

Overall Research on Electrode Coating Processes (OREO)

PI: Michael Ulsh National Renewable Energy Laboratory DOE AOP #10.2.0.502 June 6-8, 2022

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Project Goal

- The cost of MEAs is a significant portion of stack and system manufacturing cost estimates. MEA costs are dominated by material costs processing costs are generally small.
- However, extrapolations of cost at high volumes to ascertain the decrease of cell or stack cost associated with economies of scale assume roll-to-roll (R2R) processing technologies that have not been proven at scale. In particular, they have not been proven in their ability to
 - Process FC and EC materials at high quality
 - Form electrode morphologies that will provide acceptable electrochemical performance.
- Project Goal: Address these unknowns by bringing together a unique network of experts in FC and EC ink/electrode fabrication, novel materials, advanced characterization, and in situ device testing, who have capabilities to
 - Evaluate and compare material and process parameters across a wide range of different processes of interest to industry
 - Access a common and unique platform of characterization tools to enable understanding of the impact of materials, inks and processes on the nano- and micro-scale structure of the electrode, and how this impacts MEA performance.
- The intended outcomes of this project will be cost savings and acceleration of commercialization of MEAs for electrolyzers and fuel cells.

Overview

Timeline and Budget

- Project start date: 10/01/2019
 - Proposed for 3 years
- Total DOE funds received to date: \$900,000 (fully funded)
 - All partners funded separately (not by HFTO)







Barriers

Barrier	Target
A. Lack of high-volume MEA processes	\$20/kW (2025) at 100,000 stacks/yr
H. Low levels of quality control	

Partners

- Fraunhofer ISE (Ulf Groos)
 - Funded via Germany
- University of Connecticut (Jasna Jankovic)
- Colorado School of Mines (Svitlana
 Pylypenko)
 - UConn and Mines funded via NSF and the states of Connecticut and Colorado

Relevance

Hydrogen Energy Earthshot: Key Enablers for Lower Cost Electrolytic H2

- Low-cost electricity
- High electrical efficiency
- Low-cost capital expense
- Increased durability-lifetime
- Low-cost manufacturing processes
- Manufacturing at MW-scale

Bipartisan Infrastructure Law (BIL)

- Total of \$9.5B authorized and appropriated for Clean Hydrogen in Nov.
 2021 over 5-year period (FY22-FY26)
- Section 815: \$0.5B Clean Hydrogen Manufacturing and Recycling
 - "RD&D projects to advance new clean H2 production, processing, delivery, storage and use equipment manufacturing technologies and techniques"
- <u>Section 816</u>: \$1.0B Clean Hydrogen Electrolysis Program
 - Goal: To reduce the cost of hydrogen produced using electrolyzers to less than \$2 per kilogram of hydrogen by 2026

Stetson, Hydrogen Program Annual Merit Review plenary, 2021

Addressed by OREO Collaboration



Hydrogen

Hydrogen Energy Earthshot

for

\$1

"Hydrogen Shot"

1 decade

Launched June 7, 20

1 kg H₂



- Leverage broad range of coating/processing technologies and expertise at NREL and ISE
- Utilize a common and unique set of advanced characterization tools at the two university partners to understand the impacts of ink and coating parameters on electrode morphology
- Perform in situ testing at NREL and ISE to understand these impacts on MEA performance
- Leverage broad industry relationships and participation in HFTO and AMO consortia

Date	Milestone/Deliverable (status as of 4/12/21)	Complete
6/21	Complete plans for meeting or workshop in year 3	100%
9/21	Perform EC ink and coating studies exploring the limits of catalyst solids	100%
9/21	Coordinate on quarterly meetings and two joint publications	90%
12/21	Correlate between catalyst properties and ink behaviors	100%
3/22	Compare three Pt/HSC catalysts for processing differences	100%
6/22	Hold a workshop to present OREO results to the community	25%
9/22	Coordinate with ISE to compare IrOx coating processes	25%
9/22	Coordinate on quarterly meetings and two joint publications	50%



Goals:

- 1. Identify relevant process-related questions regarding fuel cell and electrolyzer electrode processing
- 2. Address those questions by performing a broad range of electrode studies to understand the impact of ink, coating, and drying conditions on electrode morphology and performance
 - Durability studies are out of scope for OREO; however, samples fabricated within OREO have been and will be used within H2NEW Task 3 (see P196c)activities to understand durability aspects

Studies during FY2022:

- Study 1: Understand the impact of Pt/HSC catalyst solids loading on electrode morphology
- Study 2: Understand the impact of support type and Pt wt.% on ink properties and coating
- Study 3: Understand the impact of differences in supplier for 50% Pt on HSC catalysts on inks and coating
- Study 4: Understand the impact of drying conditions on Pt/C electrode morphology
- Study 5: Understand the impact of coating shear on Pt/C electrode morphology
- Study 6: Understand the impact of ball milling time on Pt/C ink properties
- Study 7: Understand the impact of coating process type on IrOx anode coating window and morphology

Impact of Pt/HSC solids loading on electrode morphology

- R2R slot-die-coated electrodes fabricated from 3.5, 5, and 7 catalyst wt.% inks (all at 0.9 I:C), and coated at two target loadings
- Results: STEM/EDS shows a range of porosity and dispersedness of catalyst and ionomer
 - In situ testing pending



Impact of support type and Pt wt.% on ink properties and coating

- Used Ketjen, Vulcan, and graphitized supports with 30 and 50 wt.% Pt (see backup slides for full listing of catalysts and formulations)
- Result: Support type, Pt wt.% on support, and catalyst wt.% in ink all impact rheology



Impact of support type and Pt wt.% on ink properties and coating

 Result: Electrode surface morphology was a strong function of Pt wt.% and support type Rod 50 (0.265 mg Pt/cm²)



Rod 30 (0.211 – 0.214 mg Pt/cm²)



Comparison of Vulcan (top) and graphitized Vulcan (bottom) catalyst inks at 50 Pt wt.% and I/C of 0.9

Rod 75 (0.223 – 0.227 mg Pt/cm²)



Rod 50 (0.269 mg Pt/cm²)



Comparison of Vulcan catalyst inks at 30 (top) and 50 (bottom) Pt wt.% at I/C of 0.6

Impact of support type and Pt wt.% on ink properties and coating

- Cracking increases as thickness increases (as expected)
- Nano-scale morphology similar, possibly with slightly larger pores at higher I:C



Impact of support type and Pt wt.% on ink properties and coating

- Graphitized Vulcan has more surface structure (roughness, cracking) than standard
- Not much difference resulting from the HSC inks



Impact of support type and Pt wt.% on ink properties and coating

- Dilute inks measured with DLS
- Result: Heraeus
 Pt/HSC inks had lower
 particle size and zeta
 potential
 - Mainly comparable results from rest of the catalysts



Zeta potential (top) and Zavg particle size (bottom) analysis of dilute Pt/C inks by DLS

Impact of support type and Pt wt.% on ink properties and coating

- Property/ink correlations
 - Viscosity (at 1/s) and Zavg size from DLS correlate weakly with support surface area
 - Viscosity (at 1/s) correlates relatively strongly with zeta potential



Electrodes with same I:C, dispersion media, catalyst solids, and coating and drying conditions

Impact of supplier processing on ink properties and coating

- Performed ink and coating comparison of 50 wt.% Pt on HSC catalysts from 3 suppliers
- Result: Generally, higher high-shear viscosity and larger particle size in the ink minimized cracking in the electrode





Pt/HSC (TEC10E50E)



Umicore (ELYST Pt50-05500)



Heraeus (H2FC-50 Pt-C700)



Umicore (ELYST Pt50-0380)

Impact of drying conditions on electrode morphology

- For convective drying flows at 80C, electrode thickness (from SEM) and surface F/Pt ratio (XPS) trend as top+bottom flow > top flow > bottom flow
- Surface F/Pt and electrode thickness have non-monotonic responses to increasing drying temperature, indicating opposing behaviors
 - Surface porosity follows the same general trend, where lower and higher temperature cases are relatively smoother

See backup slide for samples and conditions



Impact of coating shear on electrode morphology

- Coated with #50 rod
- Surface SEM shows little impact of speed-induced shear
- However, coating thickness is significantly reduced with increased shear
- Surface F appears to have a minima at intermediate shear



SEM at 3 magnifications, cross-section TEM in the bottom row, EDS F/Pt (first value) and XPS F/Pt (second value) for electrodes coated with #50 Mayer rod at 4 application speeds

Fuel Cell electrode ball milling time study

- Experiment: understand impact of ball milling time on electrode morphology (I:C = 1.0, nPA-rich ink)
 - Prior results showed that electrode cracking increased with increasing milling time, from 24 to 96 hours
- Result:
 - Advanced data processing methods applied to cross-section TEM imaging
 - Agglomerate and pore size decrease with milling time
 - This matches other results where increased ink particle size correlated with decreased crack formation



Example cross-section

See backup slide for samples and conditions

Accomplishments

LTE coating process comparison study

- Experiment: understand the impact of scalable coating method on coatability and anode morphology
 - Compare slot die and gravure process windows using inks with 3 catalyst solids loadings over a range of wet thickness/catalyst loading
- Slot die Result: Due to the low typical viscosity of IrOx inks, even at high solids loading, uniform slot die coatings were observed in a limited range of conditions
 - 0.4 loading electrode with 20 wt.% ink performed comparably to sprayed comparator (see P196c)



Slot die process window depiction

LTE coating process comparison study

- SEM/EDS performed of slot die coated anodes
- Results:
 - Lower loaded samples appear to have smoother surface
 - Structure at high mag appears similar
 - F/Ir from EDS increases with thickness for the 20 wt.% inks



SEM at three magnifications for five slot die coated cases with F/Ir from EDS for each case inset in the top image of each column

Responses to Reviewer Comments

Comment: "Activity would benefit from having a parameter matrix to convey the multitude of parameters to characterize..." Response: We agree with and thank the reviewer for this comment. We have added a parameter matrix in the backup slides.

Comment: "It is unclear whether the study of Mayer rod coating method is appropriate for at-scale manufacturing processes." Response: We appreciate the reviewer's comment and heartily agree that the goal of the project should be information that is relevant to scalable processes. Fortunately, we have found that small-scale Mayer-rod coating studies correlate very well with R2R gravure coating studies. Thus, we find that Mayer rod studies are a useful scoping tool for later R2R experiments, where much less ink, substrate, and time are required to obtain results that can inform more focused (and expensive) R2R studies.

Comment: "...emphasis is needed on understanding how coating parameters control resulting structure and properties." Response: We absolutely agree, and in FY22 have been able to obtain significantly more nano- and micro-structural analysis from the university partners to understand these process-structure relationships.

Comments regarding lack of understanding of the interaction and fear of duplication of effort with H2NEW and M2FCT Response: We appreciate the comment and agree that this is something that we must work at to ensure we're leveraging but not overlapping efforts. Generally, the efforts within OREO are more process-science focused, whereas scaling studies within H2NEW and M2FCT are more related to specific materials or structures for a specific set of application targets. Also, note several interactions in our Accomplishments, for example where OREO samples were used within H2NEW and leveraged the greater emphasis on and infrastructure for performance and durability testing.

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Collaboration and Coordination

- University of Connecticut and Colorado School of Mines
 - Provide **common and unique** advanced characterization tools for inks and electrodes
 - Coordinated U.S. funding via NSF and states of CT and CO
- Fraunhofer ISE
 - Access a **different set of electrode processing capabilities** for broad comparison
- NREL hosted visiting researchers from ISE, UConn, and CSM
- Industry partners in NSF project: Pajarito Powders, Forge Nano, GM, Giner
- Industry partners via NREL relationships: GM, Plug Power, Nel, 3M, Gore
- Leveraging NREL's leadership and participation in M2FCT, H2NEW, AMO R2R Multi-lab Collaboration

Remaining Challenges and Barriers

- Need better understanding of how manufacturing processing conditions impact performance of FC and EC materials
- There is also a need to understand any limitations of specific coating methodologies or other process conditions to enable manufactures to properly select processes that will be suitable for their materials or product specifications
- Understanding integration of novel materials will speed up transition from lab-scale processes to manufacturing
- Manufacturing of electrolyzer MEAs is much less mature than fuel cells, therefore less is known about the impacts of ink formulations and processing conditions on electrochemical performance

Proposed Future Work

In the final partial year of the project (as currently funded) we will focus on:

- Collaboration and coordination with ISE
 - The ISE activity did not receive their funding until half-way through the NREL effort
- Addressing electrolysis anode-related processing challenges
- In situ electrochemical testing
 - We have had resourcing issues for in situ testing that have recently been addressed
- Publishing of the copious results from the collaboration jointly with the university partners

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

Summary

- The goals of the OREO International Collaboration directly support the Hydrogen EarthShot and the BIL Clean Hydrogen sections
- The project leverages a unique set of industrially-relevant coating processes and analytical tools to determine relationships between materials, processes, and performance
- The wide-ranging results presented herein aim to assist industry in scaling up fuel cell and electrolyzer electrodes, in coordination with H2NEW and M2FCT

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Technical Backup and Additional Information

Technology Transfer Activities

- The OREO collaboration will pursue technology transfer via
 - Direct engagement with industry through partner and consortium relationships
 - Joint publications and presentations at relevant conferences
 - Unique project-supported meetings
 - International Conference on Electrolysis and co-located fuel cell processing session, June 2022, Golden, CO

Relevance

- HFTO Multi-year RD&D Plan Manufacturing R&D barriers and milestones
 - Task 1: 1.2 Develop processes for direct coating of electrodes on membranes or gas diffusion media,
 1.3 Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste
 - Task 5: 5.5 Develop correlations between manufacturing parameters and manufacturing variability and performance and durability of MEAs
- Leverage and support FY2020 HFTO consortia scale-up-focused activities (M2FCT & H2NEW)
- 2020 DOE Hydrogen Program Plan: "...R&D efforts can help achieve economies of scale in manufacturing... key opportunities include: High-speed manufacturing techniques for processes such as... coating, roll-to-roll processing"
- 2020 "Roadmap to a US Hydrogen Economy": "...cost targets achieved driven by investments in manufacturing and process development and increasing production scale... improvements in manufacturing processes and supply chains should be prioritized."

Approach: Leveraging Unique Processing Platforms and Advanced Characterization Methods



Parameter Matrix

	Hot Press	Drying	Speed	Process	Substrate	Mixing	Solids	Disp Media	lonomer	
Cat/Sup		\checkmark		\checkmark		\checkmark	\sim	*	\sim	
lonomer		\checkmark		\checkmark			\checkmark	*		
Disp Media		*		*	*	*	\star			
Solids				\sim		\star				
Mixing				✓★						
Substrate	*			Preliminary assessment of p			ssessment of prio	rity		
Process								High priority – there will be e	- data/know-how s effects worth explo	sugge oring
Speed								-		0
Drying		\checkmark	Address	Addressed by OREO study			Medium prior confirm if the	ity – need more d re is an expected t	ata to trend	
		*	Address	sed via othe	er efforts			worth exploring	ng	

Accomplishments and Progress: GDEs Prepared to study impacts of catalyst type

Catalyst Type	Catalyst wt %	I/C	Pt loading (mg/cm ²)	C loading (mg/cm ²)	Rod size
	5	0.6 / 0.9	0.184 / 0.173	0.216 / 0.203	30
TEC10V50E (Pt/Vulcan)			0.235 / 0.229	0.276 / 0.269	40
			0.299 / 0.282	0.351 / 0.331	50
	5	0.6	0.202	0.471	60
	5	0.0	0.248	0.579	75
TEC10E50E (Pt/HSC)	3.5	0.6 / 0.9	0.218 / 0.212	0.256 / 0.249	50
	0.5		0.404	0.000	75
TEC10E30E (Pt/HSC)	3.5	0.9	0.164	0.383	75
	5		0.106	0.247	30
	5	0.6 / 0.9	0.174 / 0.177	0.204 / 0.208	30
TEC10VA50E (Pt/Graph. Vulcan)					
	0	0.6	0.270	0.317	30
	0	0.9	0.238	0.279	50
TEC10EA50E (Pt/Graph. HSC)	5	0.9	0.218	0.256	40

Sample table and electrode thickness (from cross-section TEM) for fuel cell electrode shear (a-g) and drying (h-q) studies

- Ink:
- Electrodes: rod coated onto Freudenberg H23C8 GDL
 - Coated with rods having different volume factors and at different draw-down speeds
 - Dried at room temp or in lab oven at 80C or in our R2R air floatation ovens at 30, 50, 80 and 110C, and different top and/or bottom flow conditions



Impact of drying conditions on electrode morphology

• Top-down SEM and EDS F/Pt at all 8 drying conditions



Convection, 50C Top and No Flow Bottom (n)



Convection, 80C Top and Bottom Ovens (j)



Convection, 80C Top and

No Flow Bottom (k)

Convection, No Flow Top and 80C Bottom (I)



Convection, 110C and

No Flow Bottom (o)

F/Pt: 3.4

Convection, Room Temp, No Flow (h)



Lab Oven, 80C (m)



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Impact of drying conditions on electrode morphology

- SEM at 3 magnifications and EDS F/Pt for four drying cases
 - SEM EDS results indicate segregation of F to the surface during drying is maximized by convective flow from the top (i.e., onto the wet layer)
 - Same result as from XPS



Cross-section TEM inset in bottom row

Impact of coating shear on electrode morphology

- Coated with #20 rod
- Surface SEM shows little impact of speed-induced shear
- Coating thickness is significantly reduced as shear increases
- Surface F decreases as shear increases



SEM at 3 magnifications, cross-section TEM in the bottom row, EDS F/Pt (first value) and XPS F/Pt (second value) for electrodes coated with #20 Mayer rod at 3 application speeds

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Impact of ink and coating parameters on surface F content

- GDE surface F content has been shown to be an indicator of performance
- Experiment: Pt/Vu and Pt/HSC inks at 0.6 and 0.9 I:C, rod-coated at 3 wet thicknesses (30R, 40R and 50R rods)
- Result: For low ionomer case using Pt/Vu catalyst, surface F shows little change with wet thickness
 - However, for high (excess) ionomer case,
 thicker wet films have higher surface F



XPS F/Pt data for Pt/Vu inks at 0.6 and 0.9 I:C rod-coated at 3 wet thicknesses

Impact of ink and coating parameters on surface F content

- Result: For low ionomer case we observe higher surface F for the Pt/HSC ink
- However, for the high ionomer case, we observe higher surface F for the Pt/Vu case

50 wt% 50 Rod Pt/HSC 0.6 and 0.9 I/C



XPS F/Pt data for Pt/HSC (left) and Pt/Vu (right) inks at 0.6 and 0.9 I:C using #50 rod

Fuel Cell cathode ball milling time study

- Result:
 - Advanced data processing applied to surface SEM imaging
 - Both micro- (between cracks) and macro-scale (including cracks) surface roughness observed to increase with ball milling time



LTE coating process comparison study

- Experimental design:
 - Ink: 0.2 I:Cat; 10, 20, and 30 wt.%
 catalyst solids
 - nPA:water was 50:50 for 20 and 30 wt.% inks
 - nPA:water was 75:25 for 10 wt.% ink, to increase viscosity
 - Slot die flowrates varied to achieve target loadings
 - Gravure roller volume factors changed to achieve target loadings

Slot coating	Catalyst Layer Loading (mg/cm2)				
	0.2	0.4	0.6	0.8	
10 wt%	1.91	3.81	5.72	7.63	
20 wt% (mL/min)	0.87	1.73	2.60	3.47	
30 wt%	0.52	1.04	1.56	2.08	

C	Catalyst I	Catalyst Layer Loading (mg/cm2)			
Gravure coating	0.2	0.4	0.6		
10 wt%	R60	R30	R25		
20 wt% Cylinder sizes	R120	R80	R38		
30 wt%	R150	R120	R80		

LTE coating process comparison study

- Gravure Result: Selecting cylinder volume factor enabled visually uniform coatings at all conditions
 - Gravure is generally more suitable for Newtonian inks
 - Similar to the slot die case, in situ testing of the 0.4 loaded electrode at 20 wt.% showed comparable performance to sprayed baseline
 - However, later high-resolution optical microscopy showed microvoids in some of the ~0.2 mg lr/cm2 electrodes (see P196c)

Gravure coating	0.2 mg/cm ²	0.4 mg/cm ²	0.6 mg/cm ²
10wt% IrO ₂			
20wt% IrO ₂		Report of the	
30wt% IrO ₂			

LTE coating process comparison study

- SEM/EDS performed of gravure coated anodes
- Results:
 - Low and medium mag imaging indicates larger agglomerates than slot die coated
 - Structure at high mag appears to be of finer scale than for slot die
 - Coating in 10 wt.% solids case appears discontinuous (verified later via optical microscopy)
 - F/Ir has a maxima at the 20 wt.% cases



SEM at three magnifications for five gravure coated cases with F/Ir from EDS for each case inset in the top image of each column

LTE coating process comparison study

- SEM/EDS comparison of slot die and gravure coated anodes with 10 and 20 wt.% inks
- Results
 - At the lower solids loading, the surface structures look quite different and have very different F/Ir
 - Also, the gravure-coated anode appears to be discontinuous
 - At the higher solids loading, the surface structure and the F/Ir appear similar
 - Both slot die and gravure coated anodes showed good performance at 0.4 loading (P196c)





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SEM at three magnifications (left to right) for the four labeled cases

Collaboration and Coordination: Partners in Germany (slide provided by Fraunhofer ISE)

- **German side:** lab scale to industrial scale catalyst and electrode development for fuel cells and electrolyzers
- Delay in funding → Funding started in January 2021 (project budget 4,3 Mio € and funding 2.7 Mio. €)
- *Fraunhofer ISE:* leads the project, performs ink and electrode lab scale fabrication, in-situ characterization
- NREL and ISE: coordinating selection of materials and components and discussing common protocols
- Heraeus: development of catalysts and inks
- **Coatema**: expert on the slot die coating \rightarrow advisory
- Fumatech: membrane requirements
- *Audi*: MEA manufacturing/automotive fuel cell requirements
- *Siemens:* will specify requirements for electrolyzer catalyst layers
- **Continental**: up-scaling the lab scale production at Fraunhofer ISE
- UConn and Mines: Structural characterization and structure-property-performance correlations



Progress toward DOE Targets or Milestones

- This project has the goal of <u>assisting industry</u> in accelerating the scaleup of MEA and stack materials, toward program cost and timeline targets
- The project is focused on addressing these needs for high priority applications such as water electrolyzers and fuel cells for heavy-duty applications