DOE-EERE FCTO Catalysts Working Group Briefing
27 July, 2016, Argonne National Laboratory

ILLINOIS INSTITUTE OF TECHNOLOGY

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Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEMFC

Project ID # FC145

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Performance Period: 03/01/16 – 02/28/19 **Budget: $ 3,397,431 (cost-share: $ 397,431)**

Research Objectives:

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

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

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)

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}

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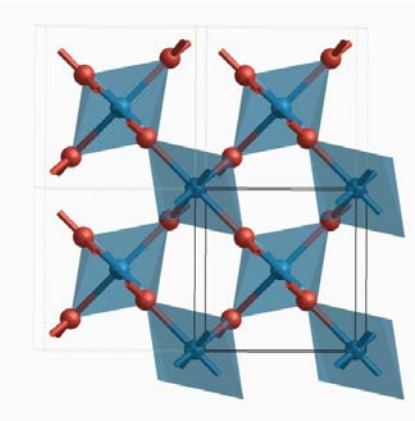
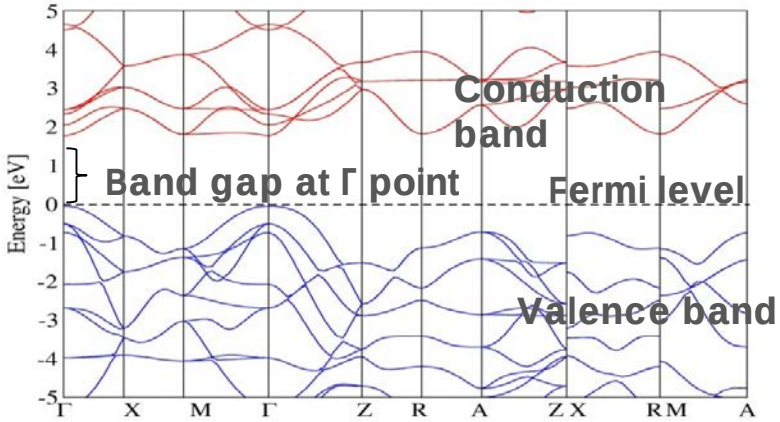
Density Functional Theory - Doping of TiO_2 with Ta

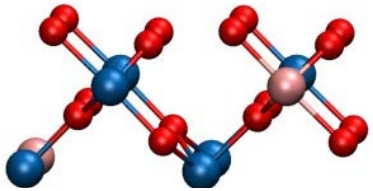
Change in the electronic structure of supports as a result of doping



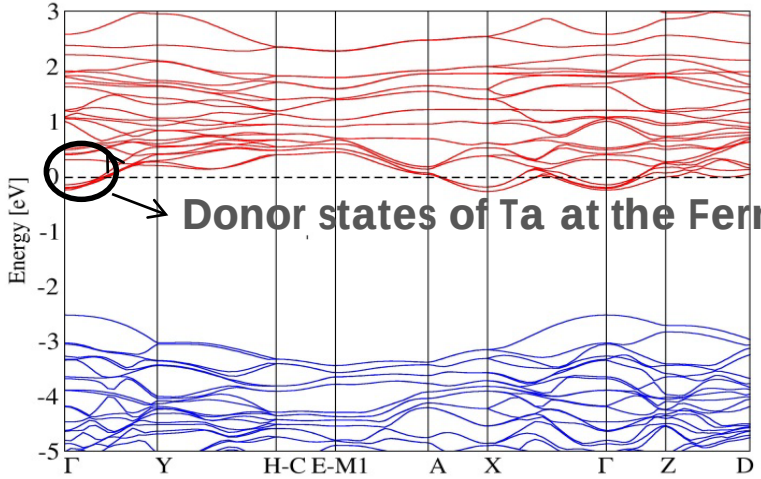
DFT optimized structure of TiO_2 (PBEsol functional).
Cell parameters
a=4.56, *b*=4.56, *c*=2.93 Å
red – oxygen, blue - Ti



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



Blue - Ti
Pink - Ta
Red - O



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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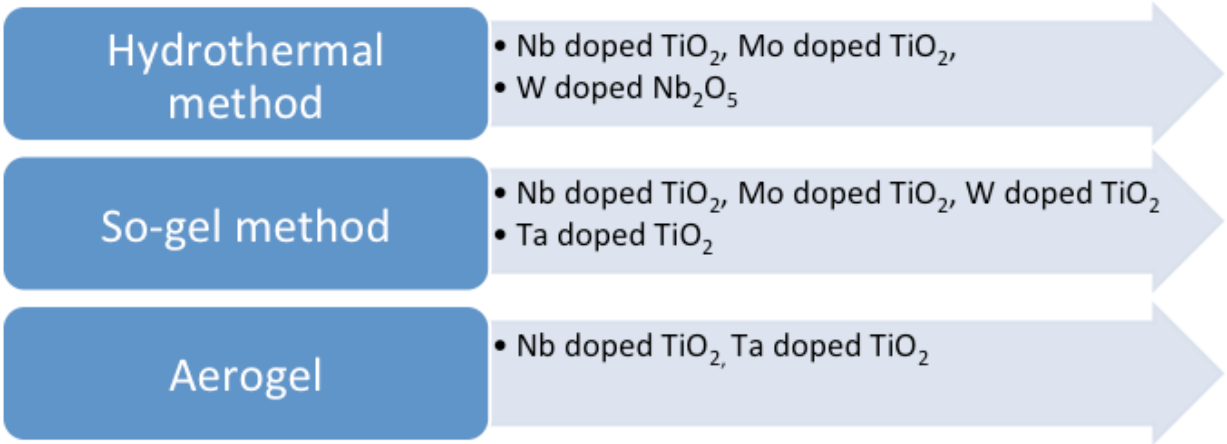
New Metal Oxides Supports Synthesis



- **Doping levels of 20-50% mol/mol**
- **Characterization:**
  Electronic conductivity,
  BET surface area and XRD
- **Objective:**
  Achieve conductivity ≥ 0.2 S/cm
  with BET surface area ≥ 30 m^2/g

1st milestone: conductivity, 0.2 S/cm;
BET surface area 30 m^2/g

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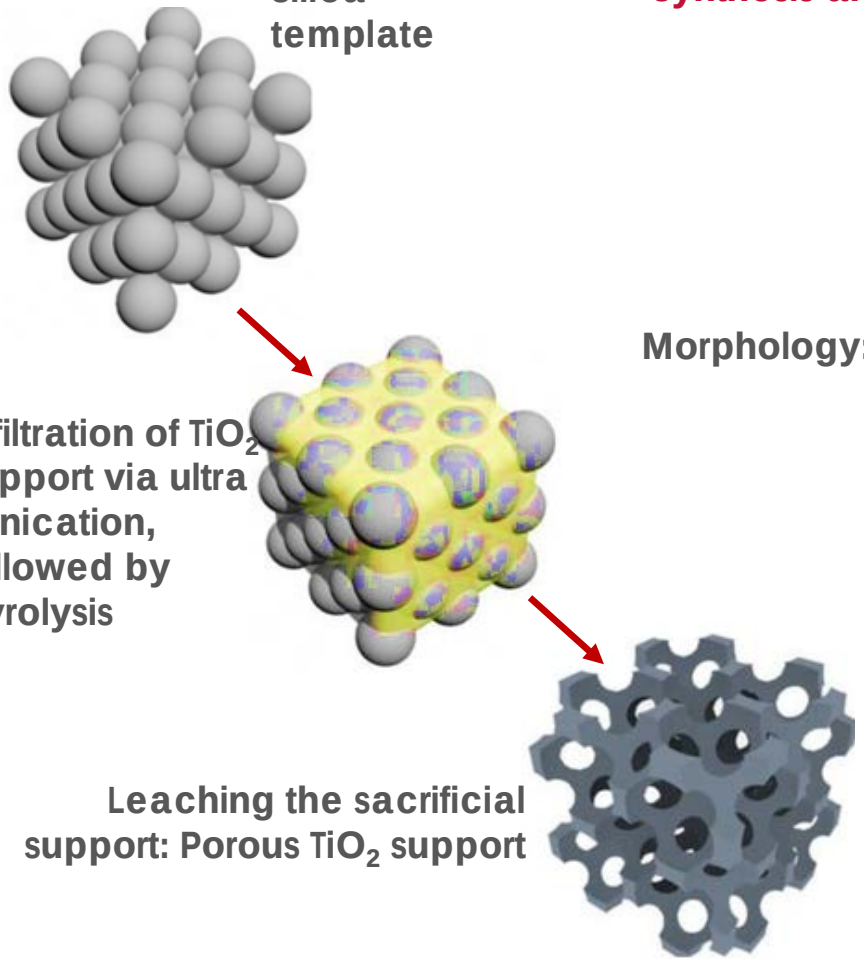
Design Porous TiO_2 supports



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)

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)

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Ongoing 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

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

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

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