High Performance non-PGM Transition Metal Oxide ORR Catalysts of PEMFCs

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Raytheon Technologies

ElectroCat Consortia Project
Project ID: **FC306**
DE-EE0008420

2020 Hydrogen and Fuel Cells Annual Merit Review

Overview

Timeline

Project Start: March 2019

Project BP1: March 2019 – August 2020

Project End: August 2021*

* Project continuation and direction determined annually by DOE

Budget

Total Project Budget:	$1,250K
- Federal Share	$1,000K
- Cost Share (20%)	$250K
Total DOE Funds Spent*:	**$473K**

*** as of 5/27/2020**

Barriers Addressed

- Low performance for PGM-free oxygen reduction reaction catalysts for PEMFCs

Target I.D. #	Characteristic	Units	2020 Targets
FC-4	Loss in initial catalytic activity	% mass loss	< 40
FC-5	Loss in performance at 0.8 A cm^{-2}	mV	< 30
FC-8	PGM-free catalyst activity	A cm^{-2} at 900 $mV_{iR\text{-}free}$	> 0.044

Funded Partners

Massachusetts Institute of Technology

Relevance

Objective: Develop *acid-stable non-PGM metal oxides* and *optimize oxide catalytic activity for ORR reactivity.*

	Barrier	Approach	2020 Impact
A	Durability	Focusing on improving the acid stability of novel materials will lead to higher durability materials for PEMFCs	• Acid-stability descriptors developed based on manganese oxides • Family of acid-stable antimony-based oxides developed
B	Cost	Development of non-PGM electrocatalysts is a key approach to reducing PEMFC cost	• Project focuses on Mn-based oxide materials that do not contain PGMs
C	Performance	Optimize the catalytic activity by the doping of acid-stable oxides with multiple metal cations to fill multiple roles including stability, catalytic activity, and electronic conductivity	• Evaluated electrocatalytic activity of Mn-based oxides

Approach

Develop acid-stable non-PGM metal oxides

- Identify descriptors for acid-stability to guide prediction of acid stable oxides
- DFT calculation of phase stability of doped metal oxides of interest as potential acid stable oxides

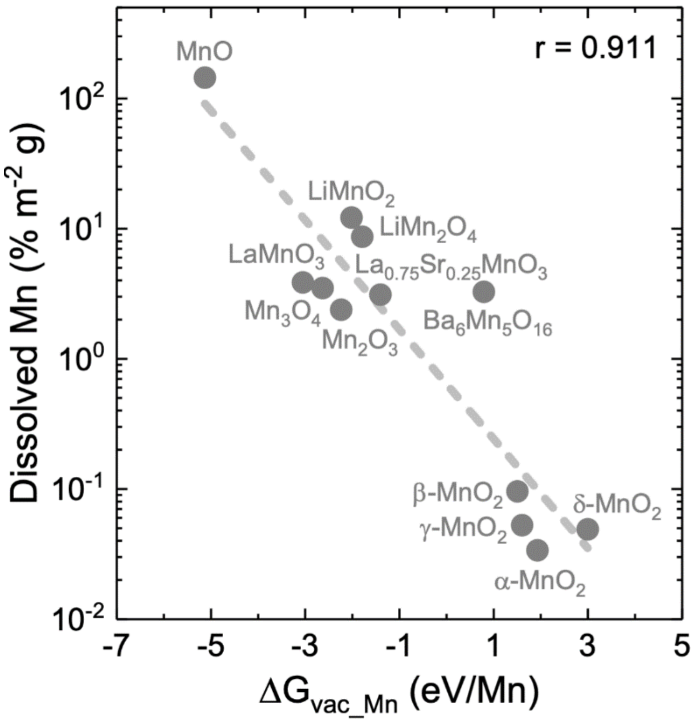
Optimize oxide catalytic activity for ORR

- Electrochemical characterization to determine intrinsic activity of novel materials
- Optimize material synthesis for high surface area
- Optimize catalyst layer composition with high-throughput ink formulations

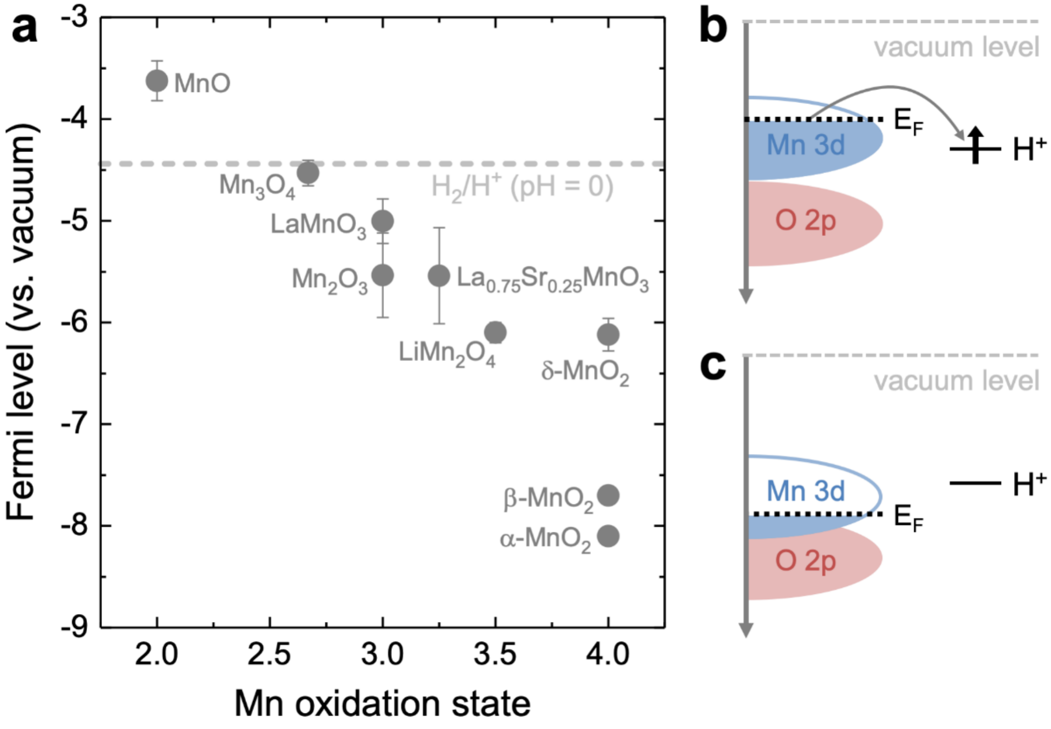
Project Milestones	Original Planned	Revised Planned	Percent Complete	Notes
Subcontracts completed	5/31/2019		100%	Completed
Evaluation of Acid Stability of A_xMnO_2	5/31/2019		100%	No doped MnO_x have been found to be acid stable under ORR conditions
Evaluation of Intrinsic ORR Activity of Acid-Stable A_xMnO_2	8/31/2019		100%	Evaluated activity of most acid-stable MnO_x systems – proceeding to 2nd generation oxides
Demonstrate intrinsic ORR activity $\geq 0.5\ \mu A\text{-}cm^{-2}_{oxide}$ at 0.9 V (iR-free) with acid stable oxide	8/31/2019	8/31/20	50%	Activity observed, but not with demonstrated acid stability
Optimize Catalyst Layer Composition with best catalyst developed	11/30/2019	8/31/20	0%	
Demonstrate intrinsic ORR activity $\geq 4.4\ \mu A\text{-}cm^{-2}_{oxide}$ at 0.9 V (iR-free) with an acid stable oxide	11/30/2019	8/31/20	0	
Demonstrate MEA with performance of 0.025 $A\text{-}cm^{-2}$ at 0.9 V (iR-free) under 1 atm O_2 and 80 °C	**2/29/2020**	**8/31/20**	**0%**	**Go/No-Go**

Progress: Acid Stability Descriptors

Mn vacancies are energetically preferred over O vacancies



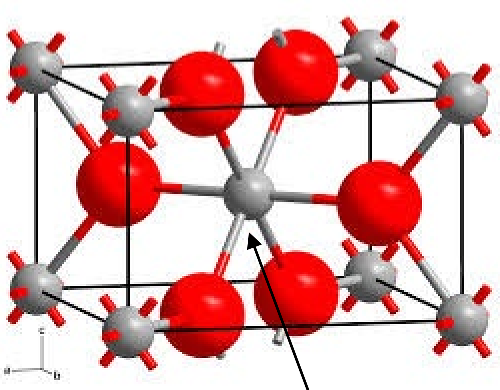
Less acidic surface favors the attack of proton, where protonation weakens surface Mn-O bonds



Acid stability descriptor developed for manganese oxides, indicating high stability of high oxidation state manganese oxides.

Identified rutile phase as a target for Mn-based acid stable oxides (β-MnO$_2$).

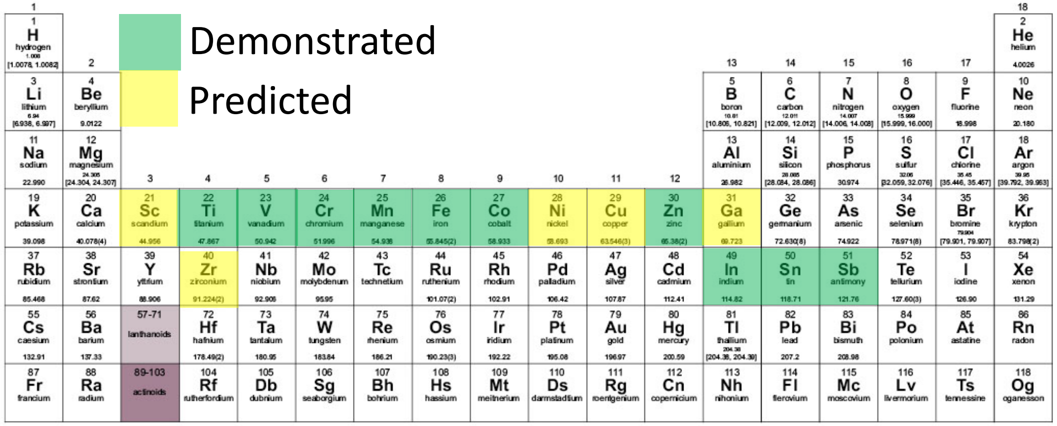
Progress: Acid Stabile Rutile Structures



½ Sb^{3+}, ½ Sb^{5+}

Overview:

Sb_2O_4 is a mixed valent (Sb^{III}, Sb^{V}) oxide
Sb^{III} and Sb^{V} are randomly disordered on the single crystallographic metal ion site (4+ site charge)



🟩 Demonstrated

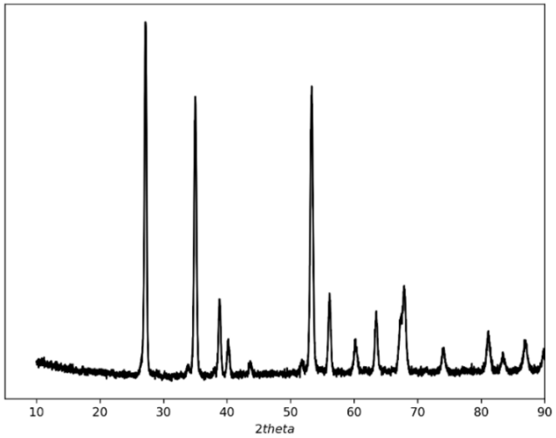
🟨 Predicted

Substitutional variation:

- Sb^{III} can be substituted with 2+ and 3+ ions
- Sb^{V} can be substituted with 5+ ions
- Miscible with other rutile materials (4+ ions)

High entropy oxides:

- Structure can stabilize disordering of up to 7 elements (demonstrated) at once
- Structure can accommodate wide range of ionic radii (68 – 94 pm)



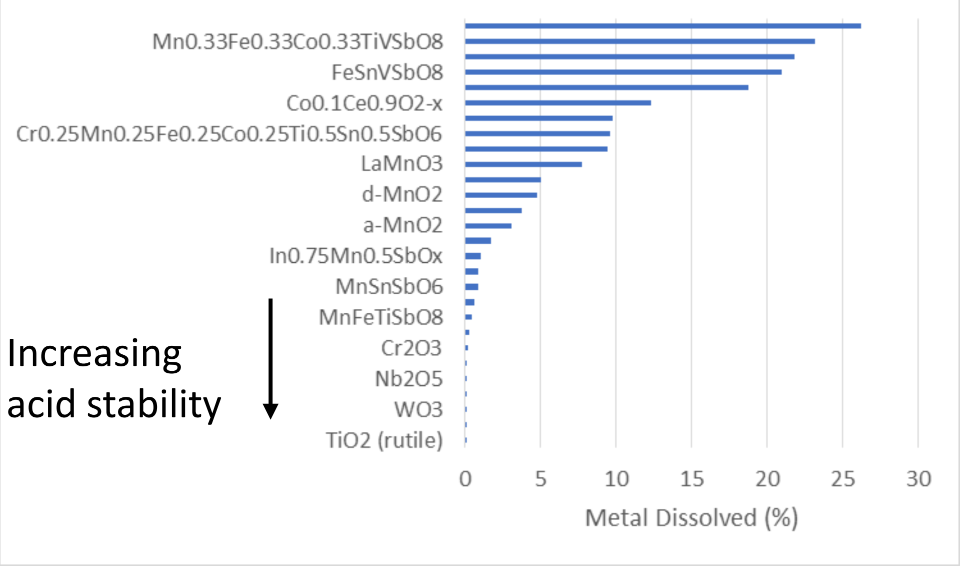
$Cr_{0.33}Fe_{0.33}Mn_{0.33}Ti_{0.33}Sn_{0.33}V_{0.33}SbO_6$

Progress: Acid Stability Rutile Structures

Acid Stability:

- Rutile antimony oxides stabilize 3+ ions towards acidic attack
- Stabilized ions include Mn^{3+}, Fe^{3+}, In^{3+}
- Other stable elements can be added (Ti^{4+}, Cr^{3+}, Sn^{4+})

Dissolution in 0.5 M H_2SO_4



Electronic Conductivity:

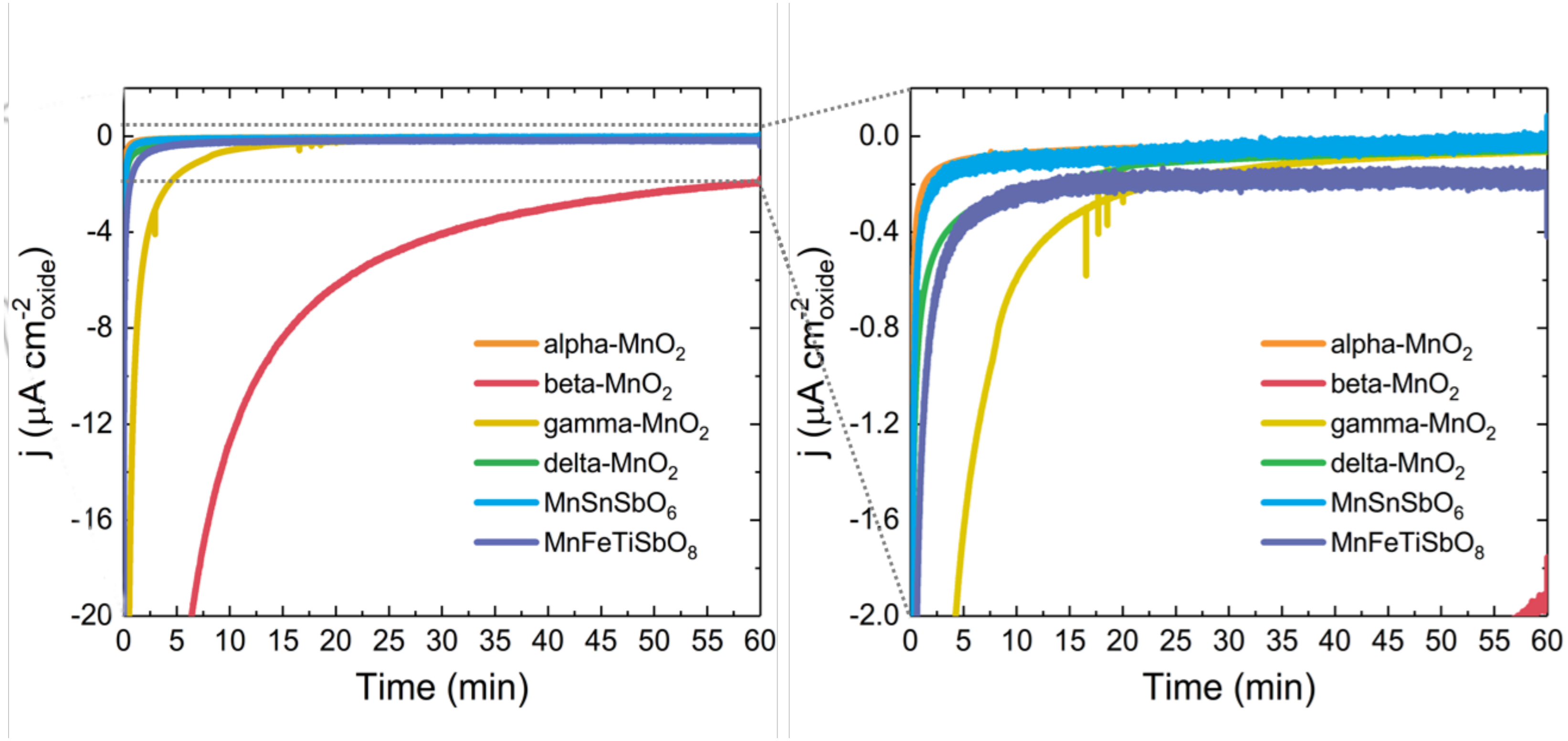
- Conductivity can be enhanced by addition of In^{3+} or Zn^{2+}

	Conductivity (mS-cm^{-1})
$InSbO_4$	220
$In_{0.75}Mn_{0.5}SbO_x$	230
MnO_2	0.005

Challenges:

- Incorporation of Mn^{4+} preferred but synthesis is challenging due to reduction
- Current Sb-based materials have low ORR activity

Progress: Electrochemical Activity



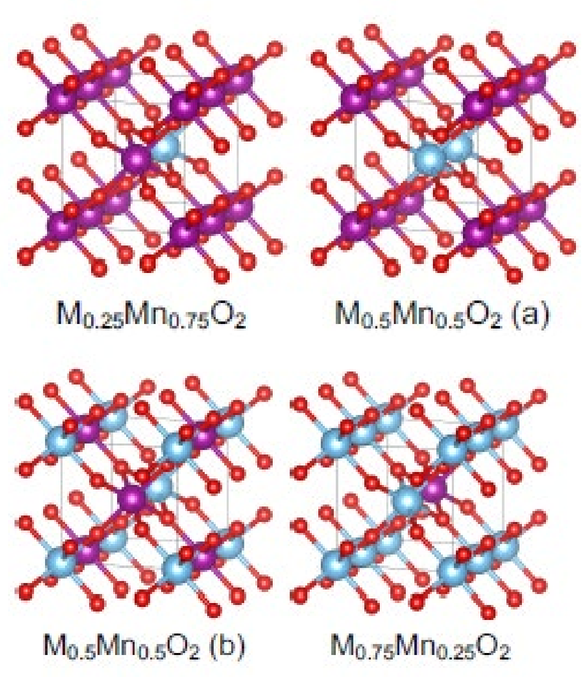
Activity of β-MnO_2 is significant over a 1-hour hold at 0.9 V (~2 µA-cm^{-2} vs. initial target 0.5 µA-cm^{-2}, final target 4.4 µA-cm^{-2})

Further durability not yet demonstrated

Mn-doped Sb-oxides are acid stable, but have low electrochemical activity to date.
Increasing Mn content (doped Mn oxide) is expected to demonstrate higher electrocatalytic activity

Progress: Computed Doped Mn Oxides

Structures Considered:



$M_{0.25}Mn_{0.75}O_2$ $M_{0.5}Mn_{0.5}O_2$ (a)

$M_{0.5}Mn_{0.5}O_2$ (b) $M_{0.75}Mn_{0.25}O_2$

Materials Computed:

B-MnO_2 with the following substituents:

Active metals: Co, Fe, Ni

Stabilization: Ti, Cr, Sb, Sn, W, Nb, Cd, Ga

Conductivity: Zn, In

Predicted stable materials:

Likely ($\Delta\phi_{hull} < 0.1$ eV/atom):

$Sb_xMn_{1-x}O_2$ (x = 0.25, 0.5)

$Nb_xMn_{1-x}O_2$ (x = 0.25, 0.5)

Possible ($0.1 < \Delta\phi_{hull} < 0.2$ eV/atom):

$Ti_xMn_{1-x}O_2$ (x = 0.25, 0.5, 0.75)

$Fe_xMn_{1-x}O_2$ (x = 0.25, 0.5)

$Sn_xMn_{1-x}O_2$ (x = 0.25, 0.5, 0.75)

$W_xMn_{1-x}O_2$ (x = 0.25, 0.5)

$Co_xMn_{1-x}O_2$ (x = 0.25, 0.75)

DFT stability calculations for a range of ternary manganese oxides were performed to determine further acid stable synthesis targets.

Responses to Reviewer’s Comments

“The project offers an alternative to the highly unstable metal nitrogen-doped carbon catalyst. If successful, this project might have significant impact on DOE technical targets.”

“The Go/No-go should include simultaneously demonstrating voltage performance and acid stability with the same formulation.”

- The project team agrees with this assessment.

“There is a lack of evidence that complex oxides can be active, stable, and conductive under the relevant conditions for PEMFCs”

- The project team has identified oxides that are both stable and conductive under relevant conditions and are working to increase the activity.

Collaborations

First principles design to membrane-electrode assembly

Subcontractor, University

Massachusetts Institute of Technology

PI: Prof. Yang Shao-Horn

- Oxide optimization for acid stability
- ORR Electrocatalytic performance optimization of acid-stable oxides

Prime, Industry

Raytheon Technologies

PI: Tim Davenport

- Catalyst Layer Optimization
- MEA Fabrication
- MEA Performance and Durability Testing

Electrocat Consortium:

Collaborator: Dr. Deborah Myers

- High-throughput synthesis of doped oxides

Challenges and Barriers

- **Challenge:** Identifying an oxide with sufficient electrocatalytic activity to meet the project goals has not yet been achieved. Successful identification of such a material is necessary to meet the Go/No-go milestone.

- **Planned Resolution:** The project team obtained a no-cost extension to meet the electrocatalyst targets.

- **Challenge:** Integration of the electrocatalyst material into a membrane-electrode assembly has not begun.

- **Planned Resolution:** The project team will leverage the high-throughput capabilities of the Electrocat consortium to optimize the MEA fabrication.

Proposed Future Work

Project Milestones	Schedule
Demonstrate intrinsic ORR activity ≥ 4.4 μA-cm$^{-2}_{oxide}$ at 0.9 V (iR-free) with an acid stable oxide	8/31/2020
Demonstrate MEA with performance of 0.025 A-cm^{-2} at 0.9 V (iR-free) under 1 atm O_2 and 80 °C	**8/31/20**
Demonstrate MEA with PGM-free ORR catalyst that meets targets FC-4 and FC-5 under "Electrocatalyst Cycle" AST protocol.	2/28/21
Demonstrate MEA with PGM-free ORR catalyst that meets targets FC-6 and FC-7 under "Catalyst Support Cycle" AST protocol.	5/31/21

- High-throughput techniques will be leveraged to synthesize targeted acid-stable oxide materials
- As identification of a highly active electrocatalyst is critical, alternative electrocatalyst materials will be considered in place of an oxide.

Any proposed future work is subject to change based on funding levels

Summary

- Discovery of acid-stable metal oxides with catalytically active elements has the potential for breakthrough ORR electrocatalytic performance
- Descriptors for acid stability have been developed to aid acid-stable oxide electrocatalyst identification
- A family of antimony-based rutile oxides has been developed exhibiting acid-stability and a wide composition space. Conductive oxide materials were identified.

Go/No-Go Technical Target:

Demonstrate MEA with performance of 0.025 A-cm^{-2} at 0.9 V under 1 atm O_2 and 80 °C

MYRD&D Targets Addressed:

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Develop durable MEAs with PGM-free metal oxide ORR catalysts

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Electrocat Consortium