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

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- Plamen Atanasov, University of New Mexico (UNM), Albuquerque, NM

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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 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 2020 targets using DOE-prescribed accelerated tests and protocols 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 (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) 2016 Objectives

- Density functional theory (DFT) calculations to evaluate conductivity and SMSI of relevant doped metal oxides (MO)
- Synthesis and characterization of Tantalum (Ta)-doped-TiO_2 and other doped MO
- High surface area support synthesis by sacrificial support method (SSM)
- Characterization of the doped MOs and derived catalysts
- Electrochemical evaluation of support and Pt/MO stability
- Investigation of SMSI in Pt/doped-metal-oxide systems using X-ray photon spectroscopy
- Measurement of beginning of life, electrochemical active surface area, and oxygen reduction reaction activity of selected catalysts in rotating disk electrode

Technical Barriers

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

(A) Durability

(B) Cost

(C) Performance

Fuel cell catalyst and catalyst support durability need to be improved, in line with DOE 2020 targets.

Technical Targets

Table 1 shows current status (with Pt/C and with Pt/RTO developed in our prior project) and proposed targets. 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, ensure 100% tolerance towards start-stop cycling, and promote SMSI between the support and Pt, which provides us a clear pathway to enhance beginning of life mass activity and stability under load cycling. Hence, the proposed approach addresses remaining challenges or technical issues and provides a pathway to advance the state of the art and meet the DOE 2020 targets.

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	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	% 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 $mV_{iR\text{-}free}$	A mg^{-1}_{PGM}	0.07	0.07	ca. 0.05	0.3	0.44

SOA – State of the art; N/A – Not available

FY 2016 Accomplishments

- DFT calculations have been performed by UNM to examine the effect of doping (with Ta and Nb) of TiO_2 on the conductivity and stability of the resultant doped oxide. The results show that doping with Ta or Nb (at 4% levels) creates an n-type semiconductor with increased conductivity due to "metallization" of the oxide.
- Nb-doped TiO_2, Mo-doped TiO_2, Mo-doped NbO_2, W-doped TiO_2, Ta-doped TiO_2 were successfully synthesized at IIT using sol-gel and hydrothermal methods, their structures probed using X-ray diffraction (XRD), and their conductivities and surface areas measured.
- Nb-TiO_2 was evaluated to have an electron conductivity ≥0.2 S/cm (above the target) and a surface area of 25 m^2/g (marginally below target).
- Using the sacrificial support method at UNM, the surface area of Ta-TiO_2 was shown to be enhanced to 150 m^2/g. We anticipate a similar effect for Nb-TiO_2, which will put us over the target.

INTRODUCTION

Carbon black is an exceptional catalyst support for polymer electrolyte fuel cell (PEFC) electrocatalysts due to its high surface area and high conductivity. However, under fuel cell operation conditions (start-stop), carbon corrodes easily [1]. To address this issue, it is necessary to explore non-carbon supports with high conductivity, high surface areas, 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 supports and supported electrocatalysts for PEFCs. The Pt/MO catalysts should meet the DOE 2020 targets for stability and approach DOE 2020 targets for the beginning of life mass activity and Pt loading.

APPROACH

In this study, as opposed to our prior work, we select the base oxide to be PGM-free oxides that are thermodynamically stable in the operative potential and pH window. Furthermore, we have refined the choice of the base oxide to prioritize those that allow for SMSI. To induce electron conductivity, we will tune the oxide structure by appropriate selection and introduction of a non-PGM dopant atom, selected from among transition metals of similar ionic size, but having an electronic structure designed to promote the n-type doping necessary to induce electronic conductivity and to induce electron donation from the support to the catalyst (SMSI). We view SMSI and support electronic properties as a route to enhance baseline mass activity and minimize platinum dissolution upon load cycling. The effect of composition (doping level) and processing parameters (annealing temperature) on surface area, porosity, electron conductivity, and SMSI with platinum will be evaluated, and tuned to achieve high oxygen reduction reaction activity and stability against Pt dissolution. 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 level. Once suitable combinations are identified and evaluated, we will employ the sacrificial support method pioneered by UNM to prepare the supports with high surface area.

RESULTS

DFT calculations performed by UNM to examine the effect of doping (with Ta and Nb) of TiO_2 on the conductivity and stability of the resultant doped revealed that that doping with Ta or Nb (at 4% doping levels) creates an n-type semiconductor with increased conductivity due to metallization of the oxide (Figure 1). These results lend credence to our doping approach, though DFT studies are still ongoing.

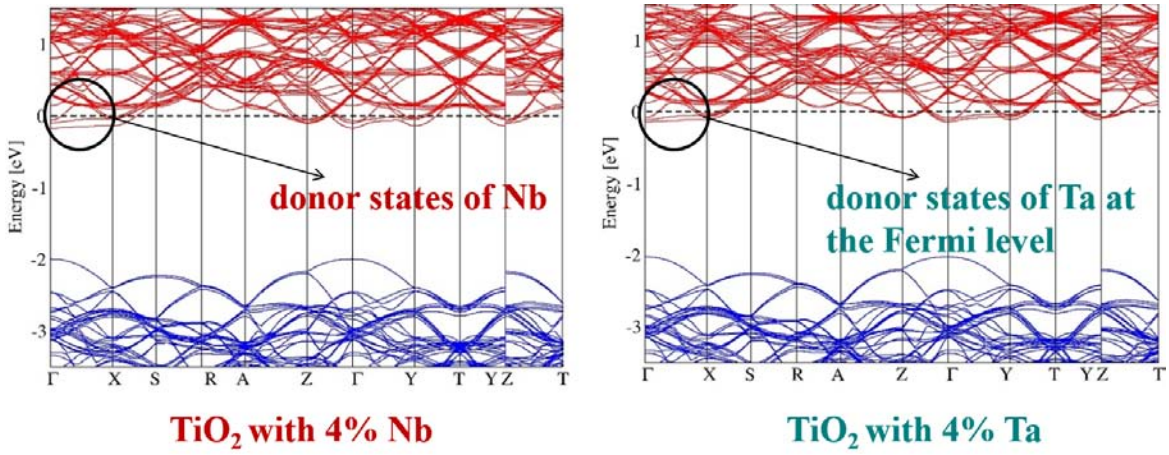

FIGURE 1. DFT modeling for Nb- and Ta- doped TiO_2 materials

We have synthesized Nb-doped-TiO_2, Mo-doped-TiO_2, Mo-doped-NbO_2, W-doped-TiO_2, and Ta-doped TiO_2 doped metal oxides and tested their electronic conductivity (Figure 2) and surface area (Figure 3). The structure of the doped MOs was confirmed through XRD. The dopant levels were set to 30% and 50% mol/mol. From the conductivity measurements we have found that $Nb_{0.3}Ti_{0.7}O_2$ and $Nb_{0.5}Ti_{0.5}O_2$ had conductivities of approximately 0.2 S/cm (commensurate with our target), after suitable processing and annealing. However, at this stage, the Nb-TiO_2 surface area (Figure 3) is still lower (25 m^2/g) than what would be required. Please note though that these were oxides made at IIT by the conventional hydrothermal and sol-gel methods, UNM has, in parallel, been performing syntheses with the sacrificial support method and have shown Ta-doped TiO_2 materials with Brunauer-Emmett-Teller surface areas approaching 150 m^2/g, well above the target. XRD peak analysis (Figure 4) of the SSM-derived supports showed (1) Ta and TiO_2 precursors mixed with silica are highly amorphous, (2) the structure goes from amorphous to crystalline following heat treatment, and (3) TiO_2 transitioned from anatase to rutile phase under annealing at 850°C. From our XRD analysis at IIT we have found that at annealing temperatures below 800°C, the material was composed partially of the anatase phase and that the electronic conductivity was much lower. For annealing temperatures above 800°C the phase transformation to the rutile structure was observed (observation replicated by UNM) and the electronic conductivity reached 0.2 S/cm. Based on these results, we can preliminarily conclude that the rutile phase is required to reach the electronic conductivity required for the milestones, especially for TiO_2-based supports.

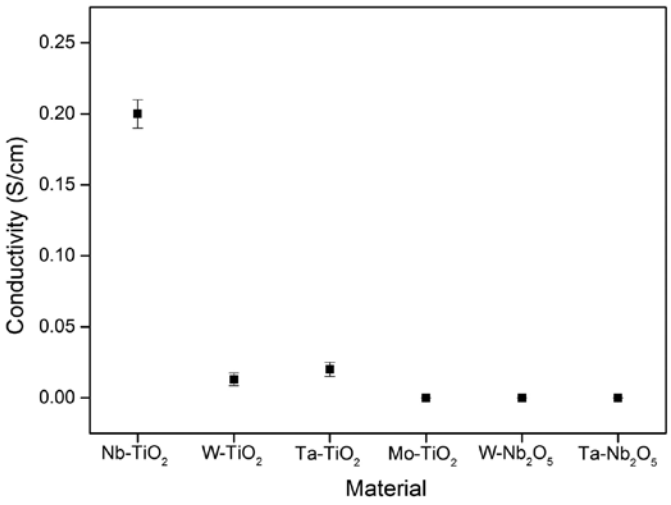

FIGURE 2. Electronic conductivity of different doped supports

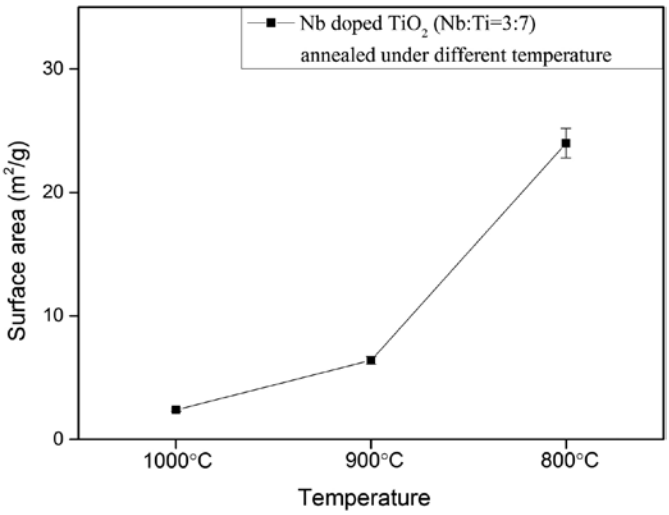

FIGURE 3. Surface area of Nb doped TiO_2 (Nb:Ti = 3:7) under different annealing temperatures

CONCLUSIONS AND FUTURE DIRECTIONS

We have found Nb-TiO_2 materials had conductivities close to or above 0.2 S/cm, and have potential to be conductive catalyst supports. We will continue to evaluate

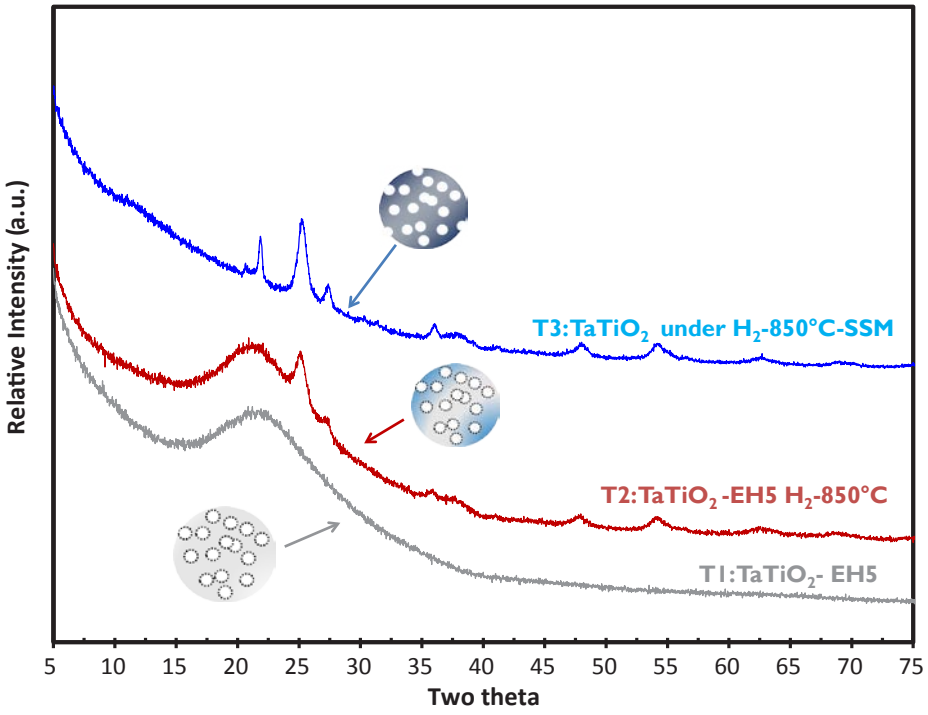

FIGURE 4. XRD patterns of Ta-doped TiO_2 prepared using SSM

these supports (for stability, SMSI, and to enhance surface area and conductivity) using both DFT and experimental methods over the rest of FY 2016.

REFERENCES

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