
High-Performance Non-Platinum-Group-Metal Transition Metal Oxide Oxygen Reduction Reaction Catalysts of Polymer Electrolyte Membrane Fuel Cells

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Overall Objectives

- Identify and develop acid-stable non-platinum-group-metal (non-PGM) oxides with high intrinsic oxygen reduction reaction (ORR) activity.
- Optimize non-PGM metal oxide catalyst particle size and morphology and catalyst interactions with ionomer and support for membrane electrode assembly (MEA) catalyst layers.
- Fabricate an MEA containing non-PGM metal oxide ORR catalyst with performance of 44 mA/cm² at 900 mV_{iR-free} at 80°C.
- Demonstrate electrocatalyst durability according to the Electrocatalyst Cycle Accelerated Stress Test in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1].

Fiscal Year (FY) 2019 Objectives

- Evaluate the acid stability of doped manganese oxides and develop descriptors for acid stability.

- Develop novel acid-stable oxide systems based on computational phase stability predictions and acid stability descriptors.
- Evaluate the activity of acid-stable oxides toward ORR.

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 Plan¹:

- Cost (the use of PGM-free catalysts will reduce the cost of MEAs)
- Performance (performance of PGM-free catalysts must be dramatically improved)
- Durability (inherent acid-stability of PGM-free catalysts will improve durability).

Technical Targets

This project is developing novel acid-stable non-PGM metal oxide ORR electrocatalysts and incorporating the catalysts into MEAs. To date, the team has focused on the development of design rules for acid-stable oxides and evaluated candidate oxides for acid stability and electrochemical performance. Catalysts developed from these studies will be incorporated into MEAs to meet the following DOE MEA performance and durability targets:

- PGM-free catalyst activity: >44 mA/cm² at 900 mV_{iR-free}
- Loss in initial catalytic activity: <40% mass loss
- Loss in performance at 0.8 A/cm²: <30 mV
- Loss in performance at 1.5 A/cm²: <30 mV
- Electrocatalyst support stability: <40% mass activity loss.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Evaluated the acid stability of manganese-based oxides and developed descriptors for acid stability.
- Developed a diverse class of acid-stable oxides based on rutile antimony oxide.
- Demonstrated stable ORR activity from an acid-stable transition metal antimony oxide.

INTRODUCTION

The ORR catalyst is a major cost driver for polymer electrolyte membrane (PEM) fuel cells due to the use of PGMs, requiring the development of catalysts with reduced PGM loading or no PGMs [1]. However, the performance and durability of PGM-free electrocatalysts must be dramatically improved to replace the use of PGM catalysts. Currently, research has focused on the development of carbon-based non-noble-metal catalysts (M/N/C catalysts) [2]. This project focuses on the development of alternative non-PGM metal oxide ORR electrocatalysts.

To date, acid-stable PGM-free transition metal oxide ORR catalysts have demonstrated low performance. This poor performance may be attributed to the limited range of simple metal oxides that are known to be stable under acidic conditions [3]. However, it has been shown that the stability of bulk solid phases toward acidic conditions can be significantly influenced by the addition of dopants to form complex metal oxides containing several metal ions with variable ratios [4]. Such complex metal oxides exhibit high performance for ORR catalysis at high temperatures in solid oxide fuel cells and in alkaline conditions at room temperature [5]. This creates the possibility that complex, multi-component metal oxides may be discovered that are both acid stable and have high activity toward oxygen reduction under acidic conditions through a rational design approach to complex oxides, the focus of this project.

APPROACH

The project will develop acid-stable PGM-free transition metal oxide ORR catalysts from first principles to incorporation into MEAs. This will be accomplished with a multi-step approach: (1) materials modeling and experimental screening to identify acid-stable oxides with high ORR activity, (2) optimization of catalyst particle size and catalyst/carbon/ionomer catalyst layer composition, and (3) fabrication of MEAs for performance and durability testing. The first step will be accomplished by a combination of computational and experimental screening. Intrinsic ORR catalytic activity will be established experimentally by electrochemical characterization, culminating in design rules to predict acid stability and activity and an optimized ORR catalyst. The initial phase of this step was performed during FY 2019.

The second step, optimizing inks for identified ORR catalysts to be used for spray coating onto MEAs, will be accomplished by optimizing the particle size of the ORR catalysts and optimization of the catalyst/carbon/ionomer composition of the ink with rapid assessment of the performance impacts through electrochemical characterization. In the final step, MEAs will be fabricated and in-cell performance will be evaluated on a PEM fuel cell test stand. The microstructure of the catalyst layer will be modeled to determine primary performance losses and determine potential mitigation pathways. The MEAs will be durability tested according to the accelerated stress tests protocols for electrocatalyst and catalyst layer durability.

RESULTS

Evaluation of the Acid Stability of Manganese-Based Oxides and Development of Descriptors for Acid Stability

The acid stability of Mn-based oxides with a wide range of chemistry, structures, and Mn oxidation states was evaluated by comparison of computational properties of the bulk oxide phases with experimental dissolution into 0.5 M HNO₃ over a 24 h period normalized to the surface area of the oxide, an estimate of the intrinsic (in)stability of the oxides. Formation energies of bulk O and Mn vacancies for each of the oxides was computed under acidic conditions using methodology developed previously [6, 7]. Density functional theory (DFT) calculations of the formation energies of O and Mn vacancies demonstrated a strong correlation between the calculated Mn vacancy formation energy and the dissolution of the oxide in acid (Figure 1a).

The formation energies of vacancies are physically connected to the electronic structures of metal oxides. Previous studies [8, 9] have suggested that the formation of vacancies in oxides can be understood by two energetics: (1) the formation enthalpies of oxides (i.e., the metal-ligand bond strength) and (2) energy penalty for electron redistribution (e.g., the energy difference between O 2p bands and Fermi levels). When Mn vacancies are formed, electron redistribution is calculated to be nearly independent of the oxide composition, suggesting that the Mn vacancy formation energy can be rationalized as increasing as the Mn-O bond strength increases, calculated as the difference between the M 3d and O 2p band centers (Figure 1b). The Mn-O bond energy, in turn, increases with increasing nominal Mn oxidation state (Figure 1c).

Apart from the Mn-O bond strength and the formation energy of Mn or O vacancies, surface acid-base chemistry also plays an important role in the (in)stability of metal oxides. Surface protonation has been shown as a crucial step in the dissolution of many compounds in aqueous solutions [10, 11], and the thermodynamic tendency of such protonation is described by the surface acidity/basicity of metal oxides, which can be estimated by their Fermi levels on the absolute energy scale [12]. Having a higher energy Fermi level indicates a higher oxide surface nucleophilicity, to a first-order approximation, which leads to easier surface protonation. This property also varies with Mn oxidation state with surface nucleophilicity decreasing with increasing Mn oxidation state, reinforcing the trends in Figure 1.

Mn-O bond strength and/or Mn oxidation states have been identified as key descriptors that interrelate the bulk electronic structures and the (in)stability of Mn oxides in acid. The trend in acid stability is most accurately described by the bulk Mn vacancy formation energy. This understanding of bulk (in)stability of oxides in acidic conditions will be utilized to design future generations of Mn oxide ORR catalysts with better stability in acidic electrolytes, and these analyses may be extended to more complex oxide systems.

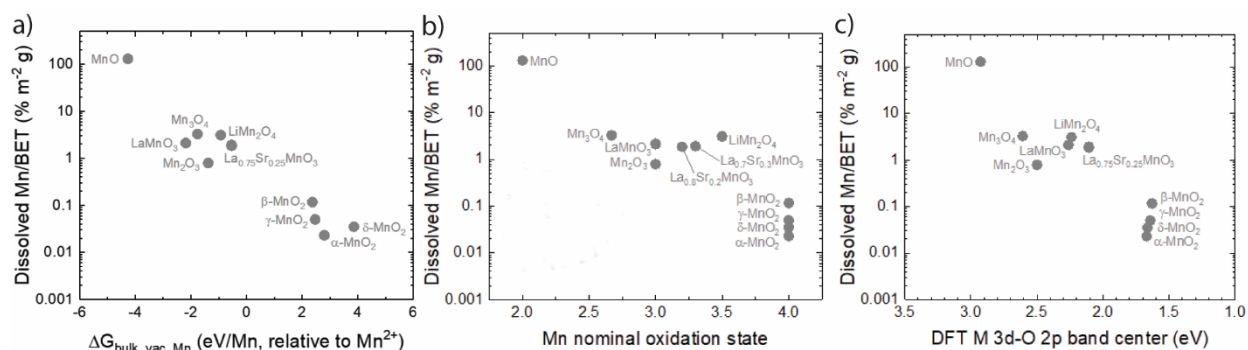


Figure 1. Mn dissolution relative to (a) Mn vacancy formation energy, (b) Mn nominal oxidation state, and (c) difference between DFT M 3d and O 2p band centers

Subsection Development of a Diverse Class of Acid-Stable Oxides Based on Rutile Antimony Oxide

Metal antimony oxides have been identified as promising manganese- and cobalt-containing acid-stable oxides with potential electrocatalytic activity [4, 13]. Other studies have shown that a rutile-type phase (with general stoichiometry of MO₂) is the most stable phase for these materials, in which the metal and antimony ions are randomly disordered over the single cation crystallographic site. It was demonstrated that at least three elements may be disordered over the crystallographic site, with a range of possible oxidation states from 2 to 5 [14]. To examine the range of possible elemental compositions that rutile-type structures may be formed and determine under what conditions each element may not dissolve into acidic solutions, a series of metal antimony oxides were formed with up to six additional metal ions from Cr, Mn, Fe, Co, Zn, In, Ti, Sn, and V using standard high-temperature solid-state syntheses. The sample Mn_{0.33}Fe_{0.33}Cr_{0.33}Ti_{0.33}V_{0.33}Sn_{0.33}SbO₆ is the first example of a high entropy rutile-phase oxide, and it demonstrates the wide range of elements that may be present on the same crystallographic site at the same time (Figure 2).

Utilizing the design rules for acid stability, high-oxidation-state Mn-bearing antimony oxides were prepared with nominal compositions of MnSnSbO_6 and MnFeTiSbO_8 , in which the oxidation state Mn is nominally expected to be 3+ and 4+, respectively. Although MnFeTiSbO_8 forms a two-phase material containing Mn_2O_3 in addition to a rutile-type phase, both materials passed a dissolution screening test in which 2% or less of each metal ion dissolved over a 24 h period in 0.5 M H_2SO_4 , suggesting the presence of the rutile antimony oxide phase may stabilize manganese oxides toward dissolution. These studies demonstrate the capability of rational design of acid-stable metal antimony oxides.

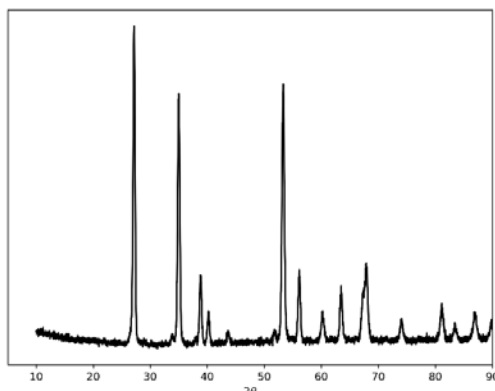


Figure 2. X-ray diffraction diffractogram of $\text{Mn}_{0.33}\text{Fe}_{0.33}\text{Cr}_{0.33}\text{Ti}_{0.33}\text{V}_{0.33}\text{Sn}_{0.33}\text{SbO}_6$

Demonstration of Stable ORR Activity from an Acid-Stable Transition Metal Antimony Oxide

The ORR specific activity of metal antimony oxides screened for acid stability was measured using rotating disk electrode techniques and compared to the activity of manganese oxides. An electrochemical activity of $0.2 \mu\text{A}/\text{cm}^2_{\text{oxide}}$ that was stable over 1 h was measured at 0.8 V vs. reversible hydrogen electrode for MnFeTiSbO_8 . This activity is higher than the long-term activities of $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$ but less than the $2 \mu\text{A}/\text{cm}^2_{\text{oxide}}$ measured for $\beta\text{-MnO}_2$. With further improvements in the electrical conductivity of the oxide and post-processing to enhance the concentration of Mn on the surface of the oxide, the target activity of $4.4 \mu\text{A}/\text{cm}^2_{\text{oxide}}$ at 0.9 V vs. reversible hydrogen electrode may be achievable.

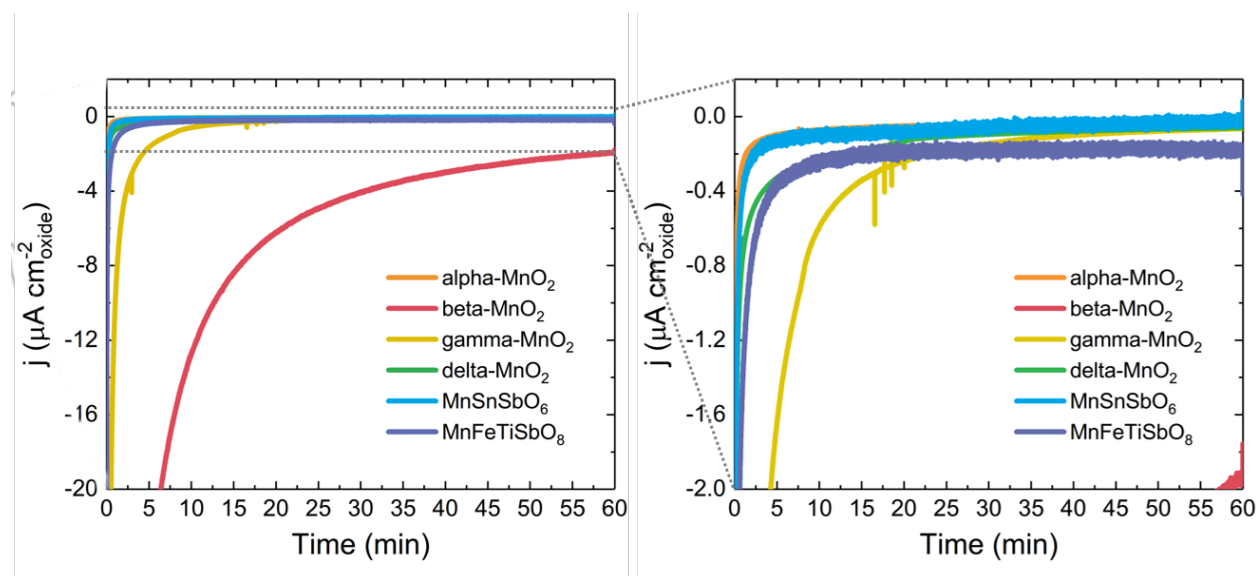


Figure 3. Intrinsic electrochemical activity of manganese oxides and Mn-bearing antimony oxides

CONCLUSIONS AND UPCOMING ACTIVITIES

This work has established descriptors for the acid stability of manganese-based oxides, which will form the foundation to design novel acid-stable oxide materials. In the upcoming activities, the generality of these descriptors to alternative oxide systems will be examined. This work has also established broad compositional variety in the rutile metal antimony oxide system with high acid stability. This compositional space is being explored for high ORR electrochemical activity combined with high acid stability. In upcoming activities, identified electrochemically active acid-stable oxides will be incorporated into MEAs with the potential to form high-performance, durable non-PGM MEAs to meet the DOE 2020 technical targets.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Timothy C. Davenport, “High Performance Non-PGM Transition Metal Oxide ORR Catalysts of PEMFCs,” presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 29, 2019).

REFERENCES

1. DOE Fuel Cell Technologies Office, “3.4 Fuel Cells,” *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan* (2016), DOE Fuel Cell Technologies Office, “3.4 Fuel Cells,” *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan* (2016), <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>
2. Minhua Shao, Qiaowan Chang, Jean-Pol Dodelet, and Regis Chenitz, “Recent Advances in Electrocatalysts for Oxygen Reduction Reaction,” *Chemical Reviews* 116 (2016): 3594–3657, <https://doi.org/10.1021/acs.chemrev.5b00462>.
3. Zhongwei Chen, Drew Higgins, Aiping Yu, Lei Zhang, and Jiuju Zhang, “A Review on Non-precious Metal Electrocatalysts for PEM Fuel Cells,” *Energy & Environmental Science* 4 (2011): 3167–3192, <https://doi.org/10.1039/C0EE00558D>.
4. Lan Zhou, Aniketa Shinde, Joseph H. Montoya, Arunima Singh, Sheraz Gul, Junko Yano, Yifan Ye, Ethan J. Crumlin, Matthias H. Richter, Jason K. Cooper, Helge S. Stein, Joel A. Haber, Kristin A. Persson, and John M. Gregoire, “Rutile Alloys in the Mn-Sb-O System Stabilize Mn³⁺ To Enable Oxygen Evolution in Strong Acid,” *ACS Catalysis* 8 (2018): 10938–10948, <https://doi.org/10.1021/acscatal.8b02689>.
5. Jin Suntivich, Hubert A. Gasteiger, Naoaki Yabuuchi, Haruyuki Nakanishi, John B. Goodenough, and Yang Shao-Horn, “Design Principles for Oxygen-Reduction Activity on Perovskite Oxide Catalysts for Fuel Cells and Metal-Air Batteries,” *Nature Chemistry* 3 (2011): 546–550, <https://doi.org/10.1038/NCHEM.1069>.
6. Kristin A. Persson, Bryn Waldwick, Predrag Lazic, and Gerbrand Ceder, “Prediction of Solid-Aqueous Equilibria: Scheme to Combine First-Principles Calculations of Solids with Experimental Aqueous States,” *Physical Review B* 85 (2012): 235438, <https://doi.org/10.1103/PhysRevB.85.235438>.
7. Xi Rong and Alexie M. Kolpak, “Ab Initio Approach for Prediction of Oxide Surface Structure, Stoichiometry, and Electrocatalytic Activity in Aqueous Solution,” *Journal of Physical Chemistry Letters* 6 (2015): 1785–1789, <https://doi.org/10.1021/acs.jpcclett.5b00509>.
8. Ann M. Deml, Aaron M. Holder, Ryan P. O’Hayre, Charles B. Musgrave, and Vladan Stevanovic, “Intrinsic Material Properties Dictating Oxygen Vacancy Formation Energetics in Metal Oxides,” *Journal of Physical Chemical Letters* 6 (2015): 1948–1953, <https://doi.org/10.1021/acs.jpcclett.5b00710>.
9. Ann M. Deml, Vladan Stevanovic, Christopher L. Muhich, Charles B. Musgrave, and Ryan O’Hayre, “Oxide Enthalpy of Formation and Band Gap Energy as Accurate Descriptors of Oxygen Vacancy Formation Energetics,” *Energy & Environmental Science* 7 (2014): 1996–2004, <https://doi.org/10.1039/C3EE43874K>.
10. Eric Laarz, Boris V. Zhmud, and Lennart Bergström, “Dissolution and Deagglomeration of Silicon Nitride in Aqueous Medium,” *Journal of the American Ceramic Society* 83 (2004): 2394–2400, <https://doi.org/10.1111/j.1151-2916.2000.tb01567.x>.

11. Bettina Zinder, Gerhard Furrer, and Werner Stumm, “The Coordination Chemistry of Weathering: II. Dissolution of Fe(III) Oxides,” *Geochimica et Cosmochimica Acta* 50 (1986): 1861–1869, [https://doi.org/10.1016/0016-7037\(86\)90244-9](https://doi.org/10.1016/0016-7037(86)90244-9).
12. J. Portier, P. Poizot, G. Campet, and M.A. Subramanian, “Acid-Base Behavior of Oxides and Their Electronic Structure,” *Solid State Sciences* 5 (2003): 695–699, [https://doi.org/10.1016/S1293-2558\(03\)00031-1](https://doi.org/10.1016/S1293-2558(03)00031-1).
13. Ivan A. Moreno-Hernandez, Clara A. MacFarland, Carlos G. Read, Kimberly M. Papadantonakis, Bruce S. Brunshwig, and Nathan S. Lewis, “Crystalline Nickel Manganese Antimonate as a Stable Water-Oxidation Catalyst in Aqueous 1.0 M H₂SO₄,” *Energy & Environmental Science* 10 (2017): 2013–2018, <https://doi.org/10.1039/c7ee01486d>.
14. Grażyna Dąbrowska, Elżbieta Filipek, and Mateusz Piz, “A New Ceramic Continuous Solid Solution in the CrSnSbO₆-FeSnSbO₆ System and Some of its Properties,” *Ceramics International* 41 (2015): 12560–12567, <http://dx.doi.org/10.1016/j.ceramint.2015.06.071>.