V.A.9 Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEFCs

Vijay K. Ramani

Washington University in St. Louis
One Brooking Drive
St. Louis, MO 63130
Phone: (312)259-0801
Email: ramani@wustl.edu

DOE Manager: Gregory Kleen
Phone: (240) 562-1672
Email: Gregory.Kleen@ee.doe.gov

Contract Number: DE-EE-0007272

Subcontractors:
- Nissan Technical Center, North America, Farmington Hills, MI (Dr. Nilesh Dale)
- University of New Mexico, Albuquerque, NM (Prof. Plamen Atanassov)

Project Start Date: March 1, 2016
Project End Date: August 31, 2019 (six month no-cost extension secured from DOE)

Overall Objectives

- Design, develop and demonstrate high-surface-area (>70 m^2g^{-1}), high conductivity (>0.2 S/cm) and corrosion-resistant (as per funding opportunity announcement requirements), non-carbon supports based on doped/mixed metal oxides (that do not contain platinum group metals [PGMs]).

- Derivatize said supports to yield functional supported platinum (Pt) electrocatalysts that leverage strong metal-support interactions (SMSI).

- Demonstrate stability, activity, and performance approaching the Department of Energy's (DOE) 2020 targets using DOE-prescribed accelerated protocols in rotating disk electrode (RDE) and membrane electrode assembly polymer electrolyte fuel cell (PEFC) experiments by optimizing the structure of the support and the structure of the electrode.

- Provide DOE with at least six 50-cm^2 membrane electrode assemblies prepared using the best down-selected formulations that (a) meet all the stability metrics and (b) provide a clear pathway to meeting DOE 2020 targets for Pt loading and mass activity metrics.

Fiscal Year (FY) 2017 Objectives

- Density functional theory (DFT) calculations to evaluate Pt dissolution and SMSI of relevant doped metal oxides.

- Synthesis and characterization of tantalum (Ta)-doped-TiO_2 and other doped metal oxides (MO).

- High surface area support synthesis by employing sacrificial support method.

- Characterization of the doped metal oxides and the derived Pt catalysts.

- Electrochemical evaluation of the stability of supports and Pt/MO electrocatalysts.

- Investigation of SMSI in Pt/doped-metal-oxide systems using X-ray photon spectroscopy and DFT.

- Measurement of beginning of life (BoL) oxygen reduction reaction activity and electrochemically active surface area (ECSA) of selected catalysts in RDE experiments.

- Electrode optimization: RDE and membrane electrode assembly.

- Evaluation of selected catalysts in a PEFC: BoL oxygen reduction reaction activity and ECSA, and fuel cell performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

(C) Performance

Technical Targets

Table 1 shows current status (with commercial Pt/C and with the Pt/ruthenium dioxide-titanium dioxide [RTO] catalyst developed in our previous DOE EERE project) and the proposed targets for the current project. The preliminary data obtained with our proposed approach (see Table 1, Pt/TiO_2-Ta) was obtained without any optimization of the support, the catalyst deposition process, or the electrode preparation process. Clearly, there is much room for improvement in performance and baseline mass activity, which is precisely our goal in this project. These

improvements, in conjunction with the enhancement in durability, will allow us to advance towards the DOE 2020 targets. The advantages of our approach over the incumbent technology and any alternate approach (and to even our prior success with RTO) are that we eliminate the noble metal in the support (cost reduction), we ensure 100% tolerance towards start-stop cycling, and we promote SMSI between the support and Pt, providing a pathway to enhance BoL mass activity and stability under load cycling conditions. Hence, the proposed approach addresses the remaining challenges and technical issues and provides a pathway to advance the state of the art and meet the DOE 2020 targets.

FY 2017 Accomplishments

- DFT calculations have been performed by University of New Mexico to examine the electronic structure of platinum supported on rutile $TiO_2(110)$ surface doped with 4% Ta, Nb, W and Mo. Based on the DFT calculated interaction energy between Pt and the doped metal oxide, the most stable Pt catalyst was on TiO_2 doped with Ta followed by TiO_2 doped with W, Mo and Nb. Preliminary DFT work on antimony-doped tin oxide have also been conducted.

- Antimony doped tin oxide was synthesized and characterized at Washington University in St. Louis using a xerogel method. The antimony doped tin oxide had an electron conductivity of 2.2 S/cm (well above the project target) and a surface area of 74 m^2/g (just exceeding the project target).

- Atomic layer deposition was used to produce a catalyst with smaller Pt particle size and a better dispersion of the Pt onto the antimony doped tin oxide. The BoL ECSA of this catalyst was 75 m^2/g_{Pt} (similar to the benchmark Pt/C; Tanaka TEC10E50E, which was about 85 m^2/g). No decrease in the ECSA of the catalyst was observed during start/stop cycling tests (performed in a RDE). A decrease of 21% in the ECSA was observed for the same catalyst when it was subjected to the load cycling protocol (RDE).

✦   ✦   ✦   ✦   ✦

INTRODUCTION

Carbon black is the commonly used catalyst support for PEFC electrocatalysts due to its high surface area and high conductivity. However, under certain automotive fuel cell operation conditions (start-stop), carbon can corrode rapidly [1], resulting in significant and irrecoverable loss in performance. To address this issue, it is desirable to explore non-carbon supports with high conductivity, high surface area, and high corrosion resistance under fuel cell operating conditions. In this project, we will design, develop and evaluate electrochemically stable, high-surface-area, metal-oxide and doped-metal-oxide supports and supported Pt electrocatalysts therein. The Pt/MO catalysts should meet the DOE 2020 targets for stability and approach DOE 2020 targets for the BoL mass activity and Pt loading (as per DOE testing protocols).

APPROACH

DFT simulations will be performed to understand the electronic structure of the oxide upon doping, and to examine SMSI between Pt clusters and the support. The DFT results will guide dopant choice and doping levels. Once suitable combinations are identified and evaluated, we will employ the sacrificial support method pioneered by University of New Mexico as well as other methods suitable for the purpose, to prepare the supports with high surface area.

The evaluation of the electrochemical stability will be performed following the start-stop DOE protocol, by sweeping (linear ramp) the working electrode potential from 1 V to 1.5 V (vs. reference hydrogen electrode [RHE]). The experiment will be performed for 10,000 cycles (at 500 mV/s). Cyclic voltammograms will be recorded at periodic intervals (at a scan rate of 20 mV/s) to investigate any changes in the pseudo-capacitance or the appearance any new oxidation or reduction peaks (sign of changes in the oxide surface). The Pt catalysts (Pt deposited onto the MO) will be evaluated by

TABLE 1. 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	N/A	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	% loss	32	33	<10%	<5%	<40
Voltage loss at 0.8 A cm^{-2}	mV	81	9	<15	<10	30
Voltage loss at 1.5 A cm^{-2}	mV	182$^+$	20	N/A; 20 mV at 1 Acm^{-2}	<20	30
Mass activity @ 900 mV$_{iR-free}$	A mg$^{-1}_{PGM}$	0.07	0.07	ca. 0.05	0.3	0.44

SOA – state of the art; N/A – not available

using the start-stop and the load-cycling stability protocols. During the load-cycling protocol the electrode containing the Pt/MO catalyst will be cycled between 0.6 V and 0.95 V (vs. RHE) for 10,000 cycles employing a square wave. Cyclic voltammetry will be performed periodically to estimate the ECSA. Linear polarization experiments will be performed to estimate mass- and area-specific activities.

RESULTS

DFT with Perdew-Burke-Ernzerhof exchange correlation functional revised for solids and full Heyd-Scuseria-Ernzerhof hybrid functional was used to further study the structural, electronic, and stability properties of TiO_2 doped with 4% Ta, Nb, Mo, and W. The order of the stability of the doped TiO_2 structures was determined to be: Ta > W > Nb > Mo (Figure 1). Moreover, defect thermodynamics calculations showed that only *doping TiO_2 with Ta will create a thermodynamically stable doped structure starting from atomic/ionic Ta*. DFT with Perdew-Burke-Ernzerhof exchange correlation functional was also used to study the electronic structure of platinum supported on TiO_2 doped with 4% Ta, Nb, Mo, or W. It is known that platinum binds to oxygen strongly, which implies that its *d*-band center is too high. Our analysis of the DFT calculated partial density of states showed that depositing Pt on doped TiO_2 lowers the *d*-band center of platinum by altering its electronic structure and Pt(111) surface on TiO_2 is expected to bind oxygen more weakly than unsupported platinum. The *d*-band center (ε_d) relative to the Fermi level (E_F) was determined to be -2.02 eV for unsupported Pt(111), -2.34 eV for Pt(111) on Ta-TiO_2, -2.32 eV for Pt(111) on Nb-TiO_2,

-2.28 eV for Pt(111) on Mo-TiO_2, and -2.30 eV for Pt(111) on W-TiO_2.

Ta-TiO_2 was synthesized using the sacrificial support method and significant changes in the both surface area and conductivity was observed following the second heat treatment post etching the sacrificial support (silica) with KOH, see Table 2. The large decrease in surface area was due to sintering and grain growth, which was expected at the synthesis temperature of 950°C. However, the increase in conductivity, by approximately three orders of magnitude, measured after the second heat treatment was attributed to the effect of n-type doping of tantalum into the TiO_2 lattice and to the reduction of TiO_2 during the second heat resulting in the formation of oxygen vacancies.

TABLE 2. Physical Properties of Step 1, High Surface Area Ta-TiO_2 Following KOH Etch, and Step 2, TiO_2 Doped with ~5 wt% Ta after Second Heat Treatment

Step	S_{BET}, m^2/g	Conductivity, S/cm	Temperature, °C
1$_{(post KOH)}$	220	1.00E-03	950
2	60	0.9	950

In parallel, $Sb_{0.05}Sn_{0.95}O_2$ (antimony-doped tin oxide [ATO], Sb-doped-SnO_2) was synthesized using the xerogel method. The resulting material had a conductivity of 2.2 S/cm and a Brunauer-Emmett-Teller surface area of 74 m^2/g. Transmission electron microscopy (TEM) pictures (Figures 2a and 2b) showed that the particle size of this metal oxide was 10±2 nm. $Sb_{0.05}Sn_{0.95}O_2$ exhibited very high
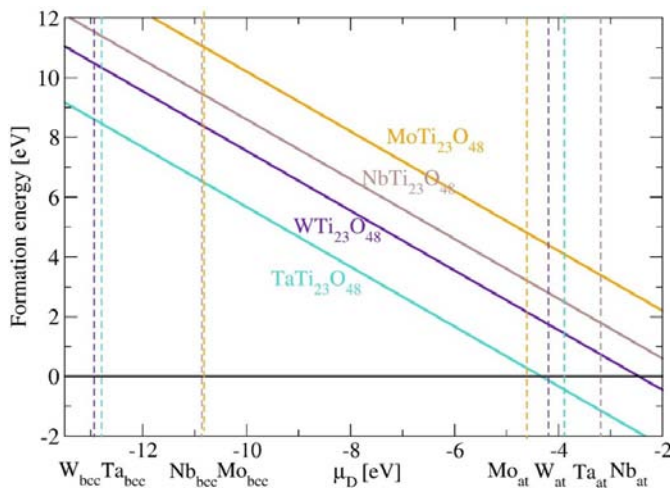

FIGURE 1. Formation energy (in eV) of the TiO_2 doped with Ta, Nb, Mo, or W as a function of the chemical potential of the dopant. Intercept of a dashed and a solid line of the same color denotes the energy required to replace 4% Ti atom in TiO_2 rutile with dopant (D), starting with a dopant in an atomic or metallic form.
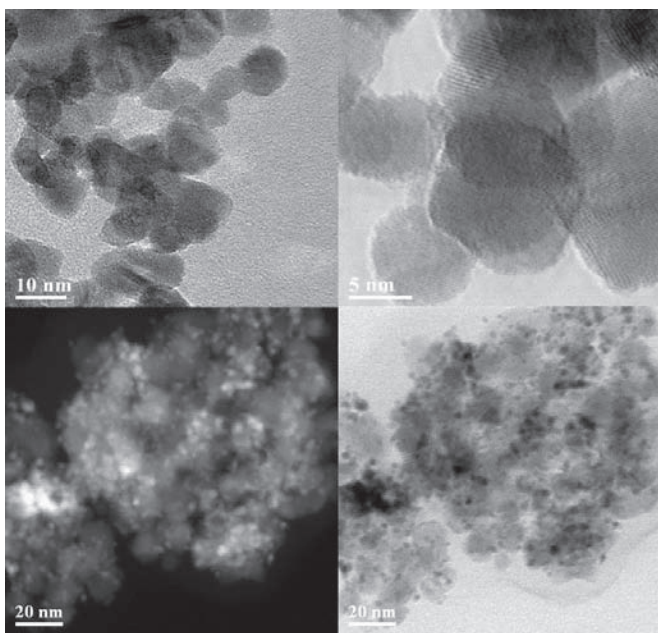

FIGURE 2. TEM and scanning TEM of ATO and Pt deposited onto ATO

electrochemical stability under the start-stop protocol, with only 1.5% change in pseudo-capacitance after 10,000 cycles, in contrast to carbon (Figure 3a). Pt supported on ATO catalyst was synthesized using the atomic layer deposition method, amongst other methods. The resultant catalyst had an ECSA of 75 m^2/g_{Pt} (Figure 4), very close to the benchmark Pt/C catalyst (85 m^2/g_{Pt}). TEM images (Figures 2c and 2d) showed approximately 2.5 nm Pt particles homogeneously dispersed onto the ATO support. Electrochemical testing (in RDE) showed good electrochemical stability under start-stop cycling protocol, with no loss in the ECSA over 10,000 start-stop potential cycles, and a loss of 21% of the initial ECSA after 10,000 cycles under the load cycling protocol (Figure 3b).
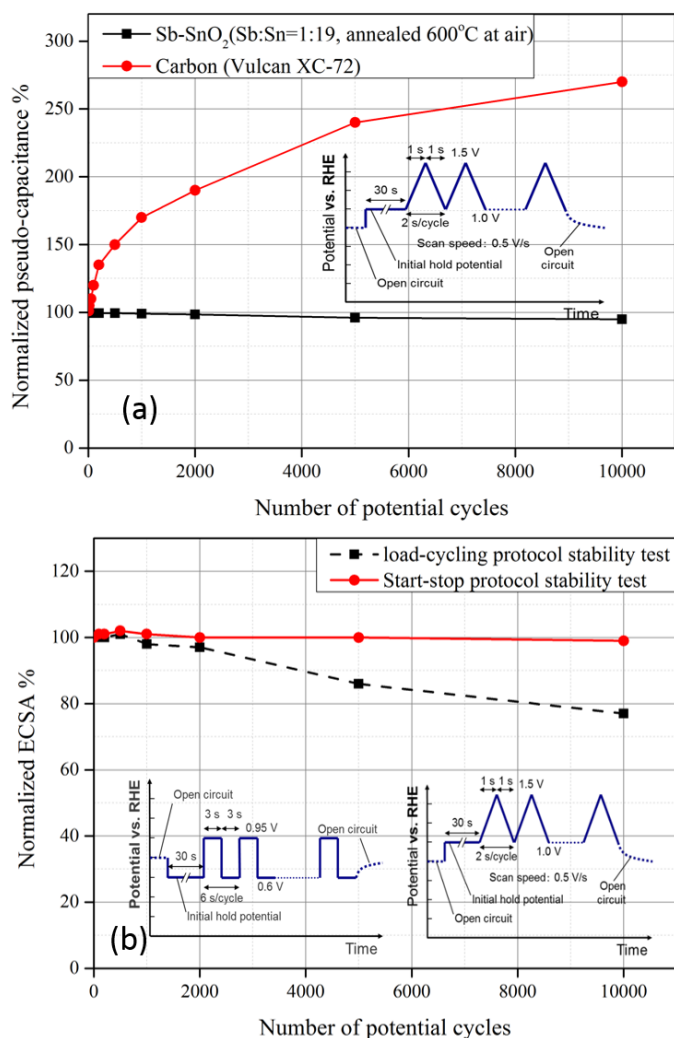

FIGURE 4. Cyclic voltammagrams for Pt/C and Pt deposited onto ATO in N_2-saturated 0.1 M $HClO_4$; sweep rate: 50 mV/s; room temperature

CONCLUSIONS AND UPCOMING ACTIVITIES

We have used DFT to identify several plausible doped-metal-oxide formulations that will provide both high conductivity and provide SMSI. In parallel, we have synthesized high surface area (74 m^2/g) and high conductivity (2.2 S/cm) ATO as a support, and successfully deposited Pt on this support to obtain a catalyst with an ECSA of 75 m^2/g_{Pt}. This catalyst only lost 21% of its original ECSA under the load cycling protocol after 10,000 cycles showing its potential to be stable catalyst under fuel cell operation. Over the next year, we will continue with the synthesis and optimization of ATO support and Pt/ATO catalyst, and its evaluation during PEM fuel cell operation. We will also in parallel prepare Ta-doped-TiO_2 supports and supported catalysts (using the sacrificial support method) and study SMSI in this and other variants suggested by our DTF calculations.

REFERENCES

1. N. Takeuchi; T.F. Fuller, J. Electrochemical Society, 155 (2008) B770–B775.

FIGURE 3. (a) Normalized pseudo-capacitance of carbon and ATO under start-stop potential cycling. (b) Loss of ECSA for Pt deposited onto antimony doped tin oxide under start-stop (support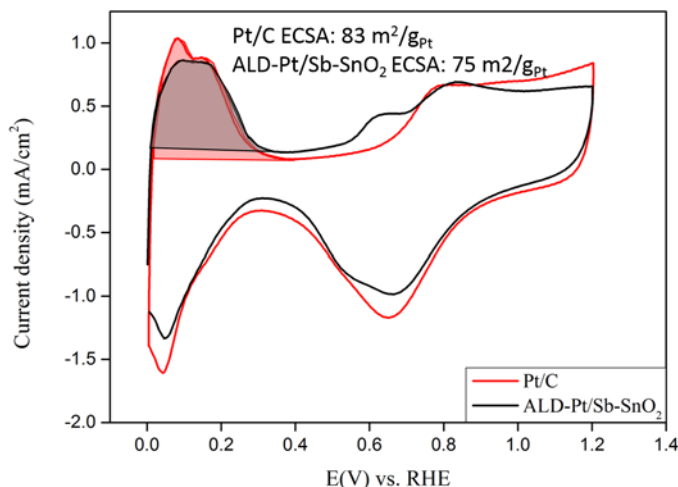 protocol) and load cycling protocols (catalyst protocol).