Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application

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Co-PIs: Tatyana Reshetenko and Madeleine Odgaard

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April 29, 2019

Project ID # FC305

Overview

Timeline

- Project Start Date: 01/01/19
- Project End Date: 12/31/20

Barriers

- Activity of PGM-free ORR catalysts should be increased
- Decrease a cost of PGM-free catalysts manufacturing
- Increase the durability PGM-free catalysts

Budget

- FY19 DOE Planned: $486,536
- Total DOE Funds Received to Date: $28,310.88

Partners

- IRD Fuel Cells, Madeleine Odgaard
- University of Hawaii, Hawaii Natural Energy Institute (HNEI), Dr. Tatyana Reshetenko

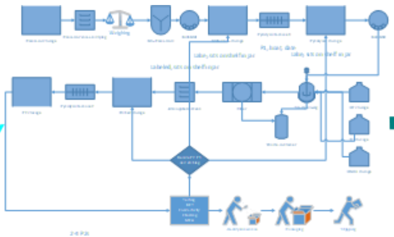
Relevance: Objectives and Targets

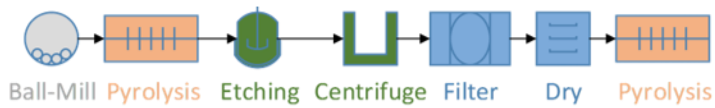
- Objectives: Development of PGM-free electrocatalysts for ORR; the catalysts will be scaled up to 50g batches (PP); PGM-free catalysts will be integrated into the industrial state-of-the-art MEAs (EWII) and comprehensively evaluated by electrochemical methods (HNEI).

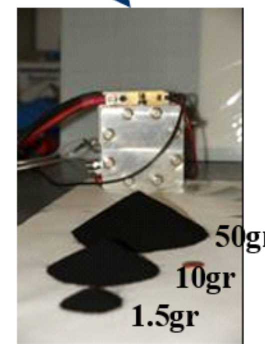
- Relevance to DOE Mission: Inexpensive, highly active and stable PGM-free ORR catalysts commercially manufactured by US catalyst company will demonstrate required by DOE performance level due to understanding the electrochemical processes relevant to **PGM-free** materials in mass-produced MEAs.

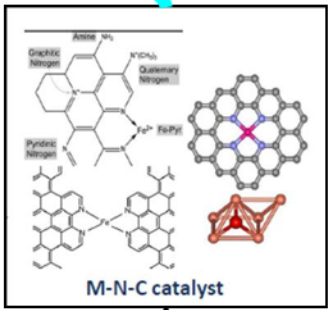
- Targets
  - Demonstrate 0.044 A/cm^2 at 0.9V (iR-free, H_2/O_2 configuration, 1bar O_2, 80ºC, 100%RH)

Approach: Catalysts and Method

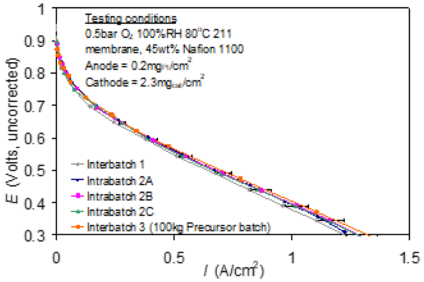


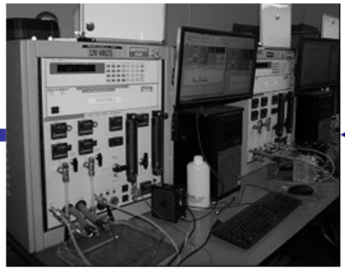






Pajarito Powder is able to manufacture up to 200g of PGM-free ORR catalysts per batch





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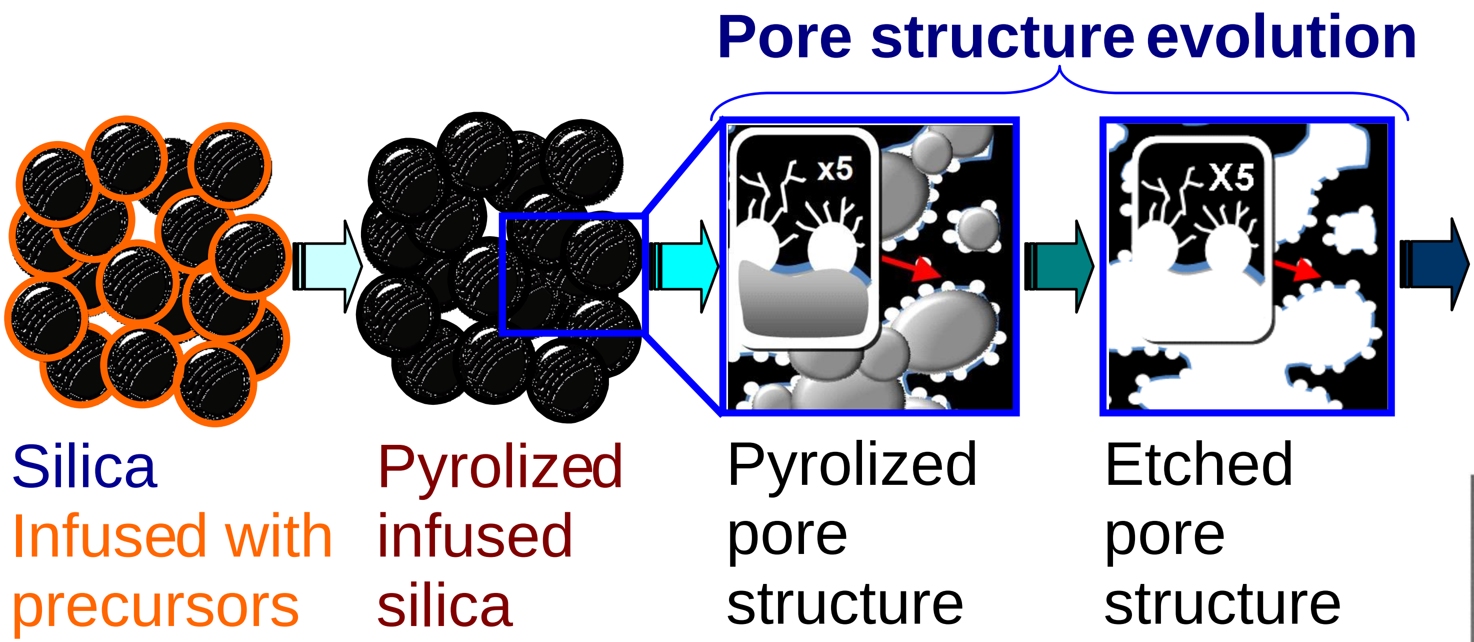
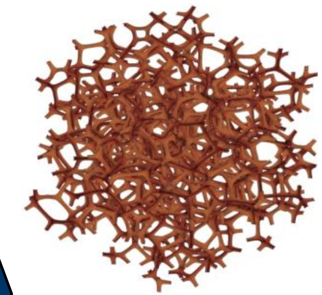
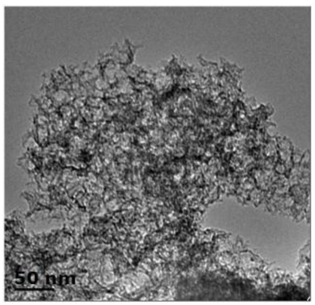
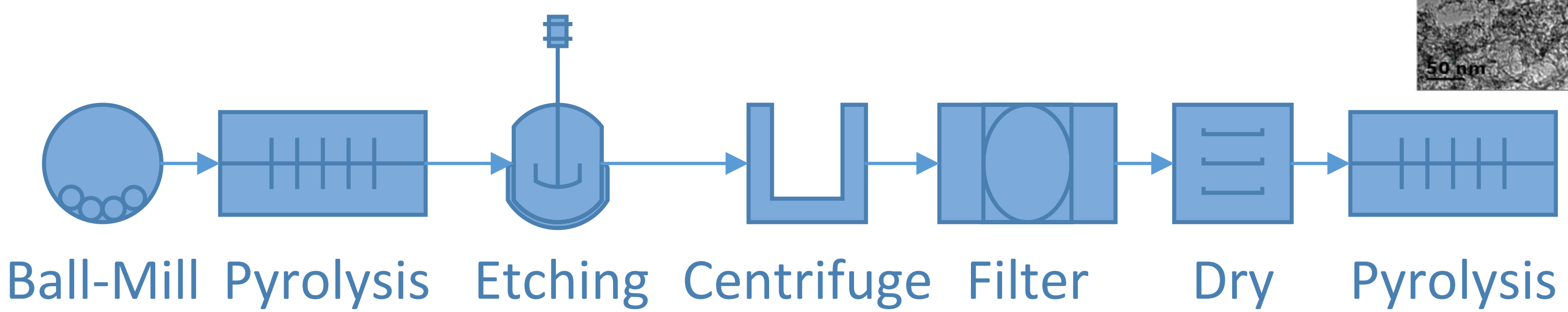
Approach: VariPore^{TM} Method





Porous
non-PGM
catalyst





Approach: Preliminary Data

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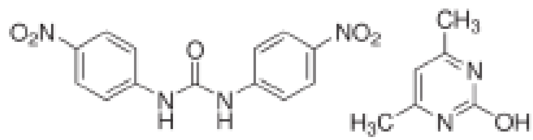
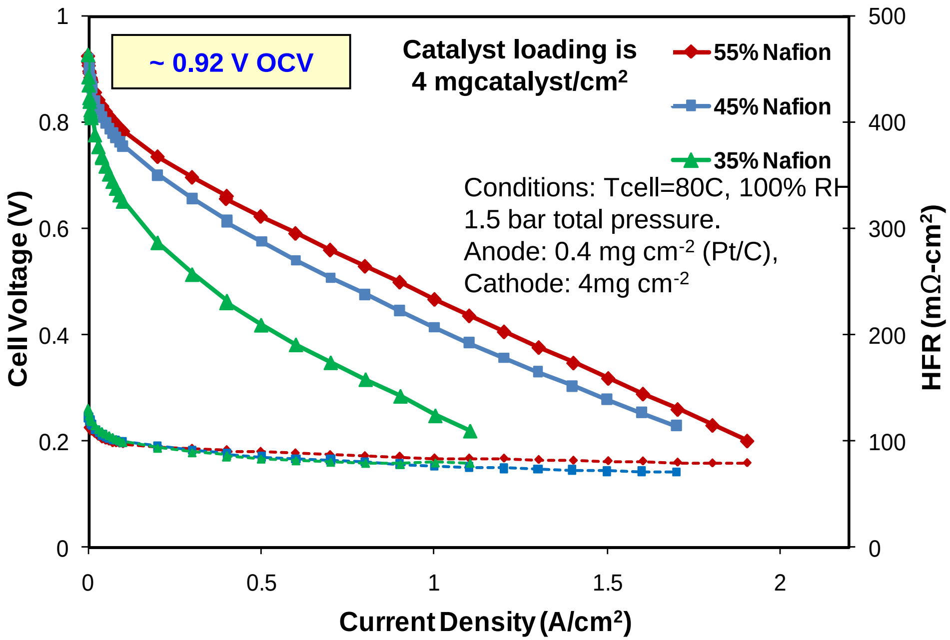
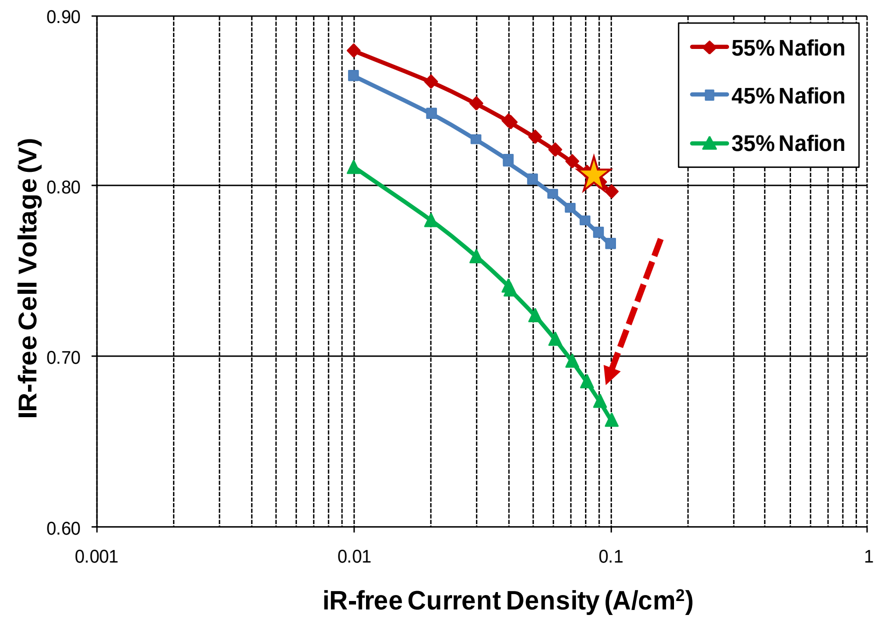






DOE EERE Project ID# FC086 AMR 2013 report, NTCNA testing

Met DOE target (2013) of 100 mA/cm² at 0.8ViR-free in Oxygen

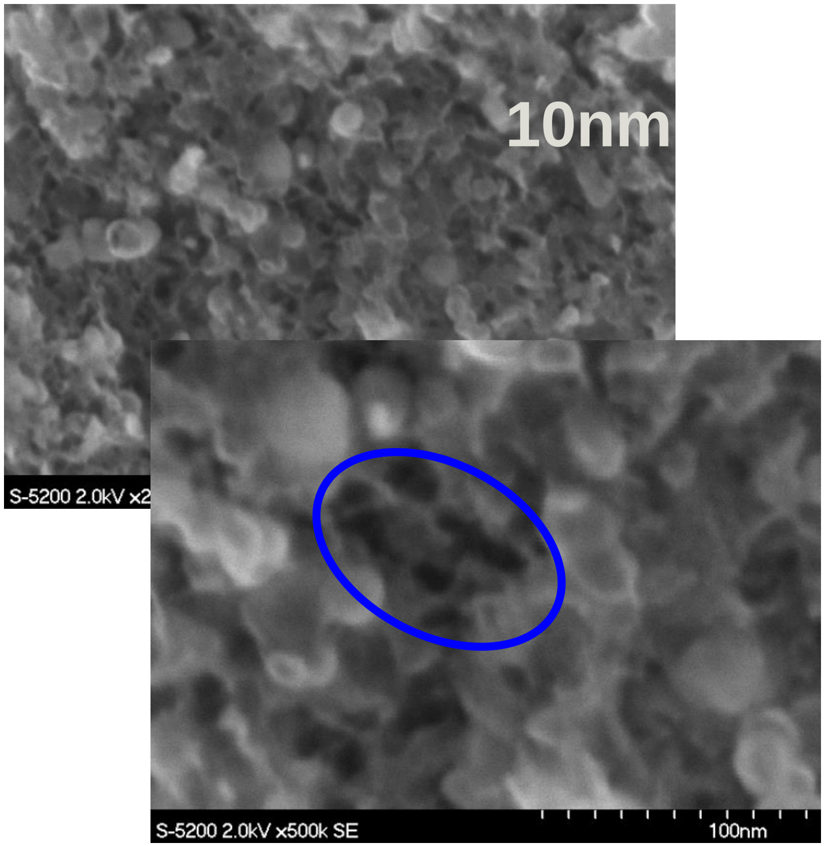
Approach: Timeline and Milestones

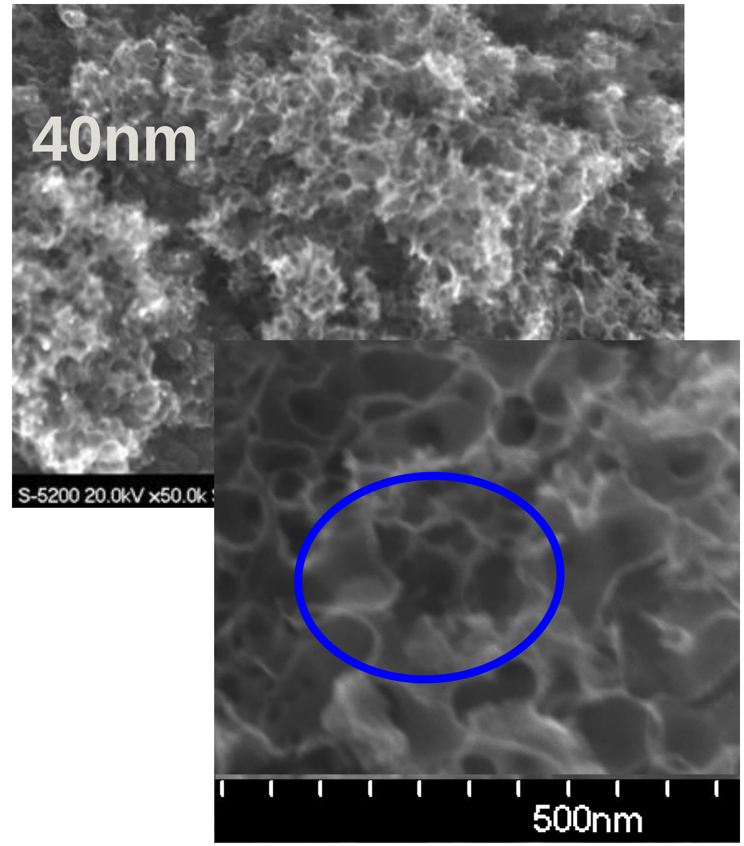
PAJARITO POWDER
FUEL CELL CATALYSTS

Milestone Summary Table

Recipient Name:	Alexey Serov, Pajarito Powder							
Project Title:	Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application							
Task Number	**Task or Subtask Title**	**Milestone Type**	**Milestone Number***	**Milestone Description**	**Milestone Verification Process**	**Anticipated Date**	**Anticipated Quarter**	**Budget Period**
1. Benchmark performance of PGM-free catalysts in fuel cell tests								
1.1	Stock Catalyst Characterization	Milestone	1.1	Correlation between synthesis parameters and morphology and chemistry of catalyst	Library of correlation. 15g of catalyst to EWII	1	1	1
1.2	Stock Catalyst integration in MEA	Milestone	1.2	Deliver 10 MEAs with stock catalyst	10 MEAs to HNEI and PP	2	1	1
1.3	Fuel Cell evaluation	Milestone	1.3	Activity will be compared with preliminary data obtained at Pajarito Powder: 0.025 A/cm^2 at 0.83V (iR-free), with H_2 /O_2 at 1.0 bar O_2, 100%RH, 80 °C	Fuel cell tests at HNEI to confirm activity and establish benchmark	3	1	1
2. Produce Gen-2 catalysts with atomically structured M-Nx active centers, integration into MEA and evaluation in fuel cell test								
2.1	Catalyst Activity Improvement	Milestone	2.1	Deliver Gen-2 catalysts	15 g to EWII	6	2	1
2.2	Gen-2 MEAs	Milestone	2.2	Deliver 10 MEAs with Gen-2 catalyst Activity Target: MEA that produces 0.025 A/cm^2 at 0.85 V (iR-free), with H_2 /O_2 at 1.0 bar O_2, 100%RH, 80 °C	Electrochemical fuel cell tests at PP, EWII and HNEI	9	3	1
2.3	Fuel Cell Tests: Active site Probing	Milestone	2.3	Recommendation to improve catalyst	Electrochemical analysis to EWII and PP	12	4	1
		Go/No-Go Decision	Go/No-Go #1	≥5cm^2 MEA that produces 0.025 A/cm^2 at 0.90 V (iR-free), with H_2 /O_2 at 1.0 bar O_2, 100%RH, 80 °C	Measured/verified at HNEI and EWII	12	4	
3. Improved morphology of PGM-free catalysts, Generation-3 of MEAs, mass transfer fuel cell evaluation								
3.1	Bi-metallic catalysts	Milestone	3.1	Deliver Gen-2a catalysts (Activity Target in 3.3)	15 g to EWII	15	5/7	2
3.2	Catalyst Morphology Improvement	Milestone	3.2	Deliver Gen-3 catalysts (Activity Target in 3.3)	15 g to EWII	15	5/7	2
3.3	Gen-3 MEAs	Milestone	3.3	Deliver MEAs with Gen-3 catalyst. Activity target: 0.044 A/cm^2 at 0. 85 V	10 MEAs to PP/ElectroCat	19	7/8	2

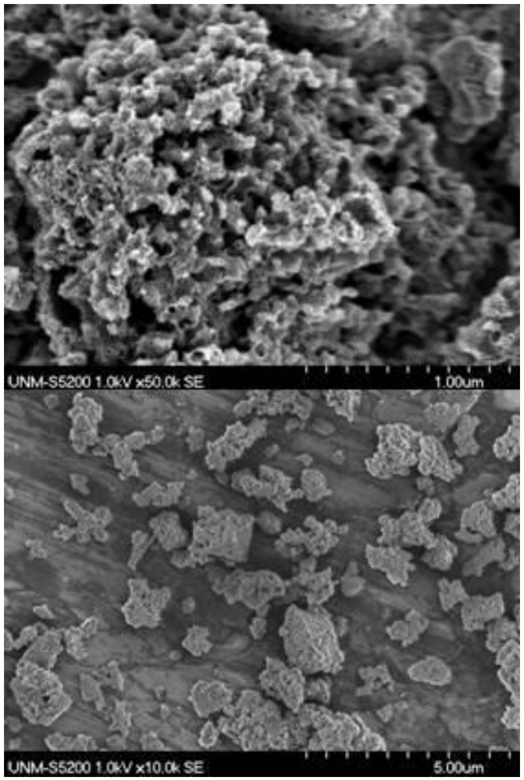
Approach and progress: Pore Size Control

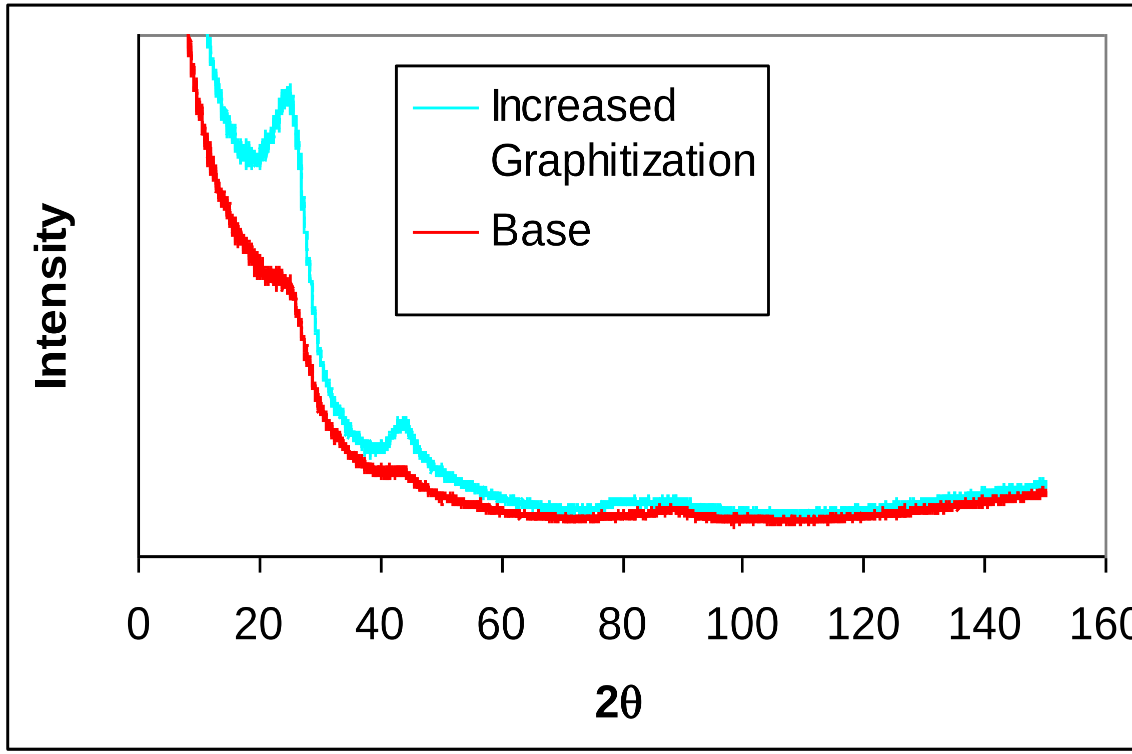




Design of M-N-C by VariPore® approach allows control catalyst morphology

Approach and progress: Graphitization





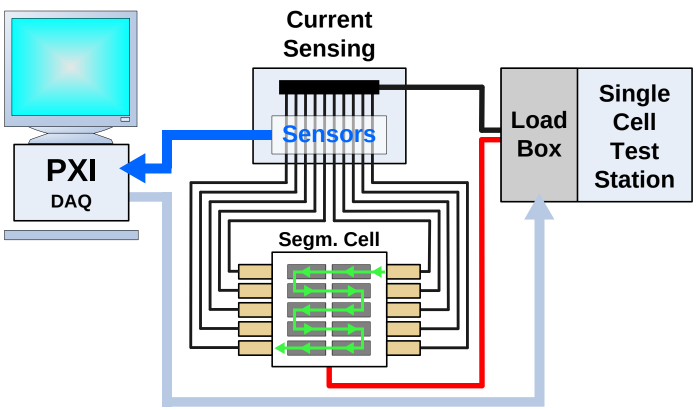
Higher graphitization leads to more corrosion resistance under Start-Stop AST protocol

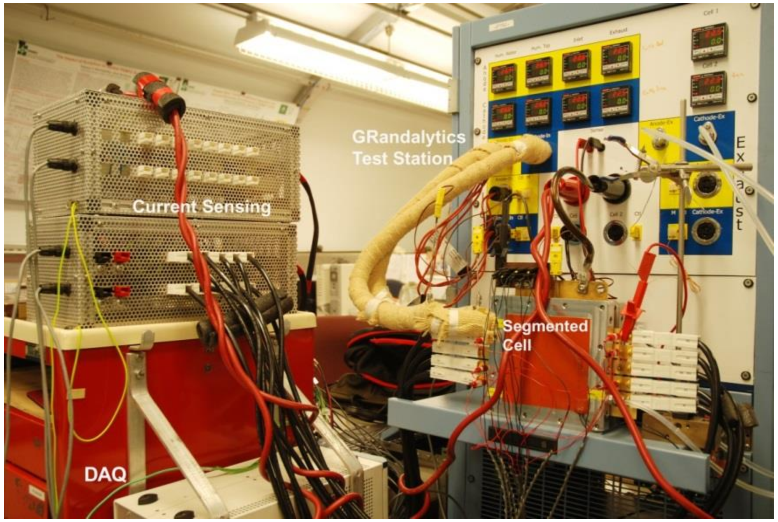
Approach: Electrochemical characterization

Subtask 1.3. Electrochemical characterization of the MEAs, standardization of activation procedure and testing protocols.

Application available characterization techniques (IV, EIS, CV)
Use single cell (25, 50 cm^2) and segmented cell (76 cm^2) systems

Segmented cell system





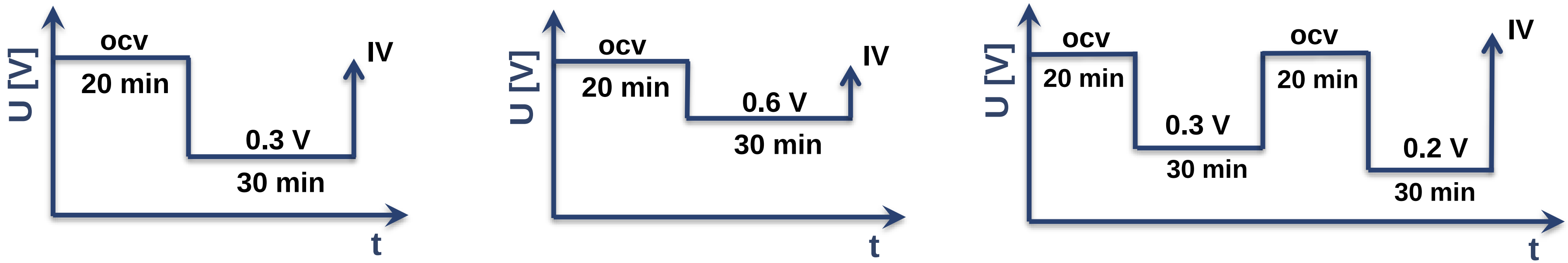
High current mode (I < 2 A cm^{-2})
- VI curve, EIS

Low current mode (I < 400 mA cm^{-2})
- Cyclic voltammetry
- Linear sweep voltammetry

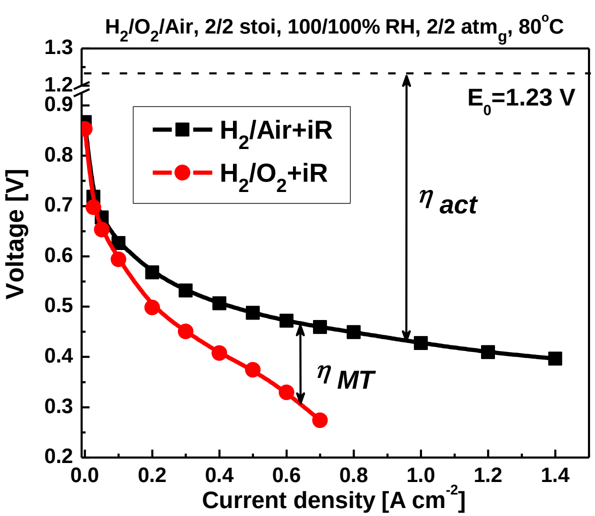
The main advantages:
- operation of the system as a single cell,
- the use of standard testing procedures.

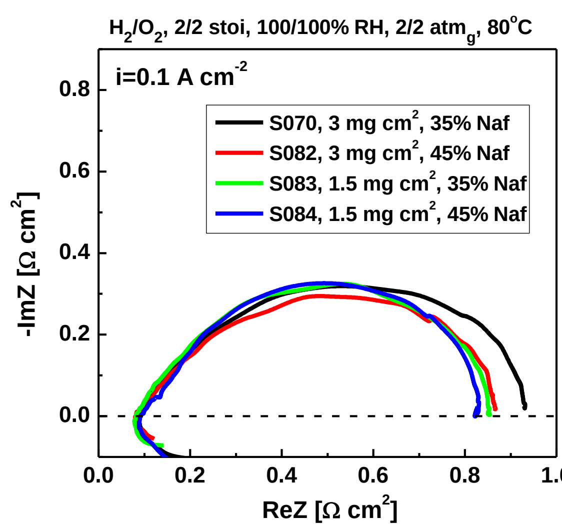
Approach: Electrochemical characterization

1. Activation protocols: Testing several promising protocols chosen from previous experience (constant voltage hold at different voltage and duration):



2. Characterization: IV (O_2/Air), EIS, EIS modeling





EIS model is based on a physical representation of the processes in MEA and provides the transport (O_2 and H^+) and kinetic parameters (Tafel slope) from the impedance spectra at relevant conditions.

Approach: Electrochemical characterization

HiSERF

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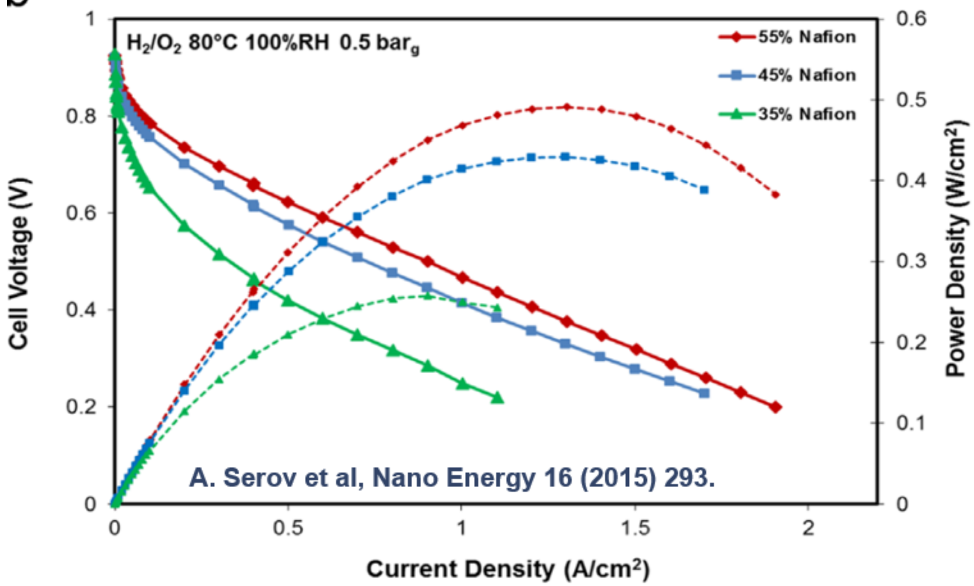
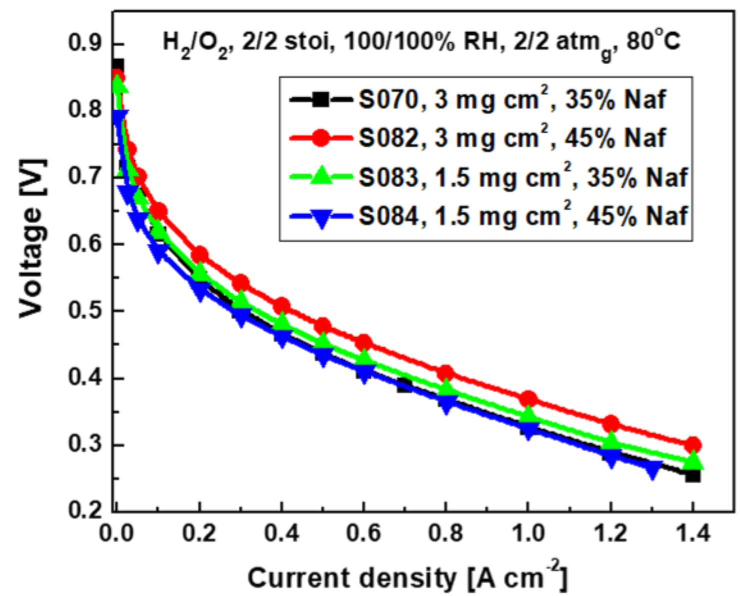
3.Testing protocols: **Galvanostatic vs Potentiostatic control of load at IV measurements**

Potentiostatic mode, 5 cm² MEA



Galvanostatic mode, 76 cm² MEA



IV measured under potentiostatic control of load has higher performance compared to galvanostatic IV. Catalyst degradation is facilitated by operation under galvanostatic conditions.
It is important to recommend a standard testing protocol for obtaining reliable performance data and for comparison of the data between different teams.

Approach: Active sites in PGM-free catalysts

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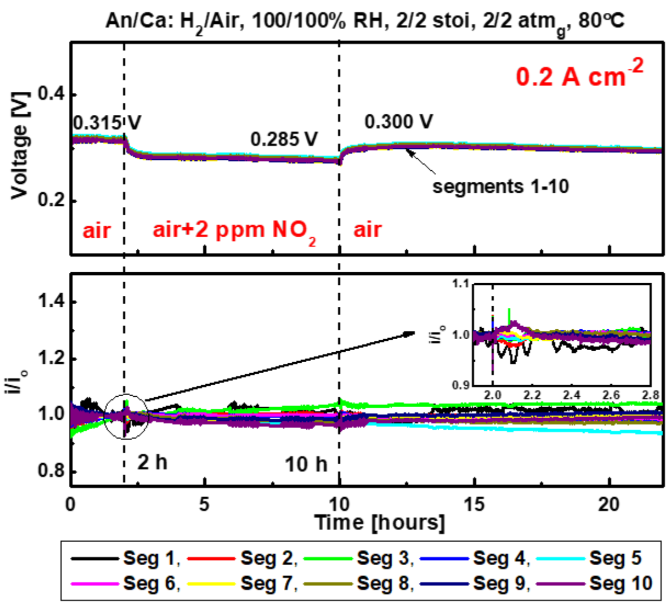
Subtask 2.3. In situ quantification of active sites in PGM-free FCs.

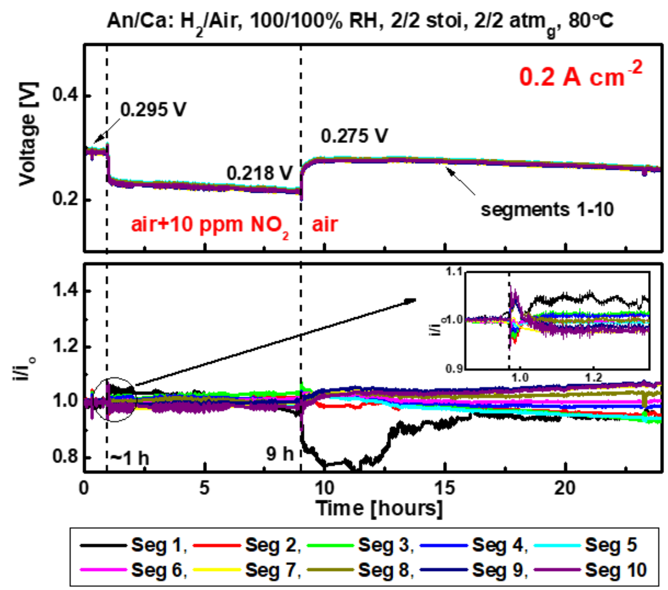
Under this subtask we propose to investigate several relevant molecular probes which strongly interact with the M-N-C: NO, NO_2, CH_3CN, HSCN, H_2S.

1) Select several potential probes and perform initial screening of their impact on PGM-free.
2) Assessment of the self-recovery of the PEMFCs.

Preliminary data

T. Reshtenko et al, J Power Sources 324 (2016) 556.





NO_2 and NO can substitute O_2 and poison Fe-N-C sites, resulting in performance loss. Thus, NO and NO_2 might be used as probe molecules to study Fe-N-C active centers.

Approach: Analysis of gas transport

Subtask 3.3. Analysis of gas transport in PGM-free electrode structure.

To address mass transport limitations imposed by high catalyst loadings and thickness, different morphologies of PGM-free electrode structure will be evaluated by two approaches:

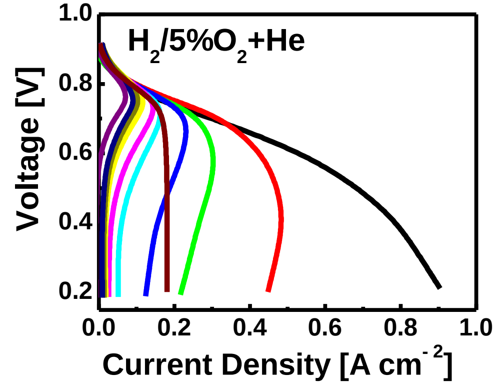
1) Deconvoluting voltage losses based on analysis of polarization curves measured with air, O_2 and HelOx;
2) Determining oxygen mass transport parameters using a novel method developed at HNEI. The method is based on a limiting current density distribution and application of diluents with varying molecular weights.

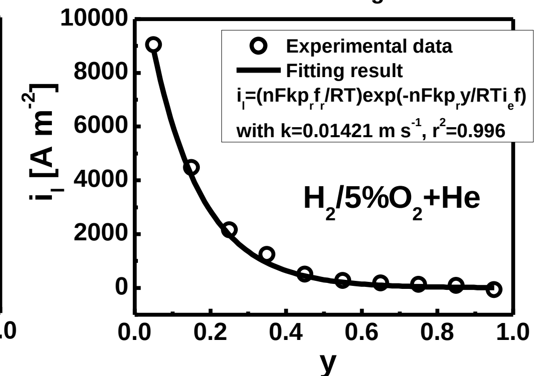
Local limiting current density

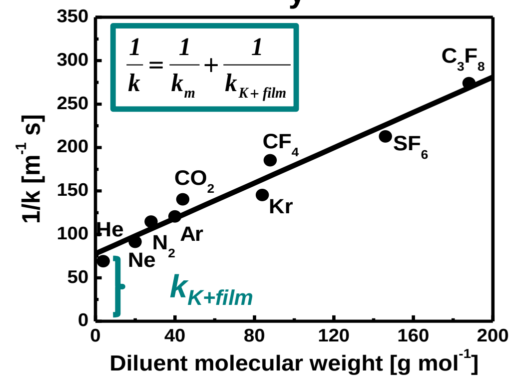
$$i_{lim}(\tilde{y}) = \frac{nFkp_r\alpha^0_{O_2}}{RT} e^{-nFkp_r\tilde{y}/RTi_ef}$$

- k - Mass transfer coefficient [m s^{-1}]
- y - dimensionless position along the flow field
- p_r - dry inlet reactant stream pressure [Pa]
- i_e – current density equivalent to inlet O_2 flow rate [A m^{-2}]
- f - inert gas to O_2 fraction in the dry inlet stream

An/Ca: H_2/5%O_2+He, 100/100% RH, 48.3/48.3 kPa$_g$, 60°C







The overall O_2 mass transfer coefficient *(k)* is a series combination of molecular diffusion in the gas (k_m) and Knudsen diffusion and diffusion through water/ionomer (k_{K+film}). Different gas diluents affects only O_2 diffusion in gas phase *(k_m)*. k_{K+film} and find k_m can be determined by extrapolation to zero diluent molecular weight.

T. Reshtenko et al, JES 161 (2014) F1089

Approach: Benchmark MEAs

Subtask 1.1. Integration of Gen-1 catalyst into MEA structure, initial testing of catalyst, down select best performing catalyst and MEAs.

Application of electrode using EWIIs standard coating technique

1-Gen Catalyst layer integration:

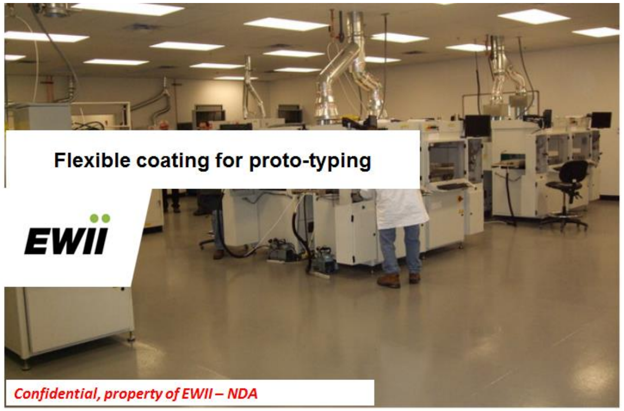
- Integration of PP stock (Gen-1) Fe-N-C catalyst into MEA for evaluation of benchmark performance.
- Establish effective material interfaces in MEAs
- Catalyst integrated into MEA using EWII standard method of catalyst layer design

The main advantages:

- Highly flexible innovative digital printing platform
- Enables rapid commercial prototyping and simple transition to high volume manufacturing.
- Aimed at all scales (from 25 cm^2 and up to industrial sizes ~5000 cm^2)
- Apply to established Quality Control procedures

Process:

- Uniform electrode coating and coat ability using EWII's industrial process routes
- Along with extremely uniform electrodes, complex electrode structures can be produced such as; spatial gradients of catalyst, ionomer and additives in all three dimensions, inter-digitated layer structures with any of the raw materials, and/or electrode patterning.



Approach: Benchmark MEAs

1. Catalyst layer structure: Input from sub-task 1.1 catalyst composition, surface area, particle size, pore size distribution and support characteristics to build 1-Gen structures:

- **Apply standard PFSA (Nafion) and pre-screen BoL performance**
- **Selection of a standard ionomer concentration**
- **Make a set of 10 catalyst coated membrane (CCM) MEAs ($25cm^2$) with a PGM-free catalyst loading on cathode of 3 mg cm^{-2}**

2. Quality Control: Apply and develop quality control on the final CCM/MEA including both in-line and off-line:

In-line:

- *Catalyst loading control*
- *Visual uniformity of electrode layers*
- *Data logging in coating equipment setup - controlled by accurate automatized ink delivery system*
- *Automated vision control*

Off-line:

- *ROI Automated Optical Tool for measurement of critical dimensions*
- *Electrochemical performance test*
- *Visual inspection*
- *Thickness*

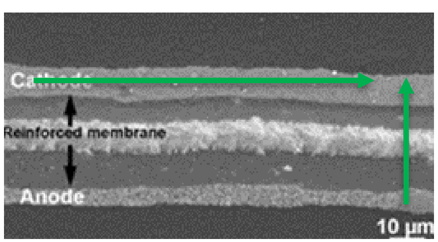
Approach: Optimization of Gen-3 MEAs

Subtasks 2.2-3.2 Optimize and develop MEAs using PGM-free catalyst with improved morphology with focus on durability and water management

Optimization of catalyst layer and coating process techniques

Optimization of Gen-3 MEAs:

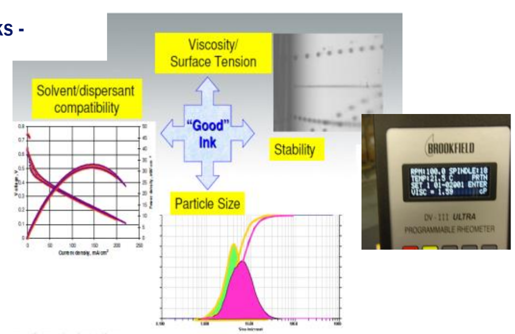
- Performance improvement by tailored electrode structures
- Fine tune catalyst-ionomer interaction: include all steps from Subtask 2.2: different solvent, additives and binders
- Emphasis will be dedicated to re-optimization of ionomer content, taking into account changed morphology of electrocatalyst.
- Adjust and develop coatings aimed for the new non-PGM catalyst system and investigate effect of spatial gradients and electrode patterning 2D (XY)

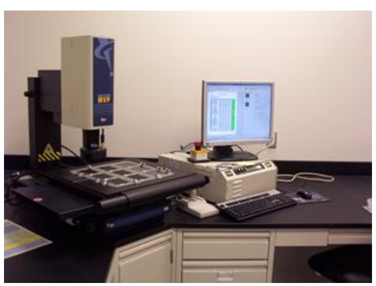


Approach and Output:

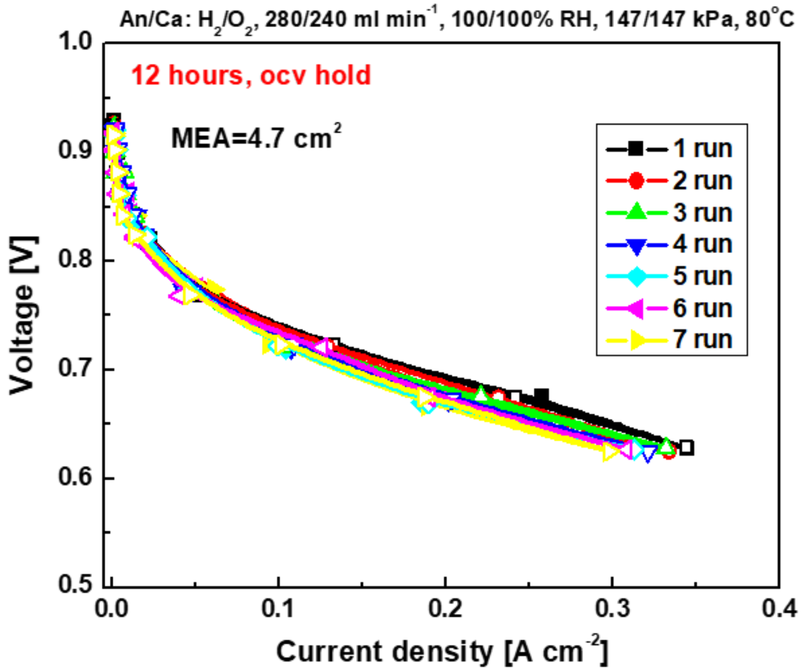
- **Maximize catalyst utilization (ECSA)**
- **Reduce Mass transport limitations**
- **Enhance durability**
- **QC** catalysts loading ± % and catalyst layer thickness (5 points thickness measurements) should be in the 15% error bar range

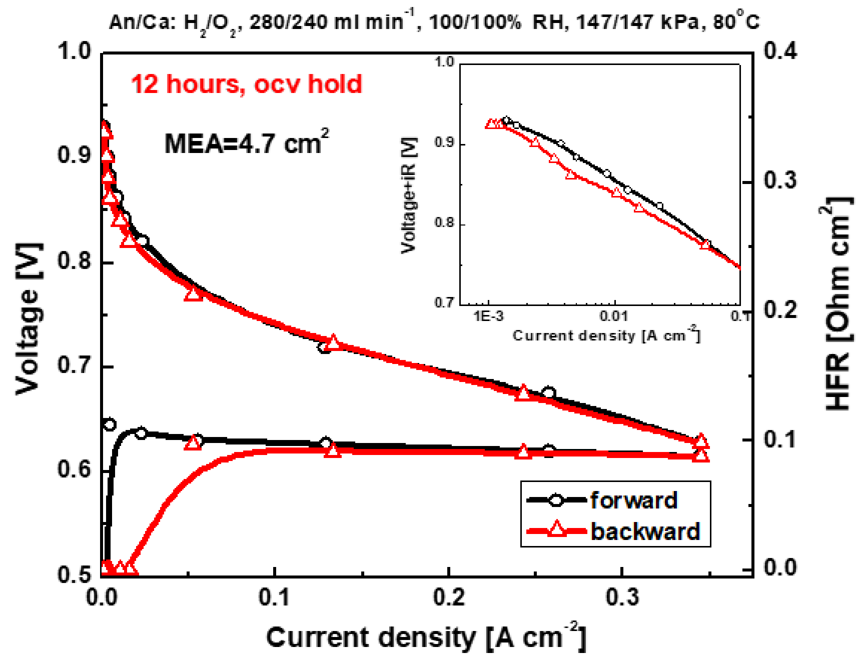
Inks -





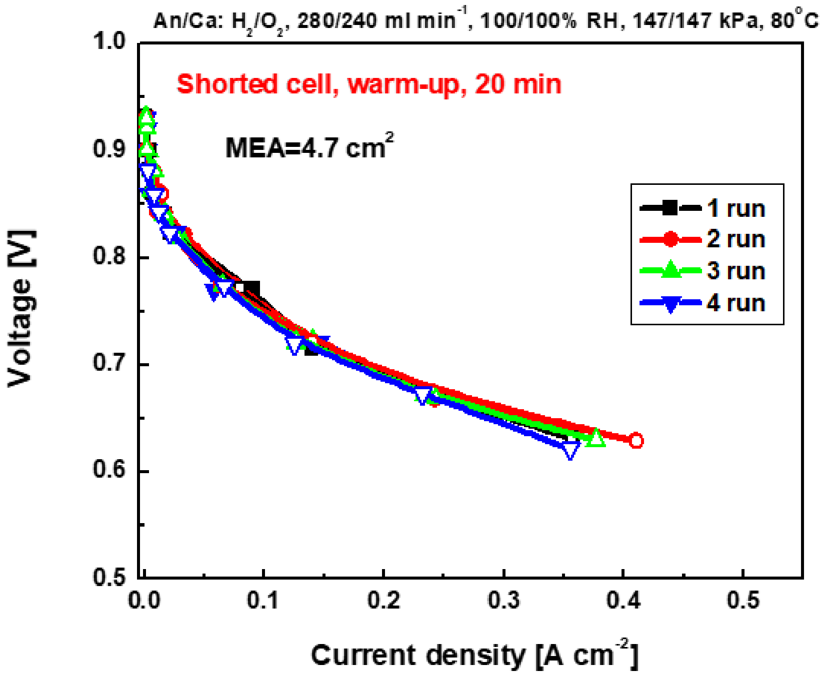
Accomplishments and Progress

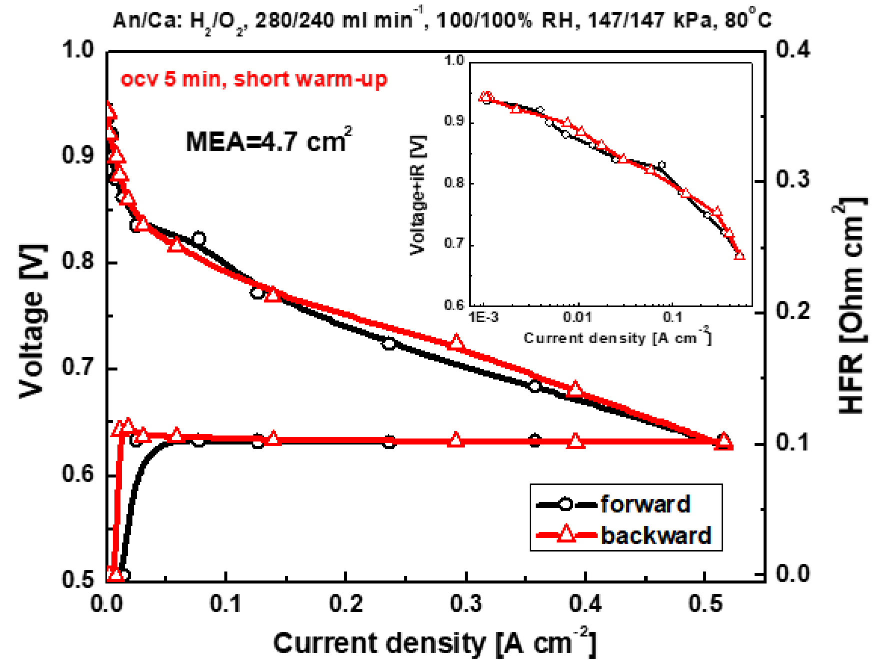




		1 IV run	2 IV run	3 IV run	4 IV run	5 IV run	6 IV run	7 IV run
fForward, iR corrected	U at 25 mA/cm² [V]	0.821	0.82	0.816	0.811	0.808	0.813	0.816
	U at 44 mA/cm² [V]	0.794	0.796	0.793	0.783	0.782	0.791	0.795
	I at 0.85 V [A/cm²]	0.0115	0.0102	0.0094	0.0107	0.0087	0.0107	0.0109

Accomplishments and Progress





		1 IV run	2 IV run	3 IV run	4 IV run
Forward, iR corrected	U at 25 mA/cm² [V]	0.829	0.836	0.83	0.825
	U at 44 mA/cm² [V]	0.813	0.815	0.805	0.8
	I at 0.85 V [A/cm²]	0.014	0.0162	0.0129	0.0085

Team achieved first milestone: 25 mA/cm^2 at 0.83V (Q1)

Collaborations

- High Throughput synthesis and testing for improved catalysts
- High Throughput electrode optimization catalysts
- Advanced characterization of catalysts and electrodes before, during, and after testing
- Degradation and degradation mechanism analysis
- Benchmark catalysts for ElectroCat method development

Remaining Challenges and Barriers

- Project is in beginning, so majority of challenges and barriers are still to be solved
- Activation protocol is critically important and should be established and harmonized
- Decrease of performance from scan to scan can be a challenging task to overcome
- Higher initial activity of PGM-free catalysts should be achieved in order to maintain required performance after initial degradation

Proposed Future Work

- Provide a Generation 1 (Gen-1) of Pajarito's catalysts to IRD for integration into the industrial quality MEAs
- Evaluate the MEAs at HNEI under different activation protocols
- Pajarito: development of Gen-2 of PGM-free catalysts based on SOPO
- Based on the results obtained from IRD and HNEI re-formulate catalysts morphology and surface chemistry

Summary

- All contractual documents are executed and project officially started
- Pajarito Powder hosted an onsite kick-off meeting in December 2018
- Team started to work on the plan described in SOPO and first series of MEAs were fabricated by PP
- Series of MEAs with Gen-1 catalyst were provided to HNEI and under evaluation
- Preliminary data confirmed the importance of the activation protocol on overall catalyst performance
- Team successfully reached a first milestone (Q1) of 25 mA/cm^2 at 0.83V (MYRD&D recommended conditions)