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: 06/07/2017

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**: $ 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 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.

Overview

Barriers and DOE target

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

	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

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

- 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)
SnO2 (4+, 69 pm)	0 - 2.2 V	No	Sb (5+, 60pm)

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)	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

Relevance

Research objectives: 1st year milestones

Q1
- 2g Ta-doped TiO_2 (or similar)
- 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 (or similar)
- B.E.T. surface area >50 m^2 g^{-1}; Particle size <70nm

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}

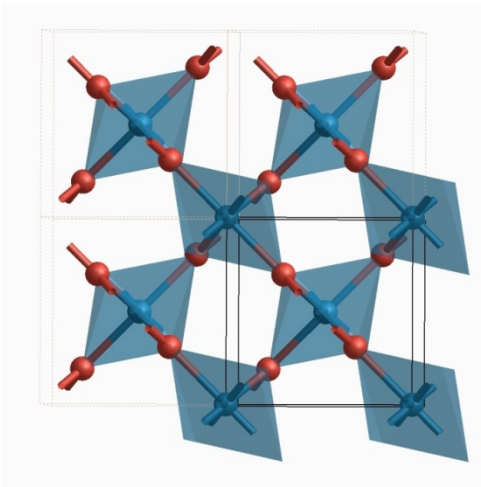
NO GO

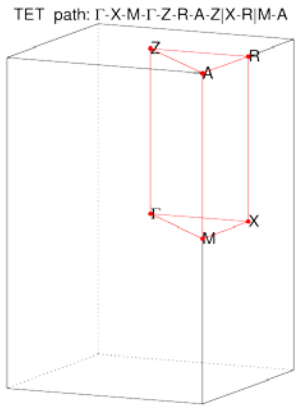
GO

Approach

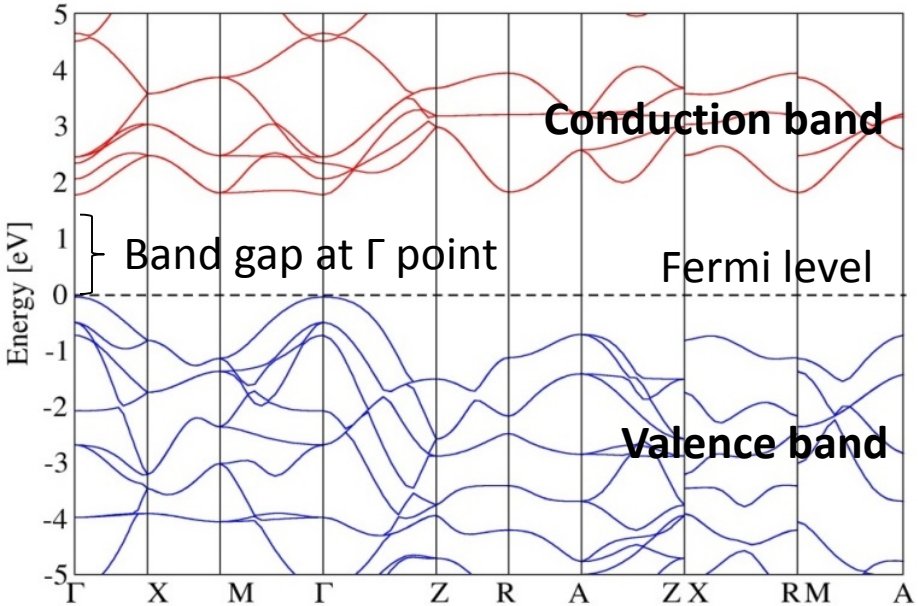
Density Functional Theory - Doping of TiO_2 with Ta

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



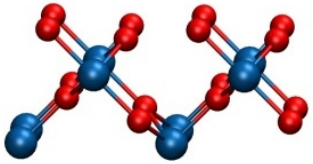
DFT calculated band structure of TiO_2. Top HSE06 level, bottom PBEsol level

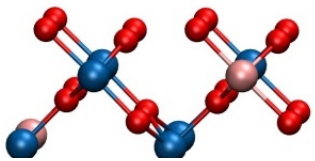
- TiO_2 is **a semiconductor, absorbs in UV.**
- Direct B-G of 1.82 eV at PBEsol level, 3.44 eV at HSE06 level (hybrid functional needed).
- Experimental reports 3.3-3.6 eV (UPS-IPS spectroscopy).

Approach

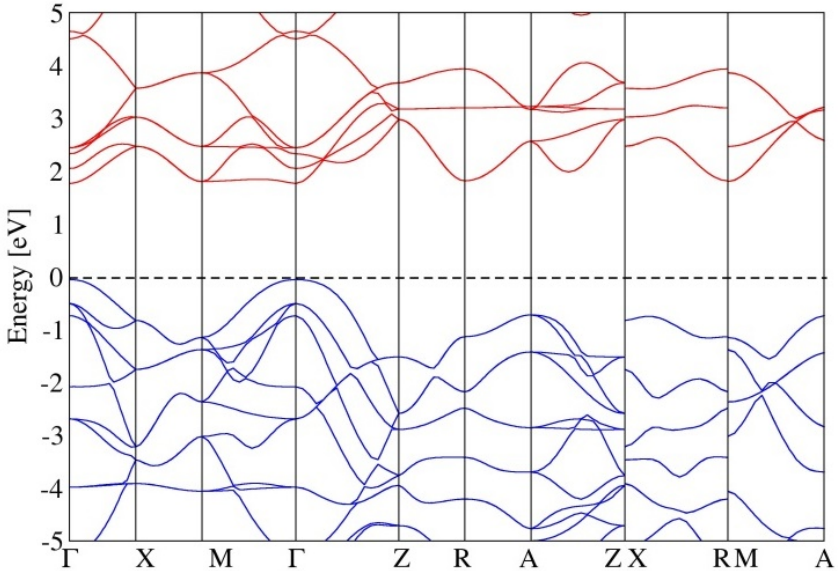
Density Functional Theory - Doping of TiO_2 with Ta

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

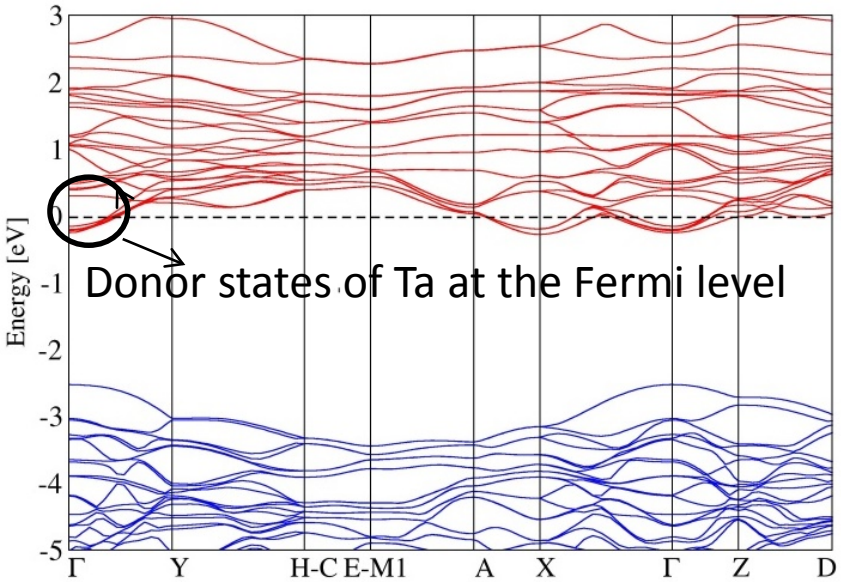




Blue - Ti
Pink - Ta
Red - O



TiO_2

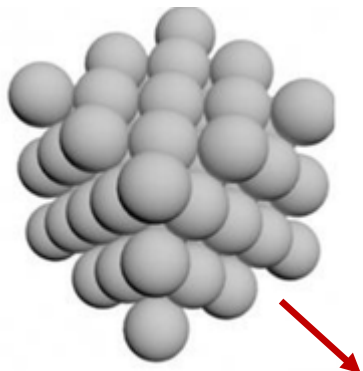


TiO_2 with 12.5% Ta (model concentration)

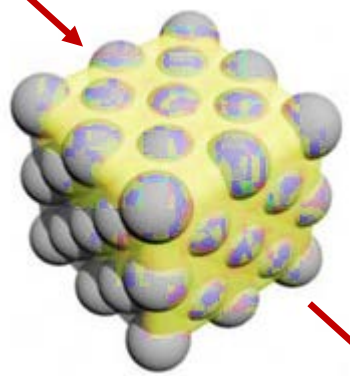
- TiO_2 is **a semiconductor**, while doping of Ta creates a ***n*-type semiconductor** with **increased conductivity** - leads to "metallization"

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)

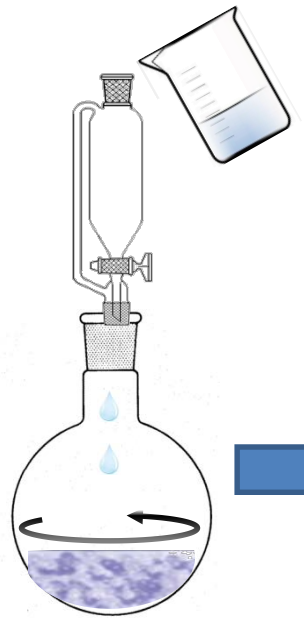
- Cab-O-Sil L90 surface area ~90 m^2 g^{-1}, 0.22 μm
- Cab-O-Sil EH5, surface area ~400 m^2 g^{-1}, 0.14 μm
- pyrolyzed at 850°C followed by leaching with 40 wt.% HF

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

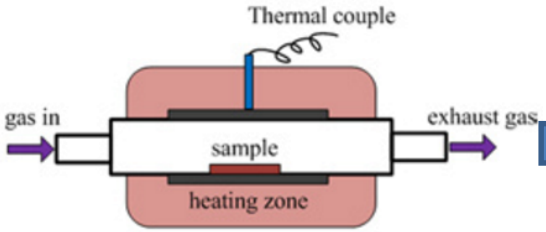
Sol-gel Synthesis



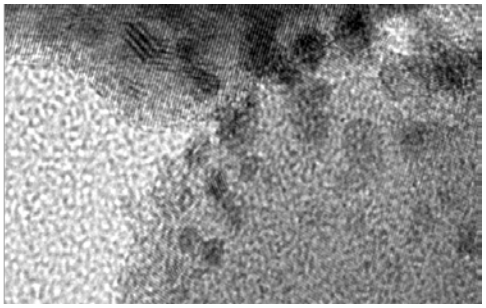
Precursors A+B in ethanol

Water+ ethanol (**or ethylene glycol**) Inert atmosphere

Centrifuge and wash the material



Anneal under 4% H_2 or air at T=200-1200°C



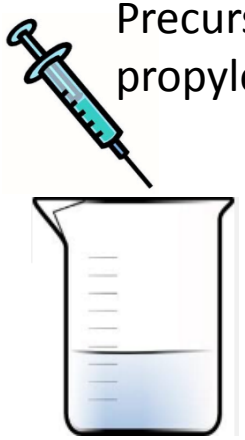
Pt deposition
(formic acid reduction)

Catalyst support

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

Approach

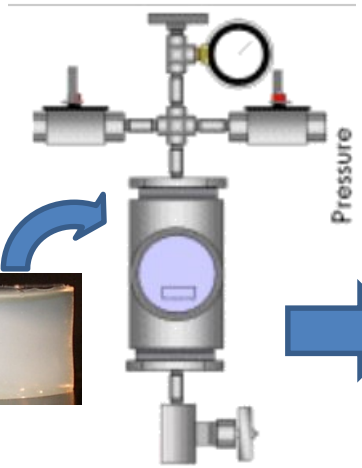
Aerogel Synthesis



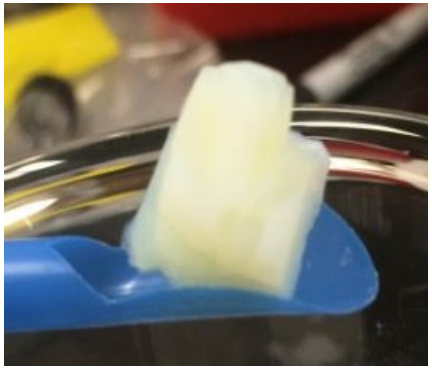
Precursor and propylene oxide

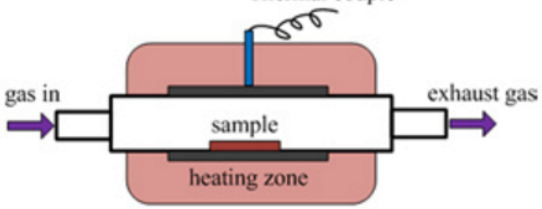
Pure ethanol

Wash the gel with pure acetone



Dry the wet gel with Supercritical dryer





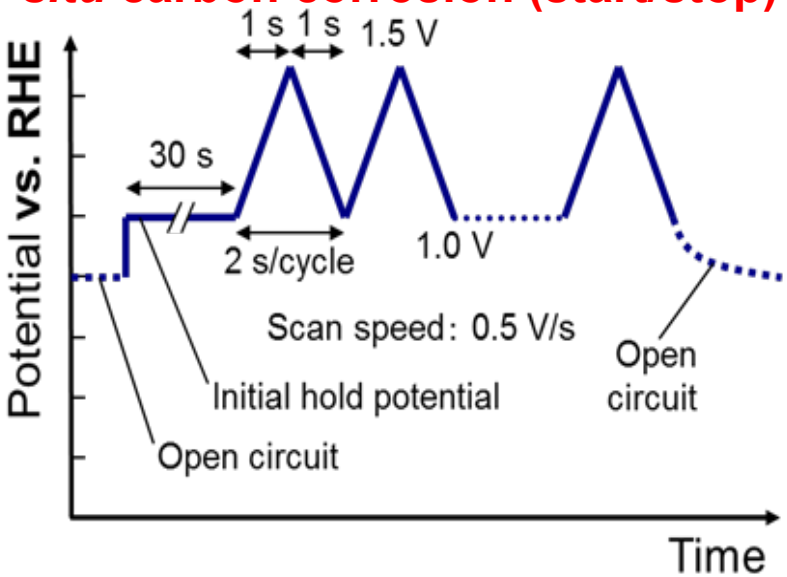
Anneal under 5% H_2 or air at T=200-1200°C

Using supercritical drying, we can synthesize higher surface area material

Approach

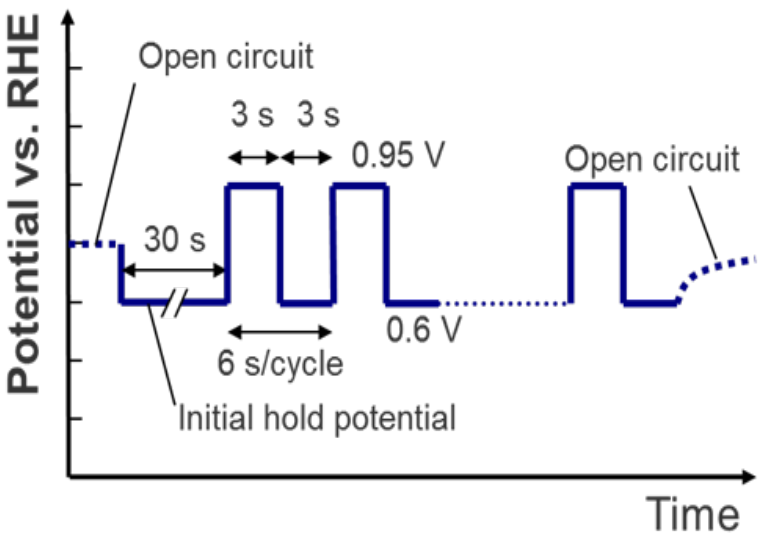
Potential cycling to evaluate support and electrocatalyst electrochemical stability/durability

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)



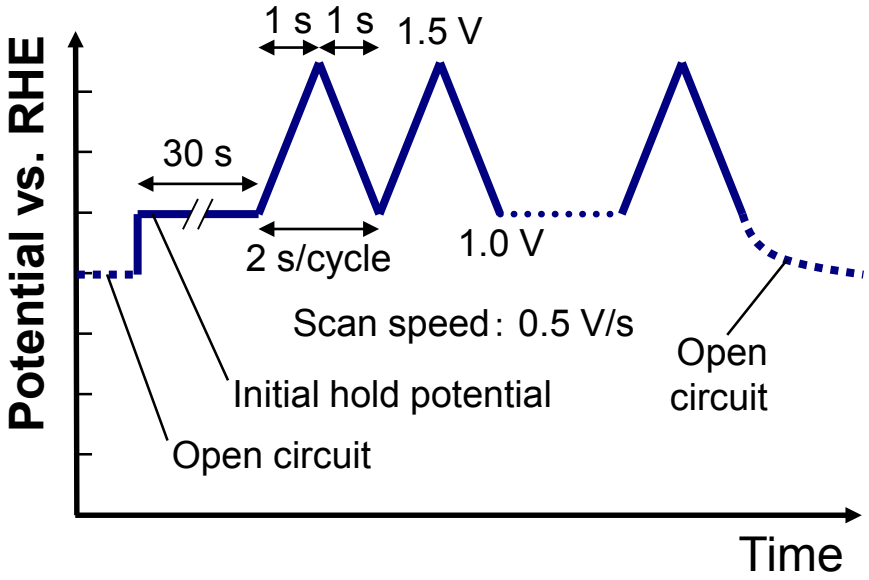
Protocol for simulating load cycling phenomena.

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

Approach

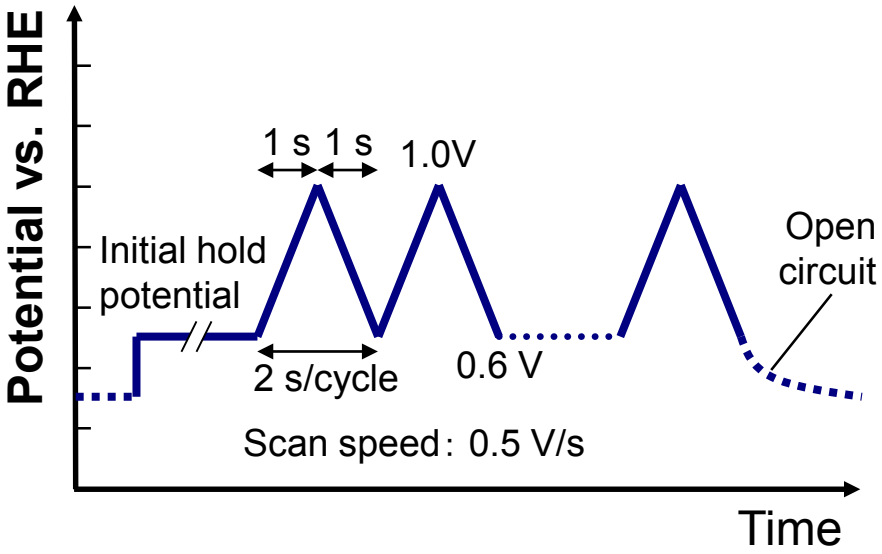
Potential cycling to evaluate support and electrocatalyst electrochemical stability/durability

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)



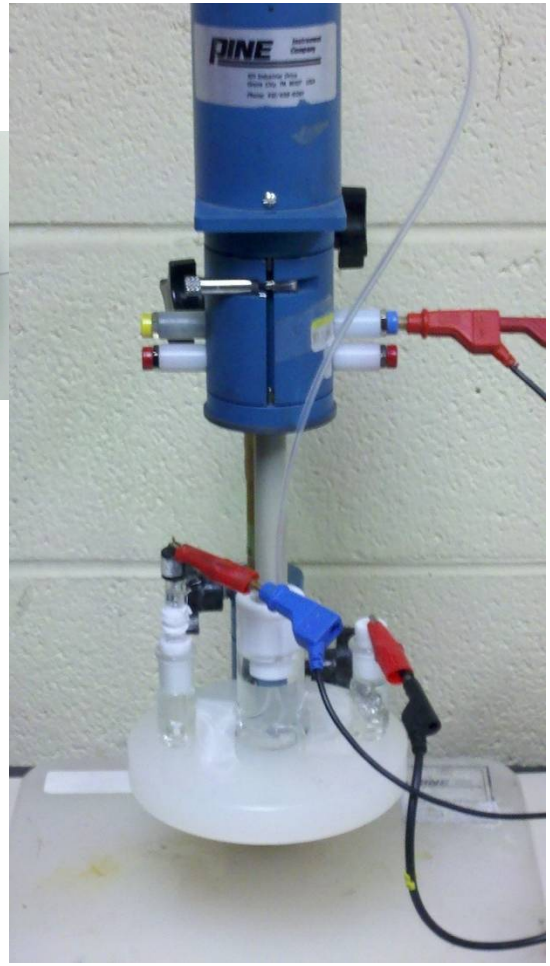
Catalyst durability – Pt dissolution

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

Approach

Potential cycling to evaluate support and electrocatalyst durability

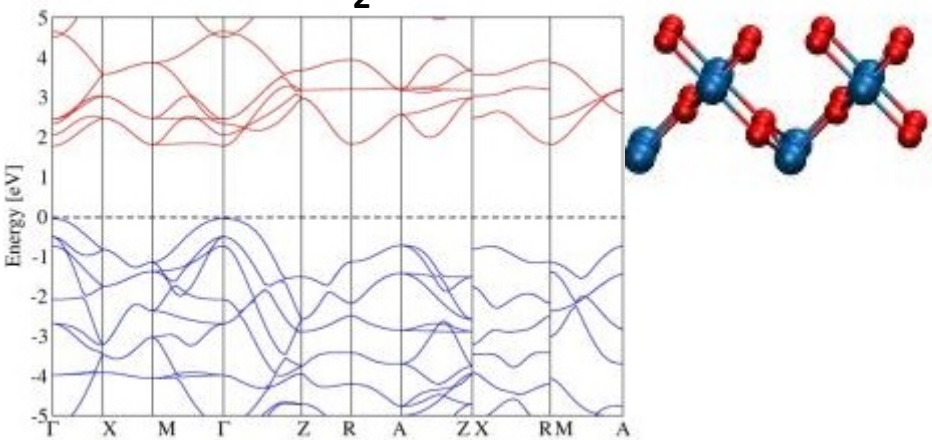
- Three electrode cell with rotating disk electrode
  - Working electrode (WE) : Glassy carbon coated with catalyst support
  - Counter electrode : Pt foil
  - Reference electrode : Saturated calomel electrode (SCE)
  - Electrolyte : N_2 saturated 0.1M $HClO_4$
- Support loading on W.E.: 200-600 $\mu g/cm^2_{geo}$ (material dependent)
- Pt loading: 17.2$\mu g_{Pt}/cm^2_{geo}$
- Potential cycling protocol



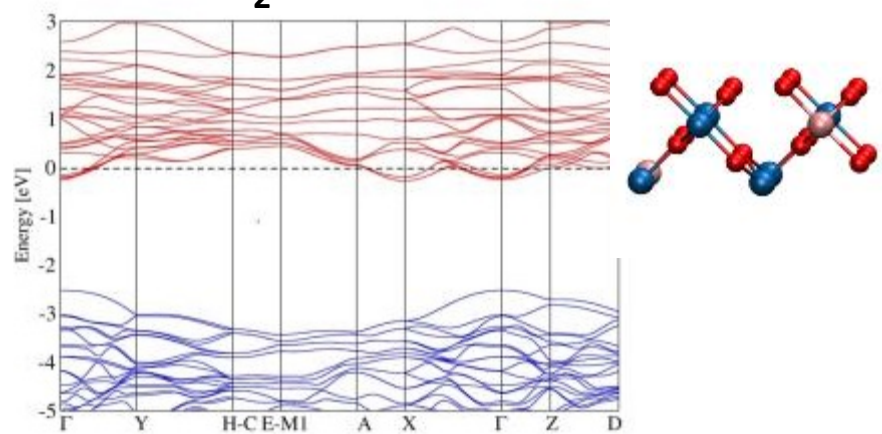
Technical accomplishments

DFT calculations for Ta-TiO_2 support

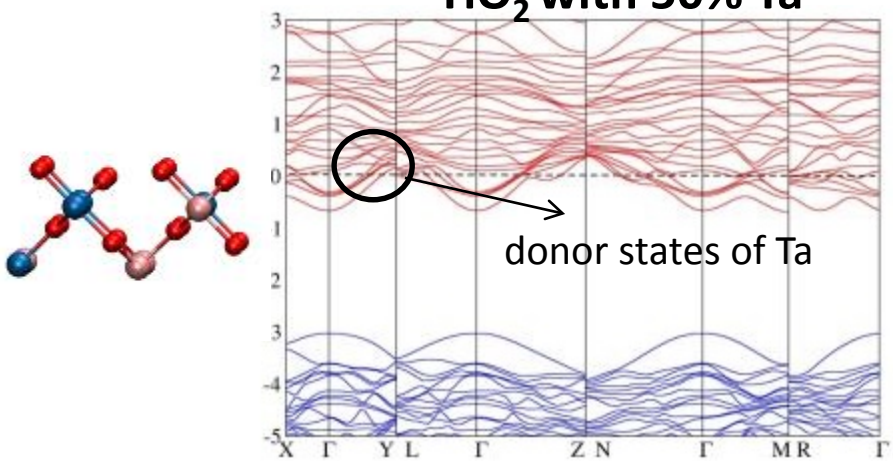
TiO_2



TiO_2 with 25% Ta



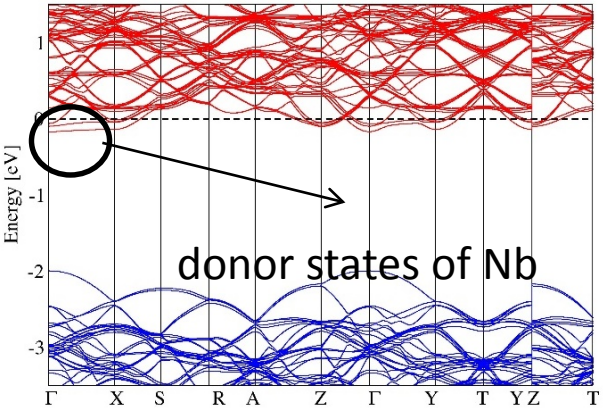
TiO_2 with 50% Ta



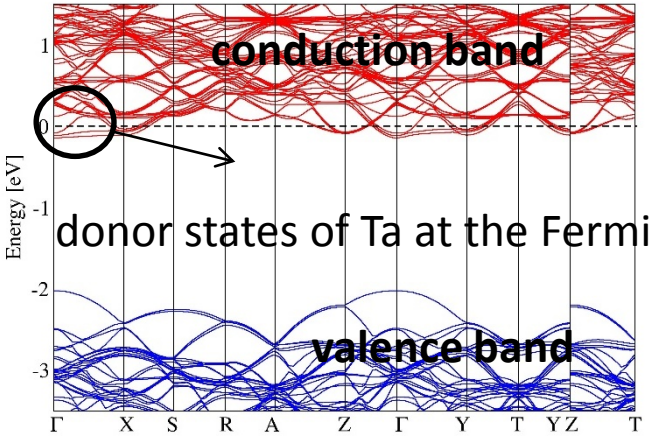
- DFT calculations show that doping TiO_2 with Ta from 25-50% reduces the Band-Gap.
- Ta-TiO_2 becomes increasingly metallic and conductive.

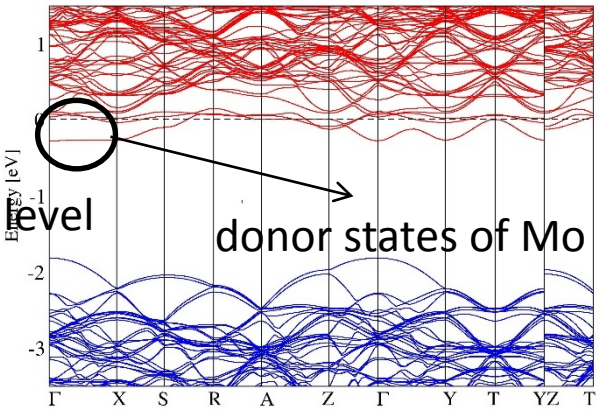
Technical accomplishments

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

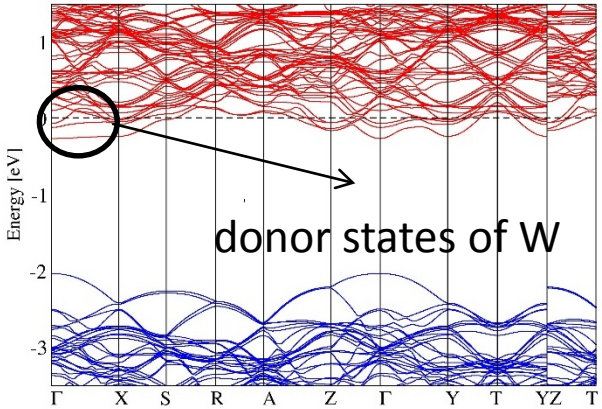


4% Nb





4% Mo

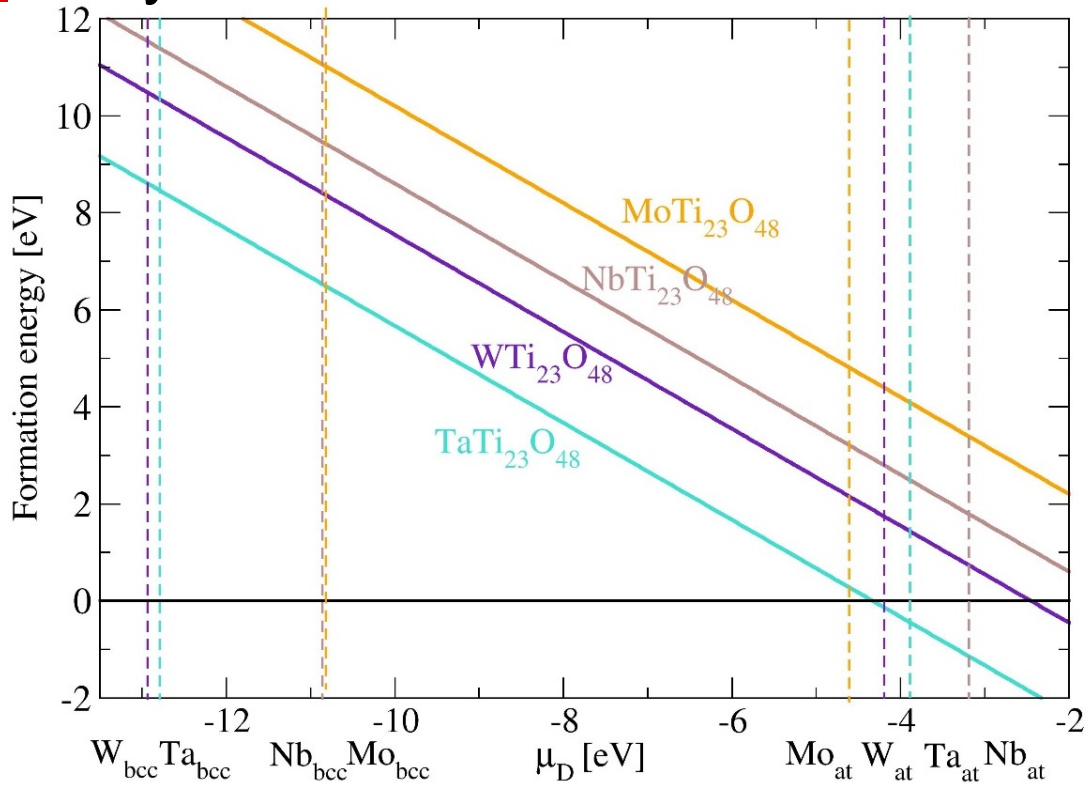


4% W

- TiO_2 is **a semiconductor**, while doping with Ta, Nb, Mo, and W (4%) creates a ***n*-type semiconductor** with **increased conductivity** =>“metallization”.

Technical accomplishments

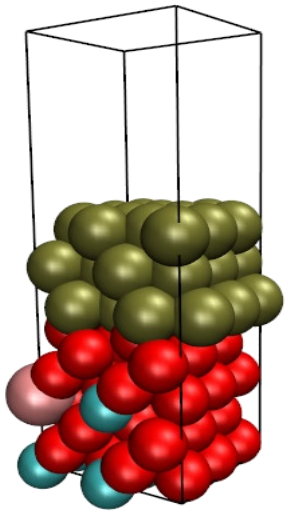
Doping of TiO_2 with Ta, Nb, W, and Mo – Defect Thermodynamics



- 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**

Technical accomplishments

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



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.

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

TiO_2(100)	a = 8.88 Å b= 9.20 Å α=β=γ=90°
Pt(111)	a = 8.32 Å b= 9.61 Å α=β=γ=90°

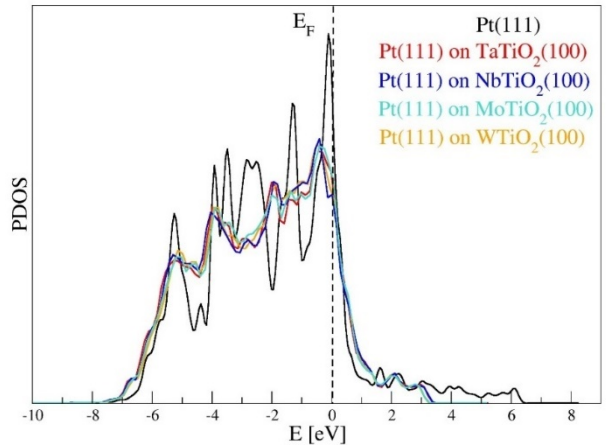
Interaction between the layers

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

- 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_2 interface

Technical accomplishments

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 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)

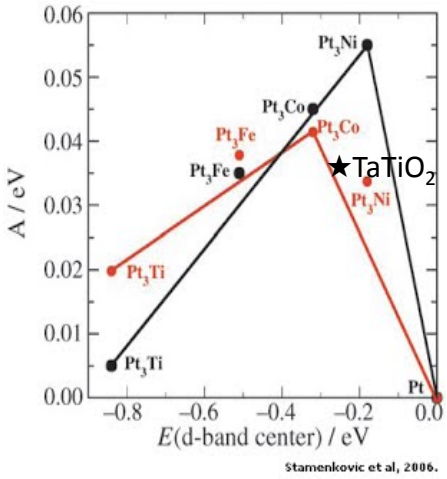
ε_d-E_F= -2.34 eV for Pt(111) on $TaTiO_2$

ε_d-E_F= -2.32 eV for Pt(111) on $NbTiO_2$

ε_d-E_F= -2.28 eV for Pt(111) on $MoTiO_2$

ε_d-E_F= -2.30 eV for Pt(111) on $WTiO_2$

the lowest *d*-band center (**larger ε_d-E_F**) for TiO_2 doped with Ta, followed by Nb, W, and Mo

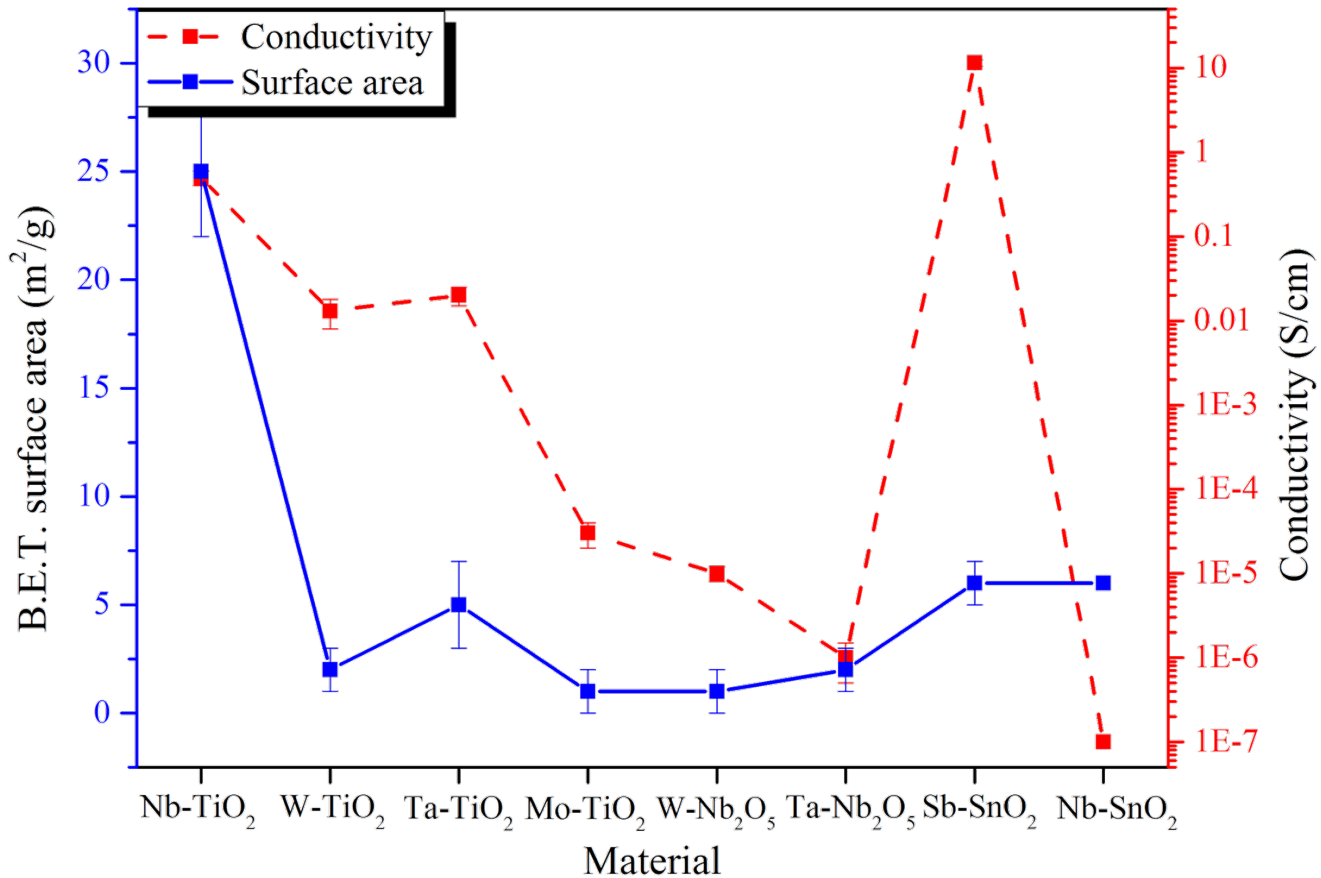


Energy of interaction between Pt and TiO_2 layer doped with 4% Ta, Nb, Mo, and W calculated as -0.13 eV, -0.08 eV, -0.10 eV, and -0.11 eV per atom

- 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_2, Pt(111) the most stable on TiO_2 doped with Ta, followed by W, Mo, and Nb.

Technical accomplishments

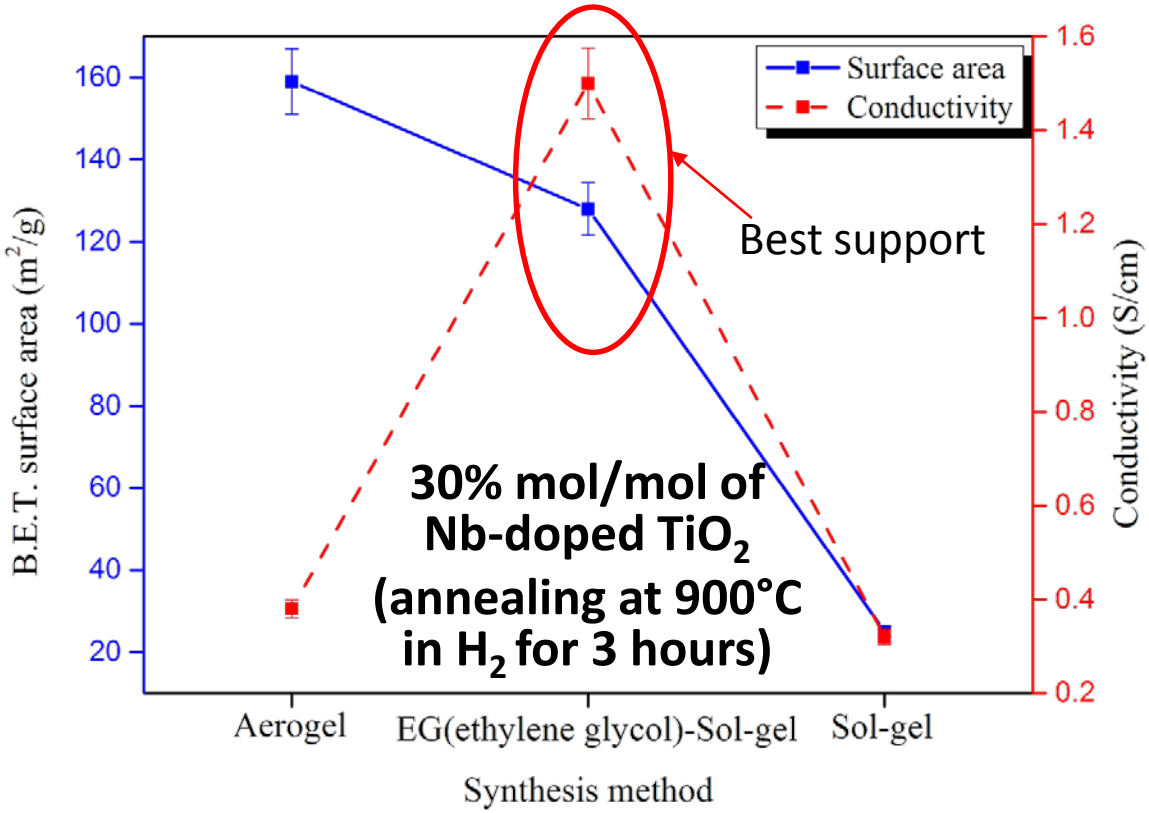
Selected Metal Oxides Synthesized



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)



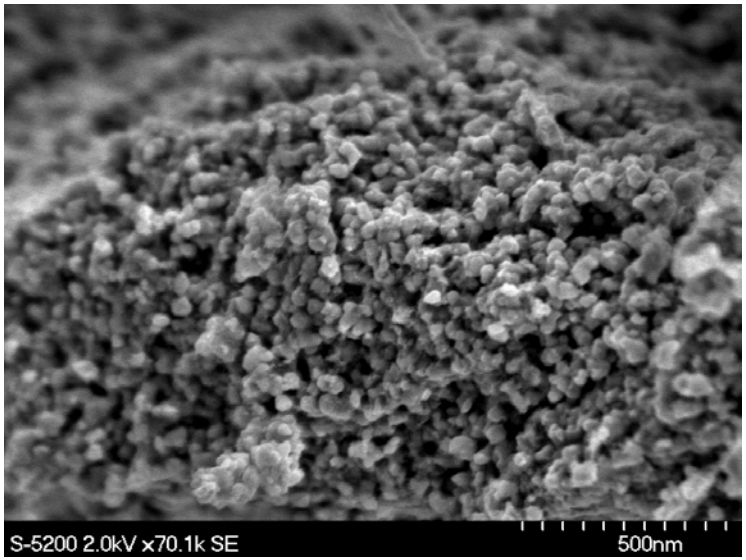
Conductivity, 1.5 S/cm & BET surface area 130 m^2/g (**Q3 milestone reached**)

Technical accomplishments

Efficacy of Sacrificial Support Method

Step:	S_{BET}, m^2/g	Conductivity, S/cm	Temperature, °C
1 (post KOH)	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.

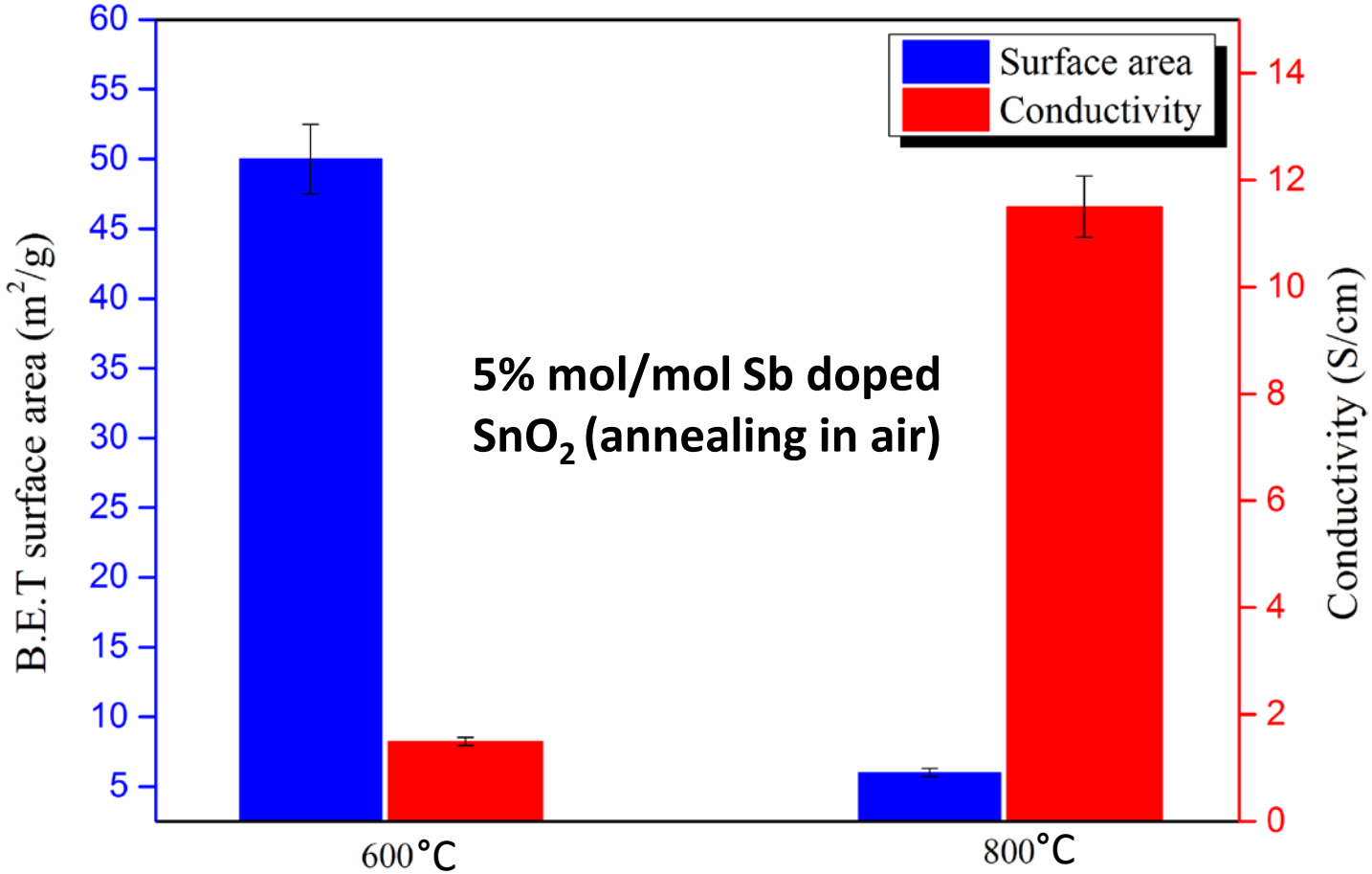


SEM image of Ta-TiO2

- 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_2 support meet Q3 milestones.

Technical accomplishments

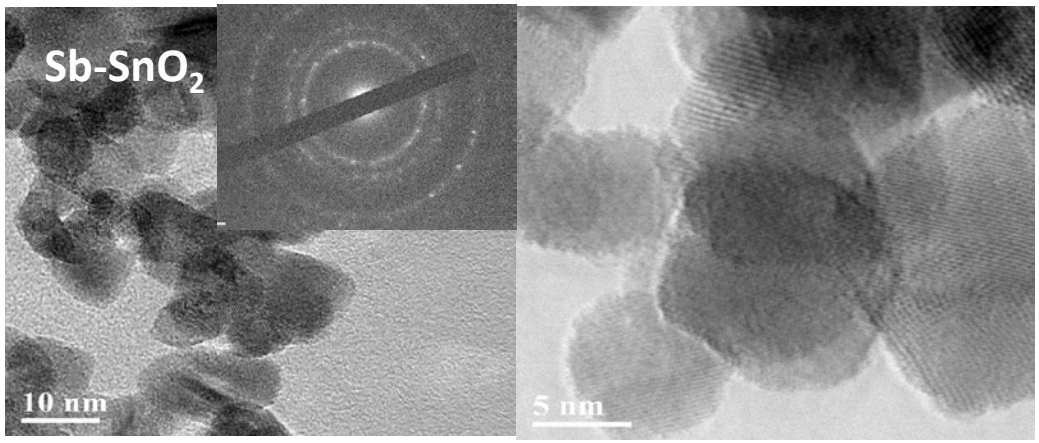
Optimization of Doped Metal Oxide Properties (annealing temperature)

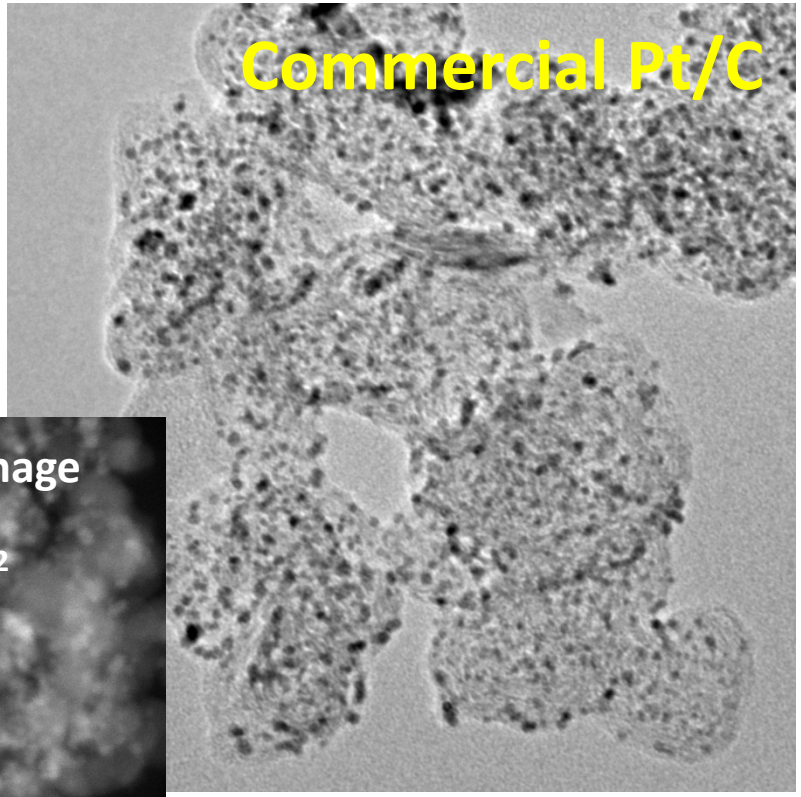


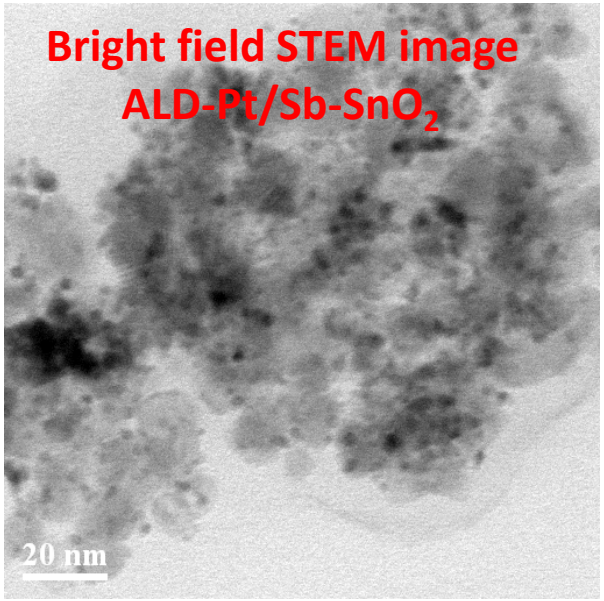
Conductivity, 1.6 S/cm & BET surface area 50 m^2/g (**Q3 milestone reached**)

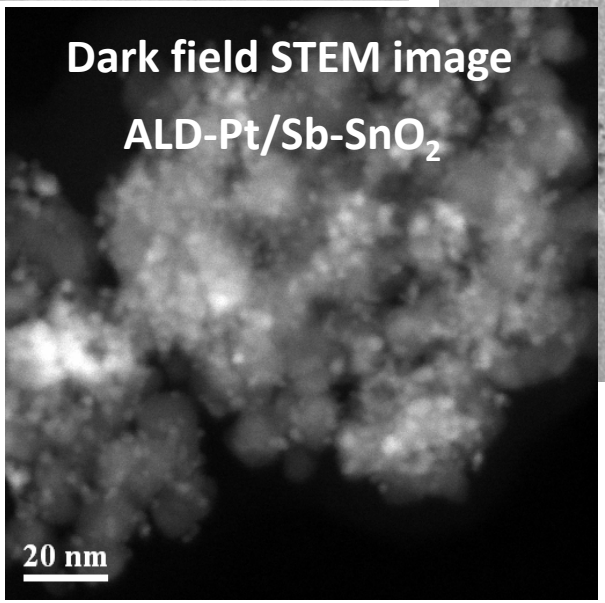
Technical accomplishments

STEM: Sb-SnO_2, ALD-Pt/Sb-SnO_2 and Commercial Pt/C



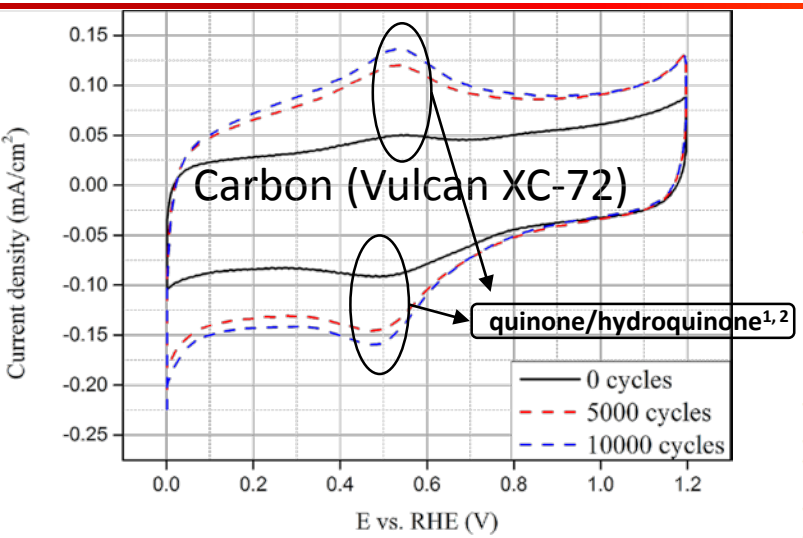


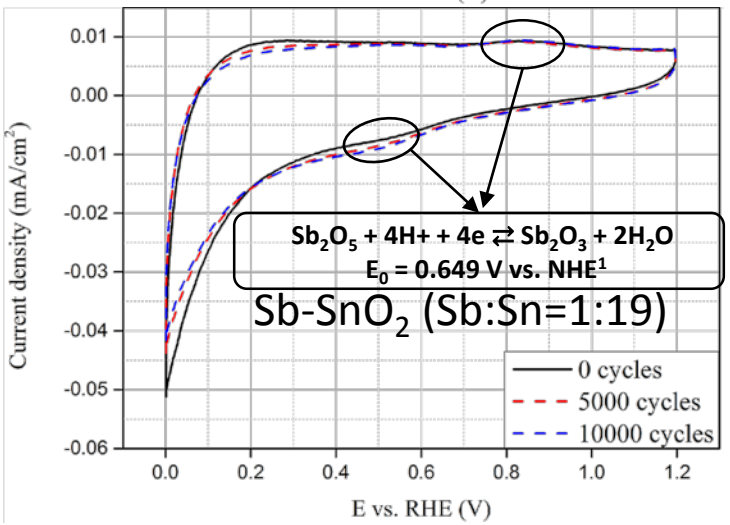


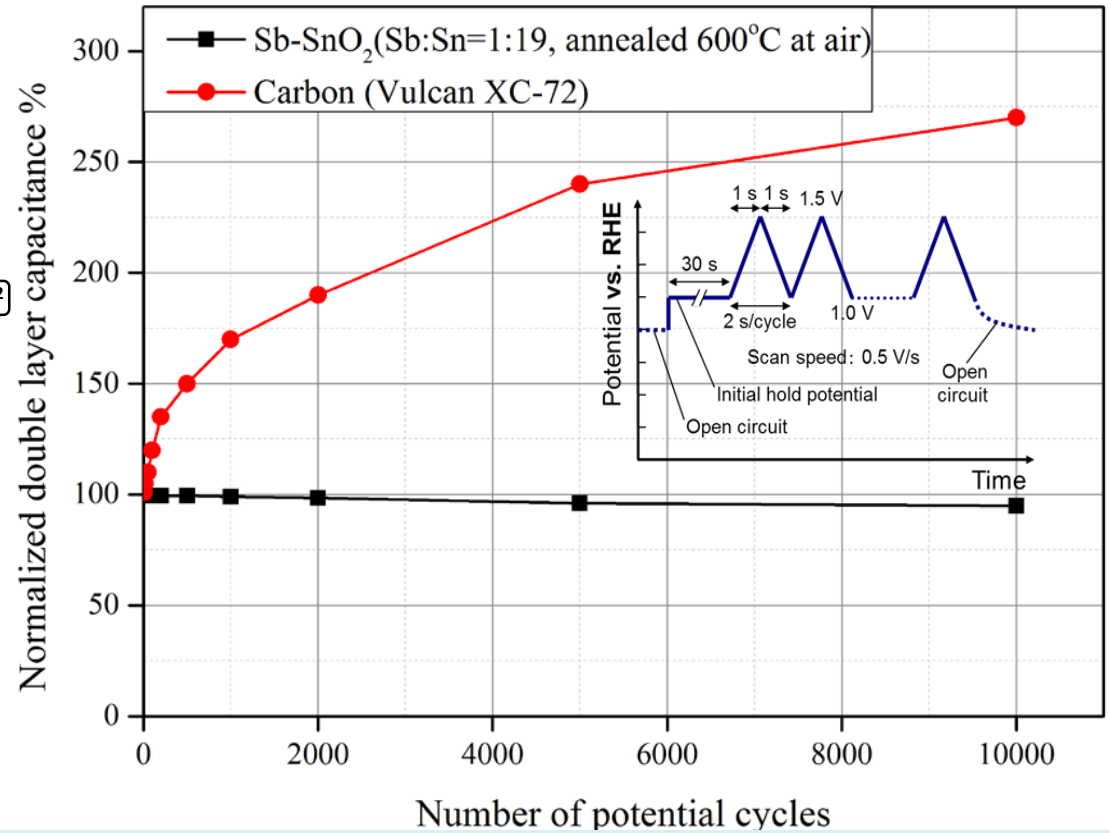


Technical accomplishments

Electrochemical stability of Sb-SnO_2 support: start-stop protocol





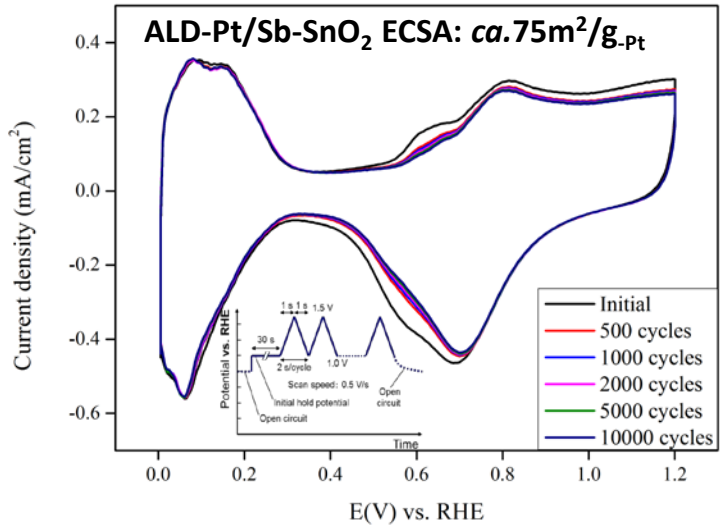


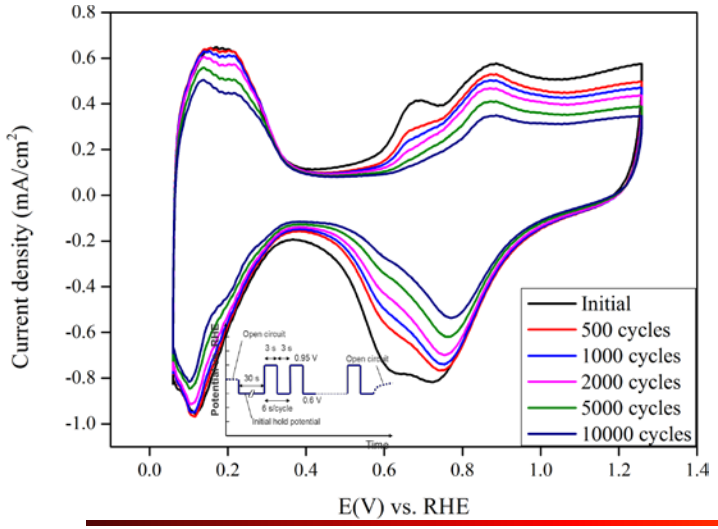
Sb doped SnO_2 (Sb :Sn =1:19) exhibited much higher electrochemical stability than the benchmark carbon material when using start-stop protocol

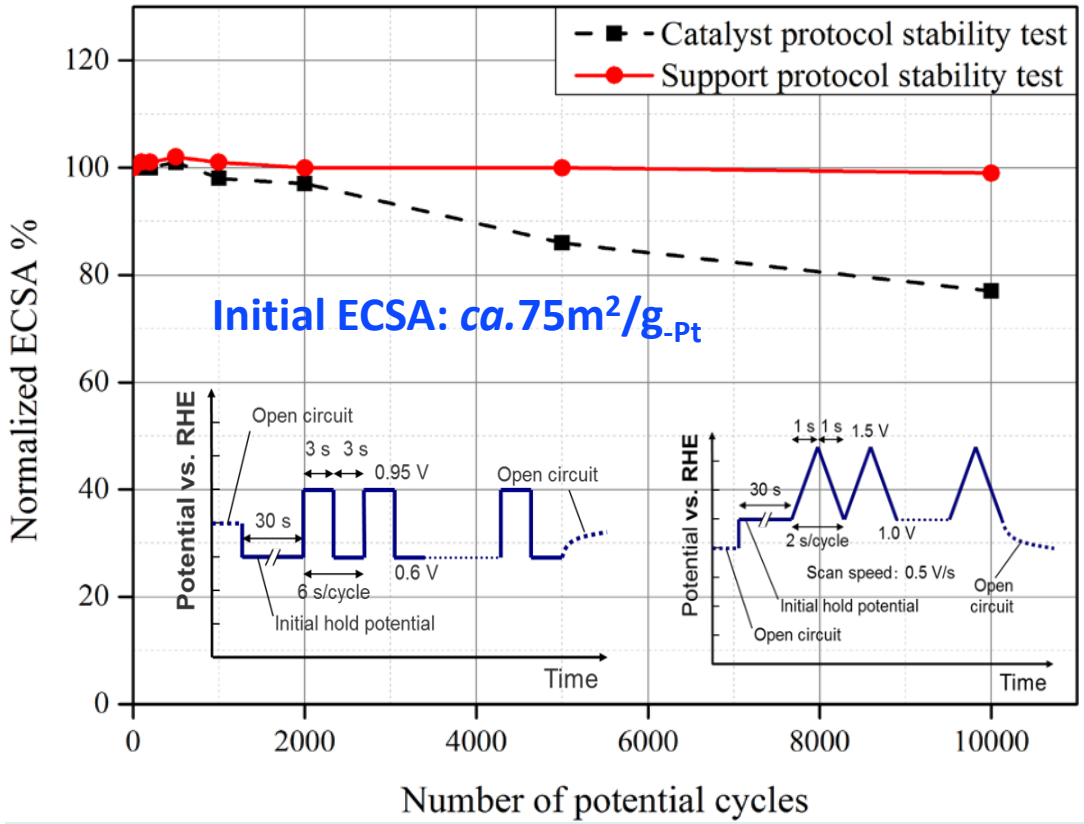
1, E. Fabbri,* A. Rabis,*Phys. Chem. Chem. Phys.*, 2014, 16, 13672—13681
2, D.A. Stevens a, J.R. Dahn a,b,*Journal of Power Sources 171 (2007) 331–339

Technical accomplishments

RDE: ECSA and electrochemical stability of Pt/Sb-SnO_2 catalyst



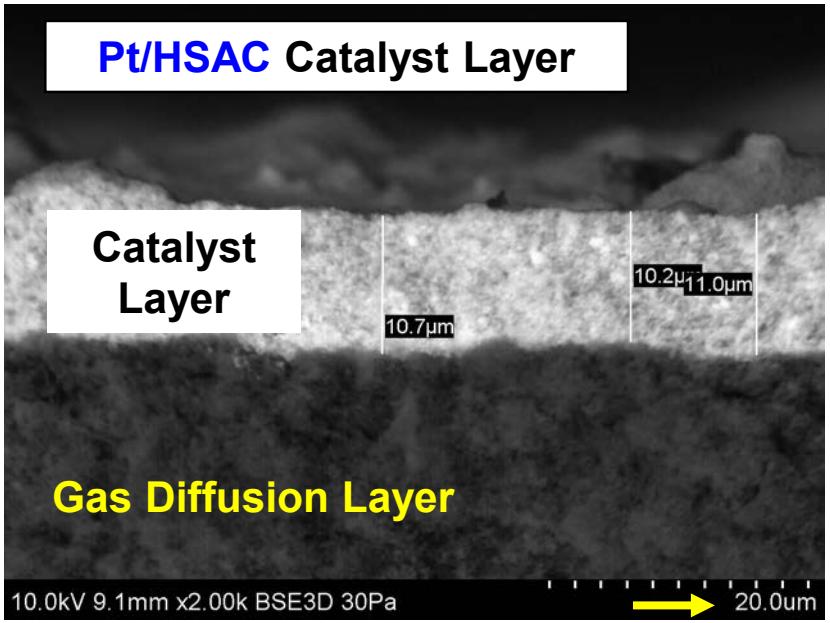


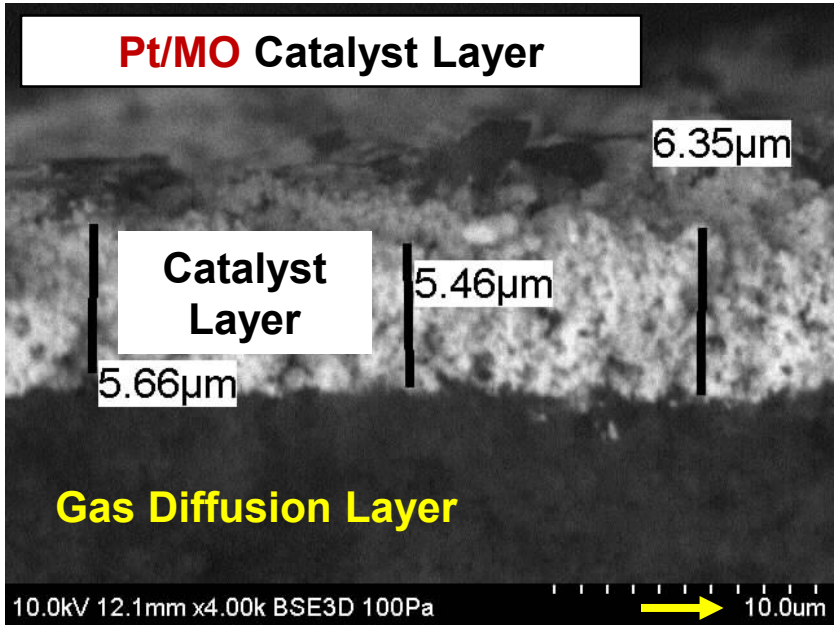


- Pt /Sb-SnO_2 was extremely stable under both catalyst loading and start/stop support protocols.
- BoL RDE ECSA for Pt/HSAC benchmark was 85m^2/g_{-Pt} and for Pt/Sb-SnO2 was *ca.*75m^2/g_{-Pt}
-

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**

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

- 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

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^2g^{-1}; particle size <70nm; conductivity ; > 0.2 Scm^{-1}; 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^2g^{-1}; 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^2 active area MEAs to DOE	Meet "End Project" durability, activity, and performance targets in Table 2	M42/Q14

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

Proposed Future Work

FY 2017

- WUSTL: Materials synthesis and characterization
  - ✓ Synthesis and characterization of Sb doped SnO_2 and other doped metal oxides (Ta,W,Nb doped TiO_2)
  - ✓ 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

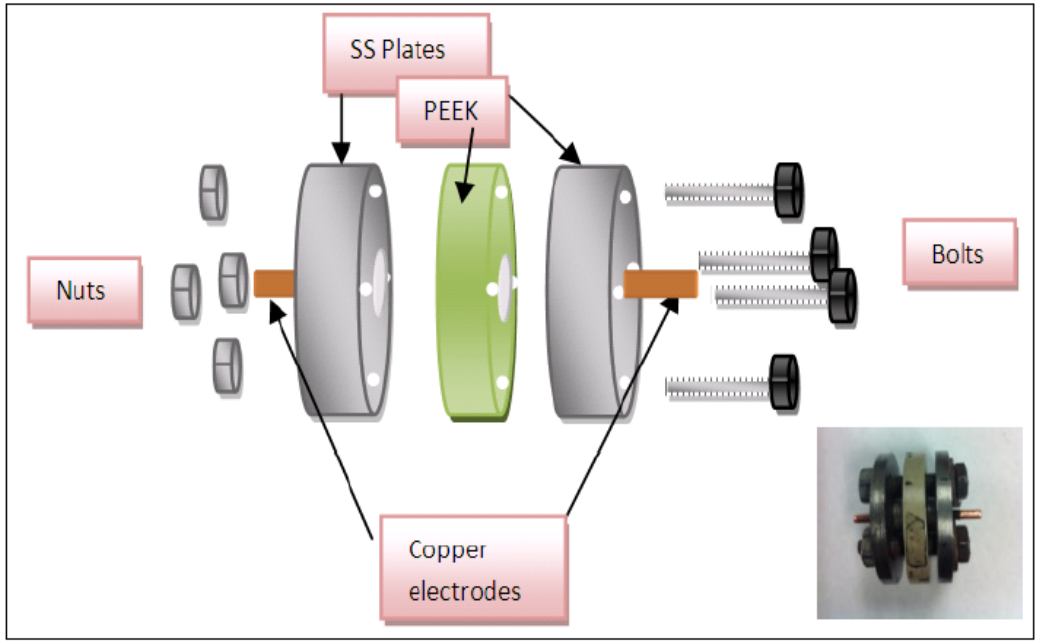
- University of New Mexico
  - ✓ DFT calculations: conductivity and SMSI of relevant doped metal oxides
  - ✓ Characterization of the doped metal oxides and derived catalysts
  - ✓ High surface area support synthesis by SSM.

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 m^2/g, and Antimony doped Tin oxide with conductivities of 1.6 S/cm and B.E.T. surface areas of 50 m^2/g.(**Achieved the Q3 milestone**)
- **Collaborations**
  - Washington University in St. Louis
  - Nissan Technical Center, North America
  - University of New Mexico

Approach

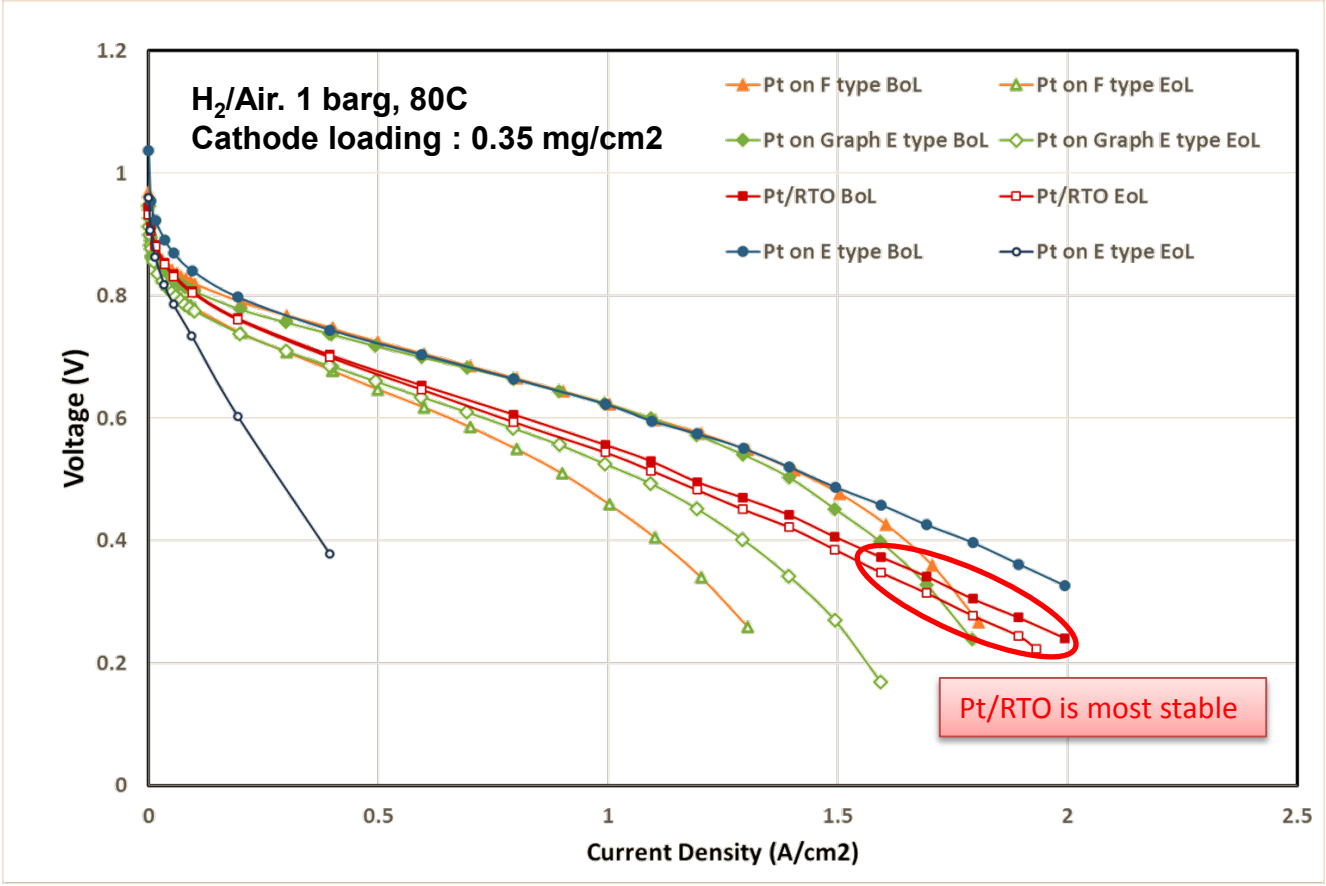
Electron conductivity measurement

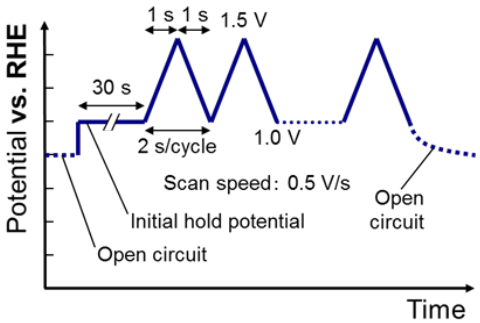


- The sample powders were pressed (25 lb x in) into pellets of 5 mm in diameter and 0.3-0.5 mm in thickness using a custom built conductivity cell.
- Sample conductivity was calculated from the slope of LSV curve
- **Vulcan Carbon Conductivity (XC72R, 250m^2/g): 51 S/cm**

Technical accomplishments

Benchmark Data





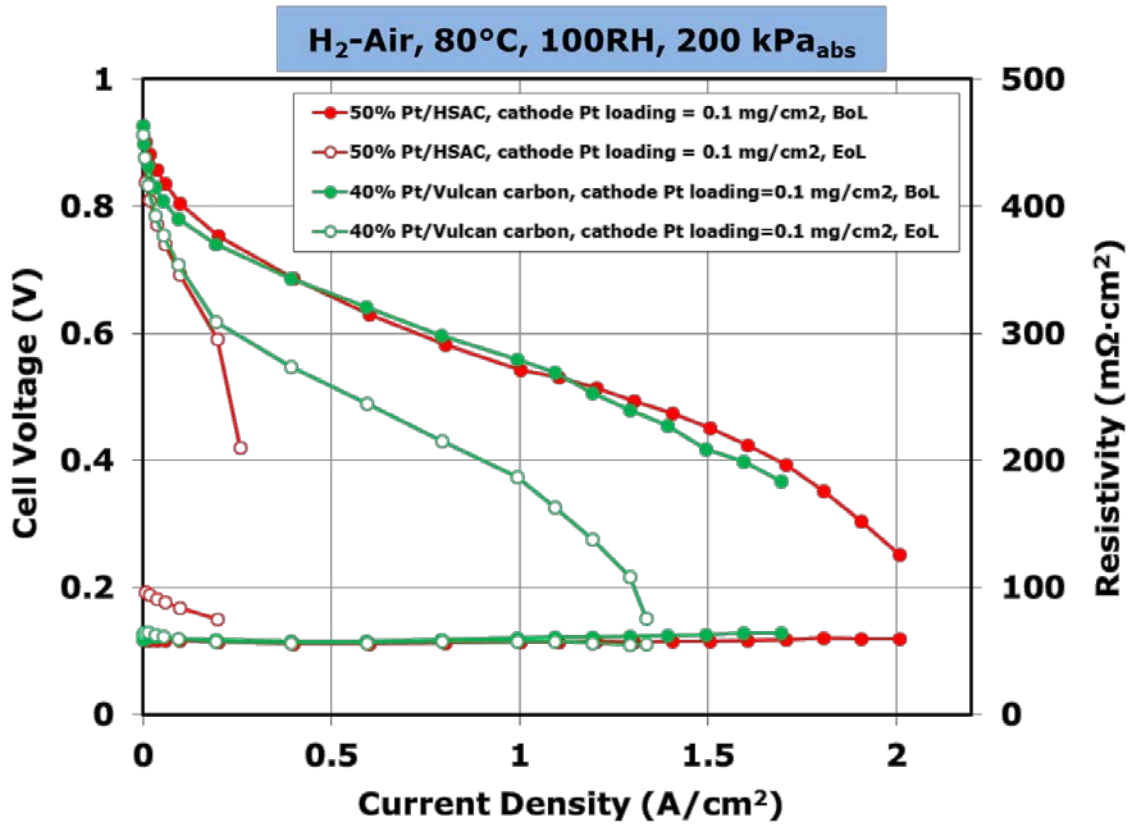
E carbon = HSAC
EA Carbon = LSAC
F Carbon = Durable HSAC

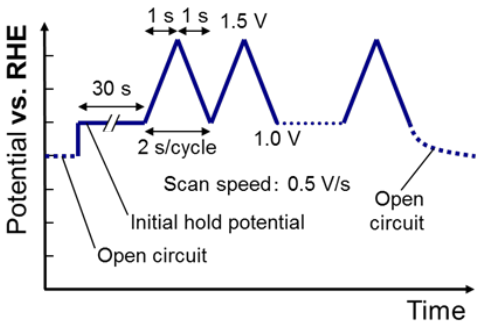
RTO = RuO2-TiO2

- **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**

Technical accomplishments

Benchmark Data

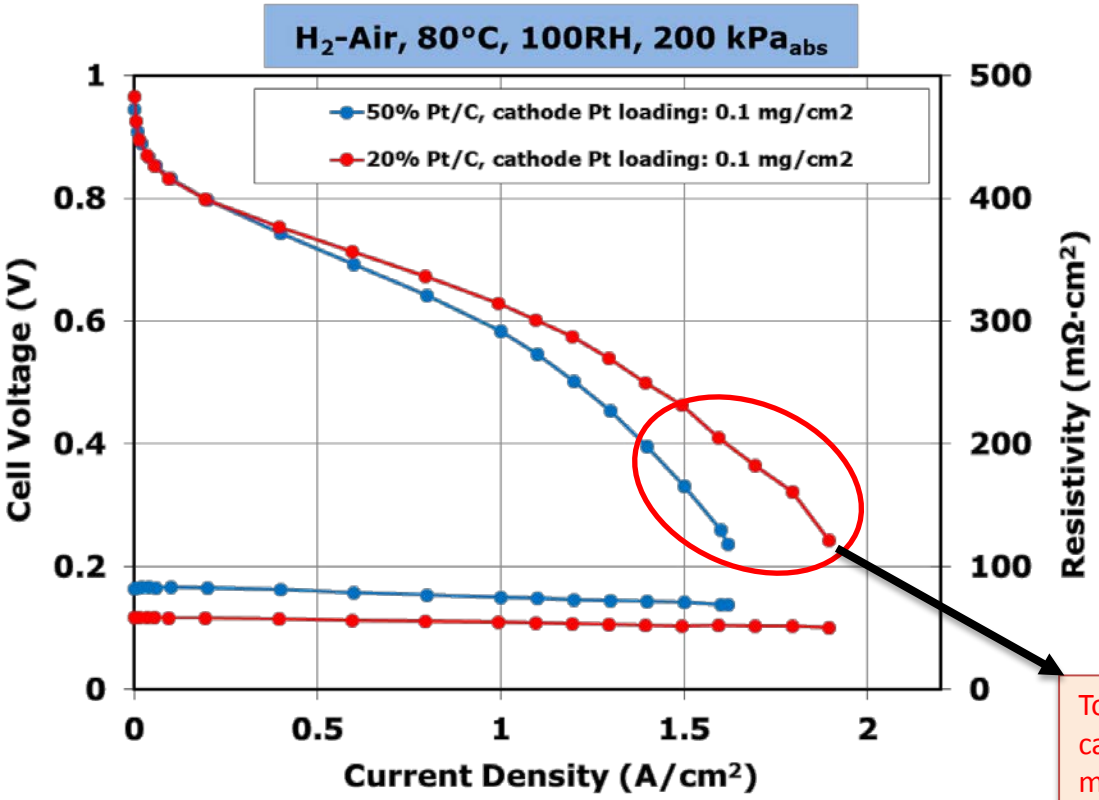




- Both HSAC and Vulcan carbon show severe degradation after 1000 cycles of carbon corrosion protocol.
- Durability of catalysts made from other carbon supports (eg. graphitized carbon and F type) under carbon corrosion protocol at low Pt loadings (~0.1 mg/cm^2) are currently under investigation.

Technical accomplishments

Benchmark Data



- Lower mass transport resistance is observed in MEA with 20% Pt/C compared to 50% Pt/C. This is attributed to the catalyst layer thickness.
- Thinner electrodes made from 50% Pt/C may result in non-uniform catalyst layer thickness and non-uniform ionomer distribution around the Pt catalyst.)

To understand mass transport losses with different catalyst layer thickness, O_2 gas transport resistance measurements are on-going

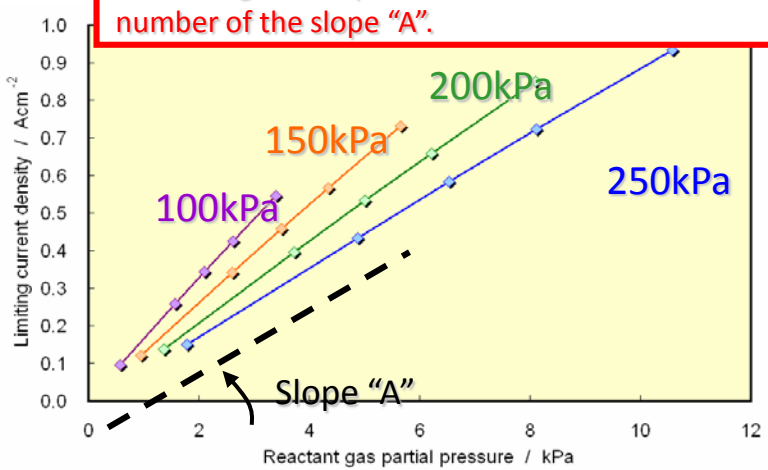
- Catalyst layer optimization (CL thickness, ionomer loadings) for low Pt loading electrodes with metal oxide supports would be key to lower the O_2 gas transport resistance and improve the performance.

Technical accomplishments

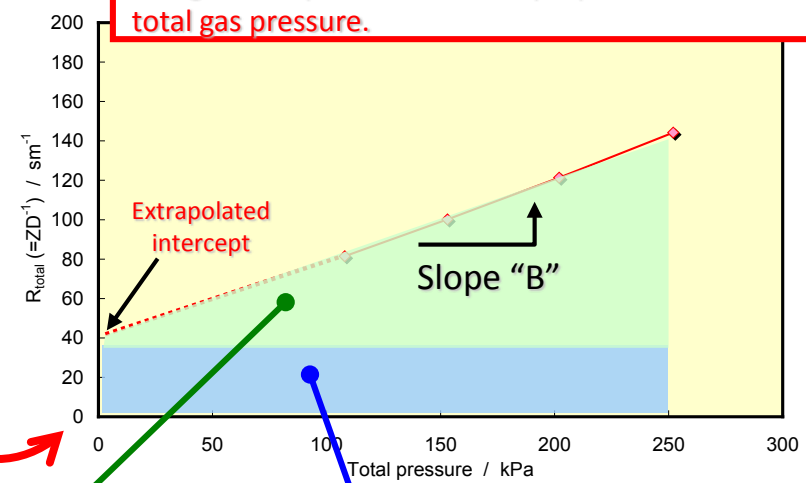
Gas Transport Resistance in a CL

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".**

Reactant gas transport resistance is the inverse number of the slope "A".



The gas transport resistance is proportional to the total gas pressure.



Total gas transport resistance

Transport resistance by molecular diffusion

Other transport resistance (Knudsen diffusion; Transport through ionomer)

$$R_{total} = R_m P + R_{0,m} + R_{0,other}$$

Slope "B"

Intercept ($R_{o,m}$ is calculated from R_m)

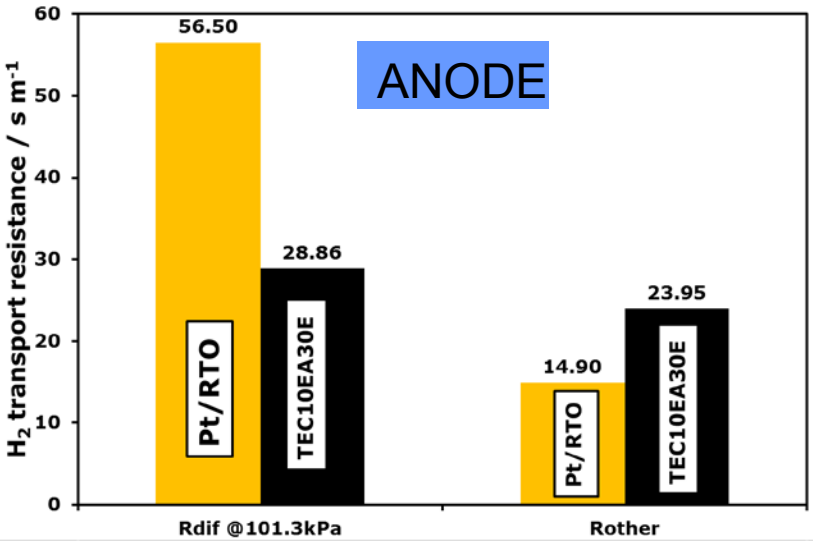
Derived from the catalyst layer (CL), without MPL.

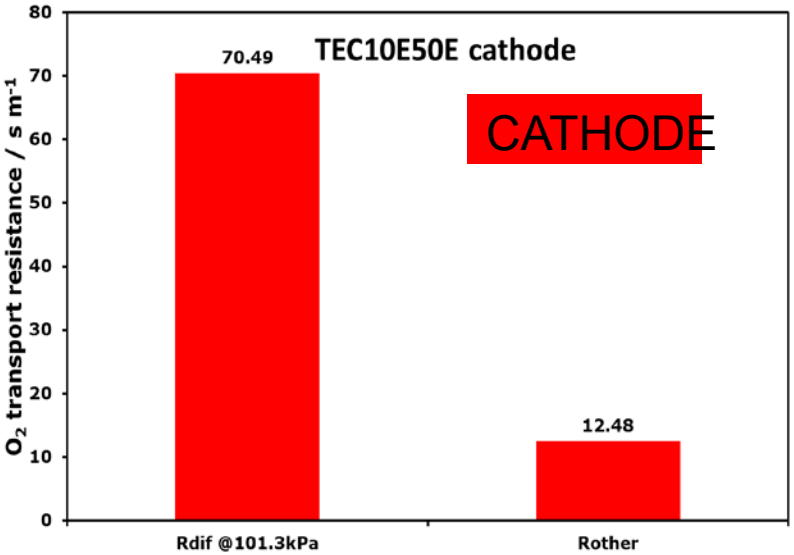
K. Sakai et al., *ECS Trans*. 25, 1193 (2009).

Technical accomplishments

Gas transport resistances

- H_2 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_{Pt}/cm^2.
- O_2 gas transport resistances of cathode catalyst layers made from Pt/Ketjen Black (TEC10E50E) were measured. Pt loading was maintained at 0.35 mg_{Pt}/cm^2 as cathode

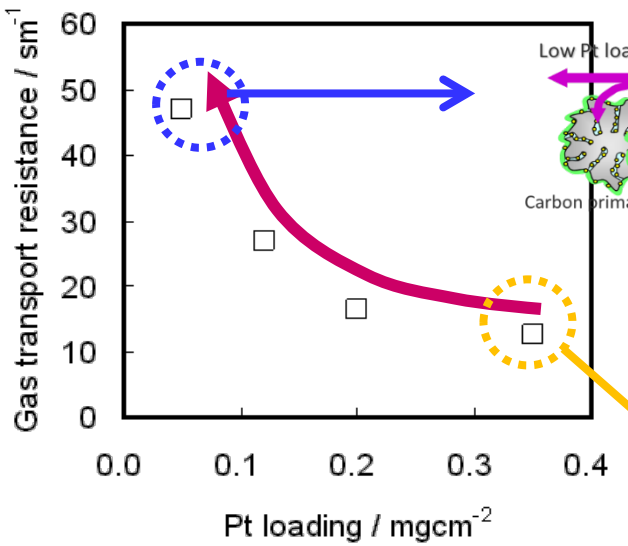


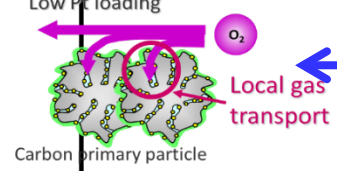


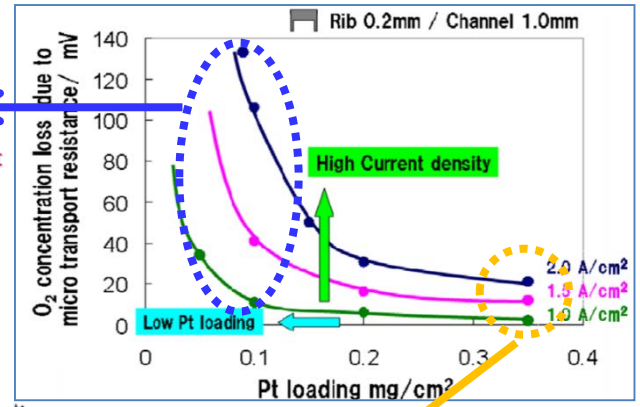
- Using limiting current experiments, gas transport resistances for both anode and cathode catalyst layers was determined.
- This diagnostic will help with the optimization of catalyst layer by varying catalyst layer porosities, ionomer content.

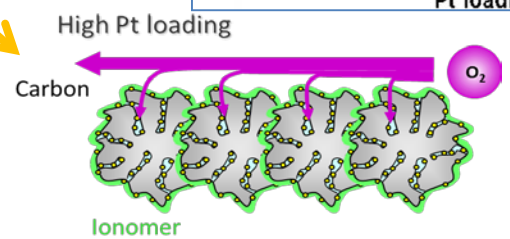
Technical accomplishments

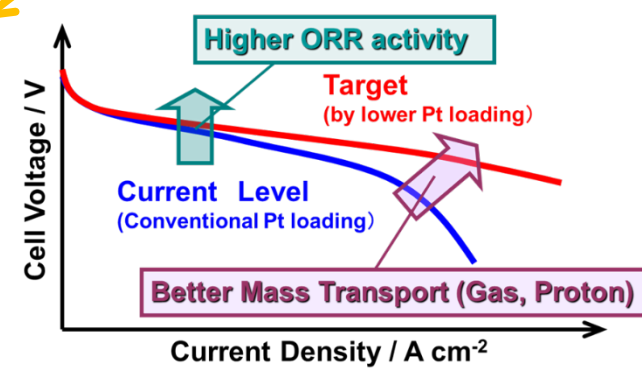
Gas Transport Losses in CL for Low PGM









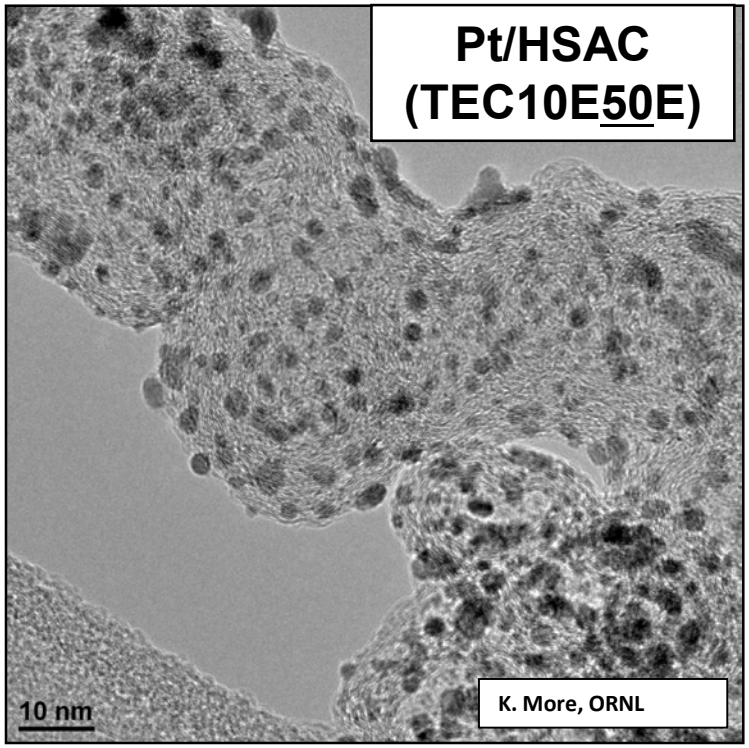


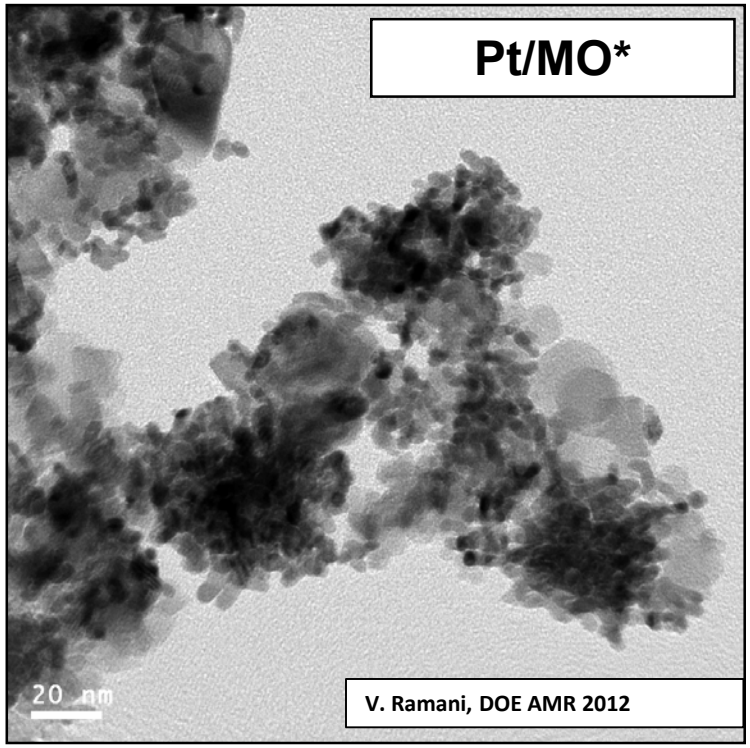
- Gas transport loss in CL is inversely proportional to Pt loading, indicating local gas transport dominates gas transport in CLs.

T. Mashio et al., *ECS Trans.* 11, 529, (2007).
K. Sakai et al., *ECS Trans*. 25, 1193 (2009).
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