

# **Overview of Proton Exchange Membrane Electrolyzer Electrocatalysis**

### H<sub>2</sub>NEW

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- Introduction to Electrocatalysis in PEMWEs
- Impact of "Thrifting" of Precious Metals on Performance and Durability
- Means to Reduce Precious Metal Loading/Decrease Overpotentials/Improve Durability
  - Alloying
  - Supports
  - Electrode structures
  - Platinum group metal-free catalysts
- Validation, Catalytic Activity Testing, Accelerated Stress Tests
- Metrics and Targets
- Summary

### **Overview of Low Temperature PEM Electrolysis**





\*Source: Guido Bender, 2018 DOE Annual Merit Review presentation





Gerhardt, et al., J. Electrochem.Soc., 168 (2021) 074503.

- Anodic oxygen evolution reaction (OER) is orders of magnitude slower than cathode reaction
- Cathodic hydrogen evolution reaction (HER) has very fast kinetics
- Anode environment very oxidizing
- Cathode environment relatively benign
- Anode kinetics and membrane resistance dominate cell overpotentials, cathode kinetic overpotential minimal
- Anode catalysts with higher OER activity are needed to improve electrolyzer efficiency, reduce hydrogen cost

### **Electrocatalysts for PEM Water Electrolyzers**



- Pt supported on high-surface-area carbon powder (i.e., PEM fuel cell anode catalyst) is the standard PEMWE HER catalyst
- Transition metal-based materials are converted to oxides at the high potentials of the PEMWE anode
- Ru oxide and various base metal oxides are near the top of OER "volcano plot" (i.e., are the most active)
- Transition metal oxides dissolve at high potentials in acidic electrolyte; carbon corrodes at high potentials of anode
- Unsupported Ir/Ir oxide is standard PEMWE anode catalyst due to balance between activity and stability



I.C. Man et al., *ChemCatChem*, 3 (2011) 1159.

C.C.L. McCrory et al., *JACS*, 137 (2015) 4347.

# **OER Activity Trends for Precious Metals and Oxides**



- Inverse relationship between OER activity and stability: Ir oxide balances activity and stability
- Materials that are initially metals more active than oxides
- Electrochemically-formed oxides are more active, less stable than thermally-formed oxides
- Crystalline material less active, but more stable than amorphous material
- A proposed catalyst metric: Activity-Stability Factor = Current at η=250 mV/Dissolution rate (ppb h<sup>-1</sup>)\*



S. Cherevko et al. / Journal of Electroanalytical Chemistry 774 (2016) 102-110

## Thrifting of Ir and Pt





• Minimal impact of decreasing Pt/C loading on cell performance (as low as 25 μg cm<sup>-2</sup>)

- Decreasing anode catalyst loading shows expected kinetic losses down to 0.6 mg cm<sup>-2</sup>
- Additional loss from anode electronic conductivity at IrO<sub>2</sub> loadings ~<0.6 mg cm<sup>-2</sup>

### **Additional Barrier to Lowering Ir Loading: Durability**



- Lower potential limit of cycling: 1.45 V
- Varying upper potential limit of cycling
- Current density loss is accelerated with decreasing IrO<sub>2</sub> loading and with cycling versus potential holds (i.e., with variable electricity supply, such as from renewable sources)

S. Alia et al., J. Electrochem. Soc., 166 (15) (2019) F1164.

### **Materials Properties and In-situ Performance**



- Catalyst variables: Ir surface area, Ir metal, Ir mixed oxide, ruthenium-containing, unsupported, supported on carbon or titania
- Ir catalysts: kinetic losses dominate and generally degradation rates increase with increasing metallic Ir content (as determined via X-ray absorption)
- Higher performance losses observed for ruthenium and carbon-supported iridium
- Performance losses with voltage cycling correlate with fraction of Ir in metallic state
- Performance loss correlates with Ir dissolution rates
- Alfa Aesar Ir catalyst is composed of a mixture of large 2-4  $\mu$ m Ir metal particles mixed with smaller amorphous IrO<sub>2</sub>; ratio can vary from batch to batch



### **Alloying of Ir to Increase OER Mass Activity**





• Alloying Ir with Ru is an effective way to increase OER mass activity – must limit amount of Ru to maintain stability

- Alloying metals that decrease the binding energy gap between O and OOH are effective at increasing OER activity
- Dealloying is an effective way to increase OER mass activity of Ir (i.e., increasing electrochemically-active surface area)

### **Catalyst Structure**



#### 3D mesoporous Conventional IrO<sub>2</sub> Electrospun IrO<sub>2</sub> Catalyst structure influences performance and IrO<sub>2</sub>-RuO<sub>2</sub> durability, but systematic study of multiple (B) IrO<sub>v</sub>-50 parameters is needed: Particle size Morphology Impacting activity and conductivity 100 nm 10 nm Composition C. Felix et al., Int. J. S. Moon et al., ACS Electrochem, Sci. 7 Appl. Mater. Interfaces S. W. Lee et al., Catal. Crystal structure (2012) 12064. 11 (2019) 1979. Today 352 (2020) 39. Atom-scale structure (segregated, core-shell, etc.) Electrospun IrO<sub>2</sub>/Sb-SnO<sub>2</sub> Catalyst-support interfacial structure **Porous Ir Nanosheets** Nanowires <sup>55 V</sup> [mA cm<sub>lr</sub><sup>-2</sup> A mg<sub>lr</sub>-SnO<sub>2</sub> (110) IrO<sub>2</sub>/Sb-SnO<sub>2</sub> NP O./Sh-SnO, NV 0.3 A mg<sub>lr</sub> 0.333 nm 50 S. Chatterjee et al., Adv. Energy Mater. 11 (2021) 2101438. S. Alia et al., ACS Catalysis, 8 (2018) 2111. G. Liu et al., J. Mater. Chem. A 3 (2015) 20791.

H2NEW: Hydrogen from Next-generation Electrolyzers of Water

### **Catalyst Supports**

Conventional OER catalysts are typically unsupported, but development of supports could enable:

- Increased OER kinetics
- Increased electrochemically-active surface area
- Higher Ir utilization
- Reduced degradation rates
- Improved electrode structure



L. Moriau et al., ACS Catal. 11 (2021) 670.





### **Catalyst Supports**



Important properties for OER catalyst supports:

- Conductivity
  - Electronic conductivity may not be needed at high IrO<sub>2</sub> loading, but becomes critical at low IrO<sub>2</sub> loading (IrO<sub>2</sub>: 10<sup>4</sup> S cm<sup>-1</sup>)
  - Protonic conductivity may be useful in some cases (e.g., porous supports)
- Chemical/oxidative stability
- Morphology (shape, porosity)
- IrO<sub>2</sub> dispersing ability
- Catalyst-support interactions (charge transfer for enhanced kinetics/durability)



E.-J. Kim et al., Appl. Catal. B Environ., 280 (2021) 119433.

### **Examples of Catalyst Supports**





P. Bhanja et al., *ChemCatChem* 11 (2019) 583.

### IrO<sub>2</sub> on TiON<sub>x</sub>



L. Moriau et al., ACS Catal. 11 (2021) 670.





E. Oakton et al., ACS Catal. 7 (2017) 2346.

### IrO<sub>2</sub> on TiN



J. S. Spendelow et al. (in preparation)

- Wide variety of supports under development, including oxides, nitrides, carbides
- General issue with transition metal oxides is low conductivity (e.g., TiO<sub>2</sub> 10<sup>-6</sup> S cm<sup>-1</sup>)
- Conductivity and other properties of oxides can be improved by doping (Nb-doped TiO<sub>2</sub>, Sb-doped SnO<sub>2</sub><sup>\*</sup>, etc.)
- Nitrides and carbides (TiN, TaC, etc.) provide good conductivity, but can lose conductivity through oxidation

\*e.g., Int. Journal Hydrogen Energy, 36 (2011) 5806.

### **Performance of Supported IrO<sub>2</sub> Catalysts**





J. Polonsky et al., Int. Journal Hydrogen Energy 39 (2014) 3072.





L. Bohm et al., Materials Today Proceed., 45 (2021) 4245.

V.A. Saveleva et al., ACS Catal. 10 (2020) 2508.

### **Electrode Structures: Conventional**





N. Danilovic and J. Fornaciari, LBNL, 2021 AMR

Conventional anode structures contain:

- IrO<sub>2</sub> (nanoscale powder, supported or unsupported)
- lonomer
- Free pore volume

Improved understanding of how catalyst characteristics, ionomer characteristics, ink properties, and deposition/drying methods influence resulting structure is needed to guide design of improved electrodes

### **Catalysts, Support, and Electrode Properties**

- Need to have sufficient electronic conductivity and good dispersion of proton conductor
  - Ohmic losses in catalyst layer can become significant with thick (high loaded) electrodes
- Catalyst must maintain sufficient water coverages at high current densities (i.e., to prevent mass transport losses)



### Variable IrO<sub>2</sub>/TiO<sub>2</sub> Loading



### Impacts of Catalyst Processing at Low Ir Loadings





- At ≥0.4 mg cm<sup>-2</sup> initial performance less sensitive to processing methodologies, formulation variations, and microscale heterogeneities due to particle sizes and agglomerates
- At lower loadings, performance can show strong dependence on processing/heterogeneities
- Electrode structure/thickness/homogeneity are additional considerations for novel catalyst development

### **Alternative Electrode Structures: NSTF (3M)**





A. Steinbach, 2019 AMR

### **Nanowire Electrode Structures**







- Coaxial Nanowire Electrode (CANE) developed at LANL uses high aspect ratio ionomer nanowires encapsulated by IrO<sub>2</sub> or Pt/IrO<sub>2</sub> thin film
- Low-loaded CANE provides similar performance to highloaded conventional IrO<sub>x</sub> electrode

### **PGM-free Catalysts for Acidic OER**



#### Challenges:

- Transition metal-based materials are converted to oxides at the high potentials of the PEMWE anode
- Transition metal oxides dissolve at high potentials in acidic electrolyte

Reports of PGM-free OER Electrocatalysts:

- MnO<sub>x</sub> where redeposition of dissolved Mn "heals" catalyst; undercoordinated sites stabilized by TiO<sub>2</sub> decoration (M. Huynh, J. Am. Chem. Soc., 136 (2014) 6002; R. Frydendal et al., Adv. Energy Mat., 5 (2015) 1500991)
- CoO<sub>x</sub> stabilized with Mn, Fe, Pb
- Polyoxometalates
- Oxidized metal organic frameworks

	CoMnO <sub>x</sub>	NiMnSbO <sub>x</sub>	Polyoxo metalate	Oxidized MOF <sup>d</sup>
<i>E</i> <sub>0</sub> (V)	1.810	1.900	1.610	1.608
<i>l<sub>0</sub></i> (mA/cm <sup>2</sup> )	1	10	10	10
$\eta_{0}(\mathrm{mV})$	580	670	340	378
<i>t</i> (hour)	50	168	0.5	250
∆ <b>E</b> (mV)	20	65	100	58
pН	2	0	0	1

a. M. Huynh et al., Chem. Sci., 8 (2017) 4779.

b. I.A. Moreno-Hernandez et al., *Energy Environ. Sci.*, 10 (2017) 2103.

c. Blasco-Ahicart et. al. Nat Chem, 10 (2018) 24.

d. D.J. Liu et al., DOE 2020 AMR p157.

#### <u>Reviews</u>

F. Lyu et al., *Small*, 15 (2019) 1804201. R. Pittkowski et al., *Curr. Op. Electrochem.*, 12 (2018) 218-224. Source for table: D.J. Liu et al., DOE 2020 AMR, p157.

### **Electrocatalyst Evaluation: Half-Cell Testing**



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\*M.F. Tovini et al., J. Electrochem. Soc., 168 (2021) 014512.



S. M. Alia, J. Manco, G. C. Anderson, K. E. Hurst and C. B. Capuano, J. Electrochem. Soc., 168 (2021) 104503. S.M. Alia, M.-A. Ha, G.C. Anderson, C. Ngo, S. Pylypenko, R.E. Larsen, J. Electrochem. Soc., 166 (2019) F1243-F1252.

### **Accelerated Stress Tests**



- Accelerated stress tests for intermittent, start-stop operation
  - Current basis
  - Focus on anode catalyst layer degradation
  - Intermittent: 1.45 V to 2 V square wave
  - Start-Stop: 0 V to 2 V square wave
- Kinetic losses larger for periodic versus steady-state and for start-stop versus intermittent





- General trends
  - Metals, Ru-inclusion saw higher performance losses
  - Kinetics drives loss (ohmic/transport secondary)



K. Ayers, https://www.hydrogen.energy.gov/pdfs/review20/p155\_ayers\_2020\_p.pdf, 2020.

## **OER Catalyst Activity and Durability Targets**



Proposed definition of OER Activity:

- Shorting-corrected current density at iR-corrected 1.45 V, 80 °C, 1 atm, 100% RH
  - ✓ Unsupported Alfa Aesar IrO<sub>2</sub> catalyst: 78 ±10 A/g<sub>Ir</sub>
  - ✓ Supported IrO<sub>2</sub>/TiO<sub>2</sub> Elyst IR75 0480 from Umicore: 54 A/g<sub>Ir</sub>, 1.58 mg<sub>Ir</sub>/cm<sup>2</sup>





Tentative OER Catalyst Targets:

- 2025 target performance target of 1.8 V at 3 A/cm<sup>2</sup> at 80 °C and 30 bar with 0.4 mg<sub>Ir</sub> cm<sup>-2</sup> requires OER activity of 100 A/g<sub>Ir</sub>
- Durability: average degradation rate over 80,000 h lifetime
  <2.25 μV h<sup>-1</sup>

Source: Xiaohua Wang and Rajesh Ahluwalia ANL, H<sub>2</sub>NEW Analysis





- Electrocatalytic challenges in PEMWEs are associated with anode (OER) catalyst and electrode
  - Majority of efficiency loss is associated with high overpotentials for OER
  - Majority of long-term decrease in efficiency is associated with increasing OER overpotentials
  - Highly oxidizing conditions lead to dissolution of even noble metal oxides
  - Balance of OER activity and stability achieved with unsupported IrO<sub>2</sub> catalysts
  - Challenges lead to the necessity for high anode loadings of unsupported Ir
- Catalysts and electrodes must balance electronic and ionic conductivity, catalytic activity, and wettability for high current density operation, while also being stable over 80,000 h
- Novel IrO<sub>x</sub> morphology and supports, such as TiO<sub>x</sub> and perylene red, have shown promise in increasing OER activity of IrO<sub>x</sub> and improving high current density performance
- Need a 20-30% increase in OER mass activity of unsupported Alfa Aesar IrO<sub>x</sub> to achieve DOE 2025 performance target, with degradation rate of <2.25  $\mu$ V h<sup>-1</sup>