Corrosion-Resistant Non-Carbon Electrocatalyst Supports for Polymer Electrolyte Fuel Cells

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- Nissan Technical Center, North America, Farmington Hills, MI
- University of California, Irvine, Irvine, CA

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Project End Date: March 31, 2020

Overall Objectives

- Design, develop, and demonstrate high-surface-area (>70 m^2/g), high conductivity (>0.2 S/cm) and corrosion-resistant (as per Funding Opportunity Announcement requirements) non-carbon supports for proton exchange fuel cells (PEFCs) based on doped/mixed metal oxides (that do not contain platinum group metals [PGM]).

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

- Demonstrate stability, activity, and performance approaching the DOE 2020 targets using DOE-prescribed accelerated protocols in rotating disk electrode (RDE) and membrane electrode assembly (MEA) (PEFC) experiments by optimizing the structure of the support and the structure of the electrode.

- Provide DOE with at least six 50-cm^2 MEAs 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) 2019 Objectives

- Synthesize and characterize niobium (Nb)-doped-TiO$_2$ and antimony (Sb)-doped-SnO$_2$.

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

- Investigate SMSI in Pt/doped-metal-oxide systems using X-ray photoelectron spectroscopy and density functional theory (DFT).

- Measure beginning-of-life (BoL) and end-of-life (EoL) oxygen reduction reaction (ORR) activity and electrochemical active surface area (ECSA) of selected catalysts in RDE experiments.

- Optimize electrodes: RDE and MEA.

- Evaluate selected catalysts in a PEFC at Nissan Technical Center, North America: ORR activity and ECSA, and fuel cell performance before and after stability test.

- Revise cost model.

Technical Barriers

- Fuel cell catalyst and catalyst support durability, fuel cell performance (mass activity), and catalyst cost need to be improved, in line with DOE 2020 targets.

Technical Targets

Table 1 shows current status (with commercial Pt/C and with the Pt/RTO [ruthenium dioxide-titanium dioxide] catalyst developed in our previous DOE Office of Energy Efficiency and Renewable Energy project) and the proposed targets for the current project. The preliminary data obtained with our proposed approach (see Table 1, Pt/Pt-aerogel-ATO) 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 toward the DOE 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 toward 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/technical issues and provides a pathway to advance the state of the art and meet the DOE 2020 targets.

FY 2019 Accomplishments

- DFT was used to study the stability and electronic properties of support material and Pt-supported catalyst. The higher conductivity and stability of antimony-doped tin oxide (ATO) was predicted and it was shown that there existed strong metal-support interaction between the support and Pt cluster.

- The Pt/aerogel–niobium-doped titanium oxide (NTO)-based MEA exhibited 26% higher currents at 0.9 V compared to Pt/C. However, MEA stability was suspect.

- The significantly enhanced durability of Pt/ATO improves the lifetime of the catalysts and hence reduces the lifetime costs by 26% compared to Pt/C.

Table 1. Technical Targets

Metric	Units	SoA (Pt/C)*	SoA (Pt/RTO)	Approach Status (Pt/Pt-aerogel-ATO)	End Target	DOE 2020 Target
Total PGM content	g/kW	0.55	0.55	0.25	0.25	<0.125
Total PGM loading	mg/cm^2	0.4	0.4	0.2	0.25	<0.125
Voltage at 1.5 A/cm^2 (air)	mV	0.45	0.48	0.49	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	< 5	<10	30
Voltage loss at 1.5 A/cm^2	mV	182$^+$	20	24	<20	30
Mass activity @ 900 mV$_{iR-free}$	A/mg$_{PGM}$	0.07	0.07	ca. 0.057	0.3	0.44

SoA – state of the art
ATO – antimony-doped-tin-oxide

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

RESULTS

We used the plane wave DFT approach and PBEsol functional to model the crystal structure of SnO_2 and SnO_2 doped with 4% Sb. Our results show that the DFT+U approach correctly predicts that SnO_2 is a semiconductor with a direct band gap of 3.5 eV, which is in excellent agreement with the experimentally determined band gap of 3.6 eV. The band structure calculations also showed that doping SnO_2 with Sb changes the electronic structure of SnO_2 from a direct band gap semiconductor to the one with the n-type metallic character. Due to the change in the metallic character caused by doping, ATO is expected to have higher conductivity than SnO_2. Our analysis of the DFT-calculated projected density of states (PDOS) showed that depositing Pt on Sb-doped SnO_2 shifts the d-band center (ε_d) of Pt by altering its electronic structure (Figure 1a). Energy and electronic structure of Pt deposited on SnO_2 was studied by using three layers of (111) Pt on four layers of (110) or (100) SnO_2 (Figure 1b). The convergence of the results with respect to the number of the Pt/SnO_2 layers was also performed. The ε_d of surface Pt atoms relative to Fermi level (E_F) was determined to shift to more negative values in the following order: Pt (111) on Sb-doped SnO_2 (110) > Pt (111) > Pt (111) on Sb-doped SnO_2(100) (Figure 1c). DFT calculations and analysis of the DOS of Pt (111) and Pt (111) supported on Sb-doped SnO_2 thus show that depositing Pt on ATO (100) lowers the d-band center of Pt by altering its electronic structure. Consequently, a decreased overpotential for ORR is predicted for Pt supported on ATO (100). In addition, due to the lattice mismatch between SnO_2 (100) and Pt (111) (f_a = 14%, f_b = -0.5%) and SnO_2 (110) and Pt (111) (f_a = 15%, f_b = -7%), DFT predicts the formation of grain boundaries on the Pt surface (Figure 1b) leading to the increase in ORR activity [2].

For fuel cell evaluation, $Nb_{0.3}Ti_{0.7}O_2$ was synthesized by the aerogel method and Pt was deposited by the formic acid reduction method. The Pt/aerogel-NTO-based MEA exhibited higher currents at 0.9 V compared to Pt/C, indicating higher catalytic activity. At 0.9 V a kinetic current of 155 mA/mg$_{PGM}$ was recorded on Pt/C whereas Pt/aerogel-NTO exhibited a current of 195 mA/mg$_{PGM}$, a 26% higher performance (Figure 2). Nevertheless, it was observed that Pt/aerogel-NTO lost a greater percentage of its initial activity as compared to Pt/C after 500 cycles stability test (start-stop potential cycles, DOE-recommended support accelerated stress test).
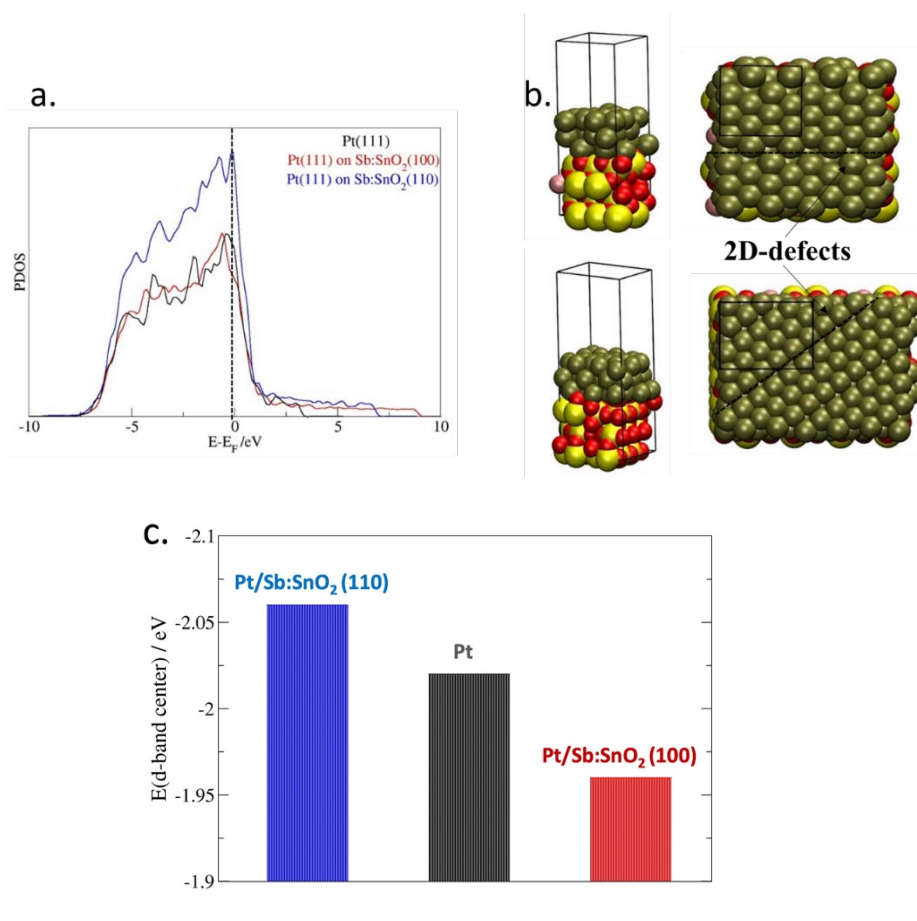
Figure 1. (a) Projected DOS for d-orbitals of Pt (111) supported on Sb-doped SnO$_2$ (100) and Sb-doped SnO$_2$ (110) surfaces; (b) DFT-optimized structure of Pt (111) on Sb-doped SnO$_2$ (100) (top) and Sb-doped SnO$_2$ (110) surface (bottom); and (c) comparison in the center of the d-band calculated for unsupported Pt and Pt supported on Sb-doped SnO$_2$ (110) and Sb-doped SnO$_2$ (100) surface. Red: O, tan: Pt, yellow: Sn, pink: Sb.
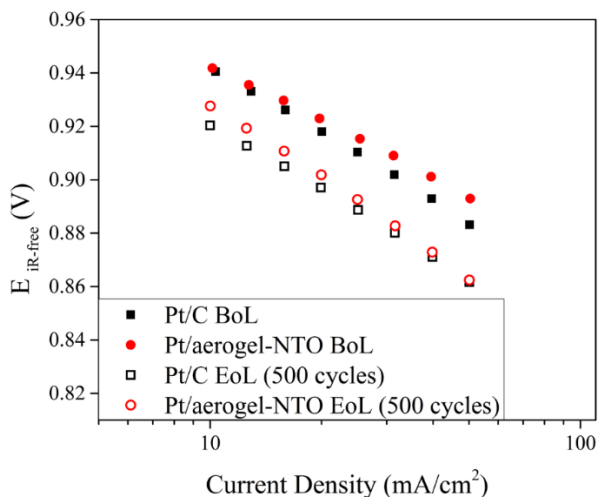

Figure 2. Comparison of fuel cell performance (H$_2$/O$_2$) at the kinetic region of Pt/aerogel-NTO, Pt/C before (BoL) and after (EoL) accelerated stress test over 500 cycles at 80°C, 80% RH, and 200 kPa$_{abs}$. Pt loading at the cathode: 0.20 mg$_{Pt}$/cm^2. Pt loading at the anode: 0.10 mg$_{Pt}$/cm^2.

To understand the different fuel cell performance obtained with different catalysts, scanning electron microscopy was used to study the morphology of the MEA with different catalyst. The Pt/xerogel-ATO MEA (Figure 3) exhibits micrometer-scale catalyst particles on the surface of the catalyst layer leading to non-uniform contact between the cathode and the separator. Lack of contact between the MEA and the separator over large areas results in significant increases in the contact resistance [3]. Thus, Pt/xerogel-ATO MEAs exhibited the highest non-electrode ohmic overpotential. The thinner Pt/xerogel-ATO and Pt/Pt-aerogel-ATO layers (Figure 3) lead to lower proton transfer resistance and more than compensate for the negative effect from lower support electronic conductivity.
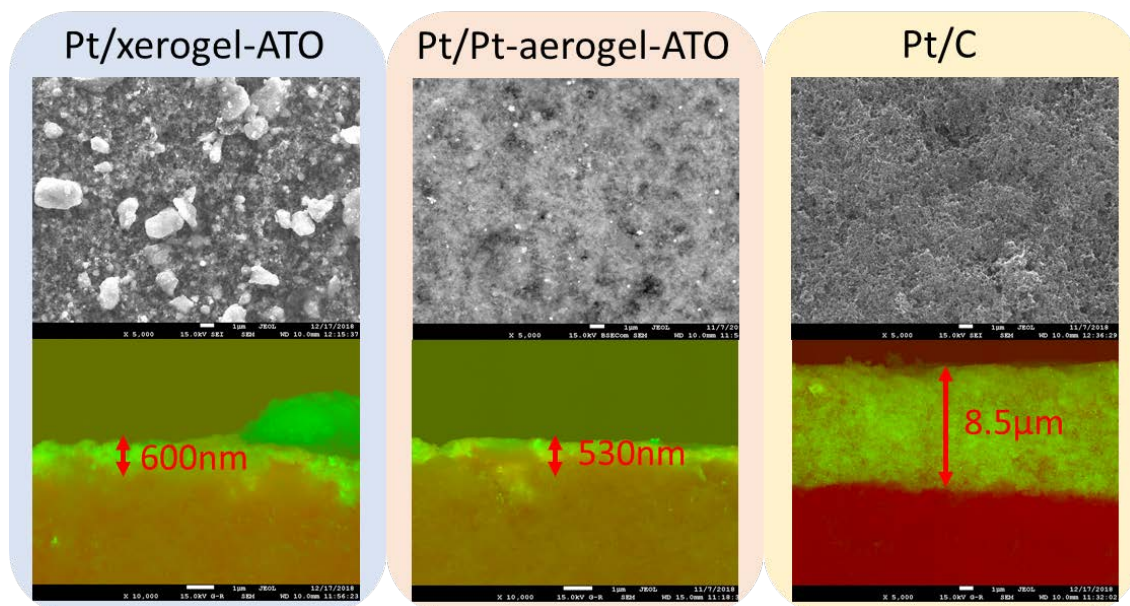

Figure 3. Scanning electron microscopy image of catalyst layer surface and cross section. Highlight green region corresponded to Pt-based catalyst layer.

Material costs for production of Pt/ATO electrodes as compared to Pt/Vulcan XC-72 were evaluated to assess the feasibility of metal oxides as supports for PEMFC catalysts. Figure 4 shows the cathode material cost breakdown. The ATO support is more expensive than the Vulcan XC-72 carbon support, but the total material cost is still dominated by the platinum. The key consideration was to examine the effect of the improved catalyst durability on the lifetime costs of Pt/ATO catalysts compared to Pt/C. The increased support costs reduce the Pt contribution to materials cost from 99% to 93%. Despite the added cost of the support, the significantly enhanced durability of Pt/ATO improves the lifetime of the catalysts and hence reduces the lifetime costs by 26% compared to Pt/C. The various cost components are listed in Table 2 and the impact of the durability is illustrated.

Table 2. Durability Considerations for Cost: Pt/ATO vs. Pt/Vulcan XC-72

	Pt/ATO	Pt/Vulcan XC-72
Cathode Pt loading (mg/cm^2)	0.10	0.10
Rated Power (mW/cm^2)	283	285
Pt	$841.32	$837.48
ATO	$57.05	-
Other	$3.00	$3.44
Total Material Cost ($/stack)	$901.37	$840.91
Total Material Cost ($/kW$_{net}$)	$11.27	$10.51
Durability Factor	1	0.69
Total Material Cost after Durability Considerations ($/kW$_{net}$)	$11.27	$15.23

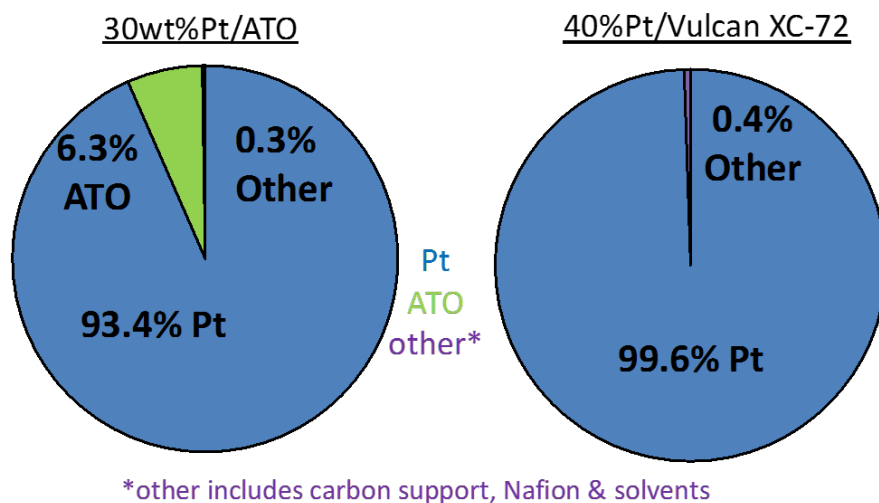*other includes carbon support, Nafion & solvents

Figure 4. Comparison of cathode material cost breakdown for Pt/ATO and Pt/Vulcan

CONCLUSIONS AND UPCOMING ACTIVITIES

- We have used DFT to understand the conductivity and stability of Sb-doped SnO_2 and predicted SMSI in Pt/ATO leading to the increase in ORR activity.

- Fuel cell performance at 0.9 V with Pt/aerogel-NTO was better than that obtained with Pt/C. However, the stability of NTO support still needs to improve to mitigate the change in oxidation state of Nb and Ti during the stability test.

- After considering the durability advantage of Pt/ATO, a preliminary cost model for Pt/ATO showed that one utilizing Pt/ATO costs about 25% less than one with Pt/Vulcan XC-72.

- We plan to deposit Pt alloy using atomic layer deposition. It is expected that atomic layer deposition deposited Pt-alloy catalyst would result in better BoL performance and mass activities.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Cheng He, Shrihari Sankarasubramanian, Ivana Matanovic, Plamen Atanassov, and Vijay Ramani, "Understanding the Oxygen Reduction Reaction Activity and Oxidative Stability of Pt Supported on Nb-Doped TiO_2," *ChemSusChem* 12 (2019): 3468–3480.

2. Cheng He, Xiaofeng Wang, Shrihari Sankarasubramanian, Kaustava Bhattacharyya, Xinhua Liang, and Vijay Ramani, "Atomic Layer Deposition (ALD) of Pt on Sb-SnO2 Nanoparticles Produces Ultra-Stable, Active Catalysts for PEMFC Application," *The Electrochemical Society* Meeting Abstracts.

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2. H. Cheng, S. Liu, Z. Hao, J. Wang, B. Liu, G. Liu, X. Wu, W. Chu, C. Wu, and Y. Xie, *Chem Sci.* 10, no. 21 (2019): 5589–5595.

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