DOE Hydrogen Program

2021 Annual Merit Review and Peer Evaluation Meeting

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

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June 8th, 2021

Award# DE-EE0008419

Project ID # FC305

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Goal

- Develop *scalable* method for synthesis and manufacturing of PGM-free (Fe-N-C types) electrocatalysts for Oxygen Reduction Reaction for PEMFC application.
- Increase *activity and durability* of Fe-N-C catalysts to required by ElectroCat consortium values.
- Integrate PGM-free ORR catalysts into *industrial quality* Membrane Electrode Assemblies through design of cathodic catalyst layer (optimization of ionomer type and loading, deposition method, additives type and concentration).
- Using electrochemical techniques and modeling estimate proton conductivity, oxygen permeability and ORR mechanism in *thick* cathodic layers.

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Overview

Timeline and Budget

Timeline

- Project Start Date: 01/02/2019
- Project End Date: 12/31/2020*

Budget

- Total Project Budget: $1,251,209
  - Total DOE Share: $999,814
  - Total Cost Share: $251,395
  - Total DOE Funds Spent**: $744,239.00
  - Total Cost Share Funds Spent**: $194,676.03

* No cost extension: 12/31/2021

** As of 01/31/2021

Barriers

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

Partners

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

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Relevance

- 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 (IRD) 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 and Go-No-Go
  - ElectroCat target: demonstrate 0.044 A/cm^2 at 0.9V (iR-free, H_2/O_2 configuration, 1bar O_2, 80ºC, 100%RH)
  - Project Go-no-Go: demonstrate 0.025 A/cm^2 at 0.9V (iR-free, H_2/O_2 configuration, 1bar O_2, 80ºC, 100%RH)

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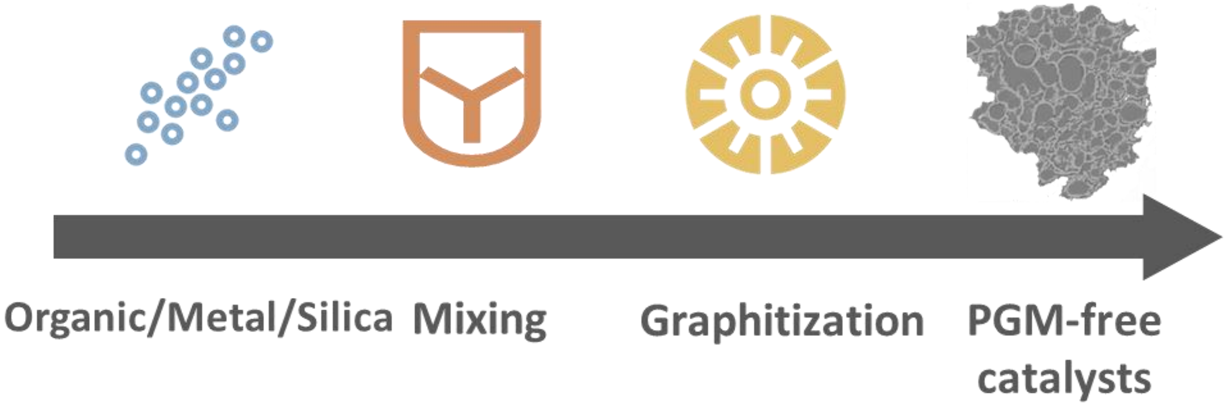
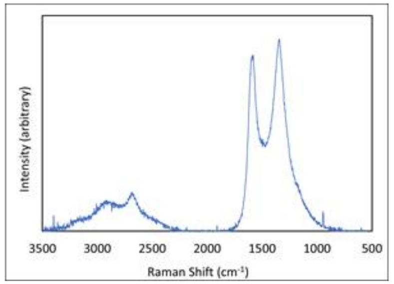
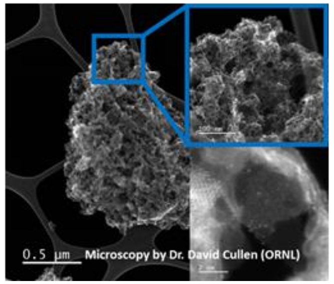
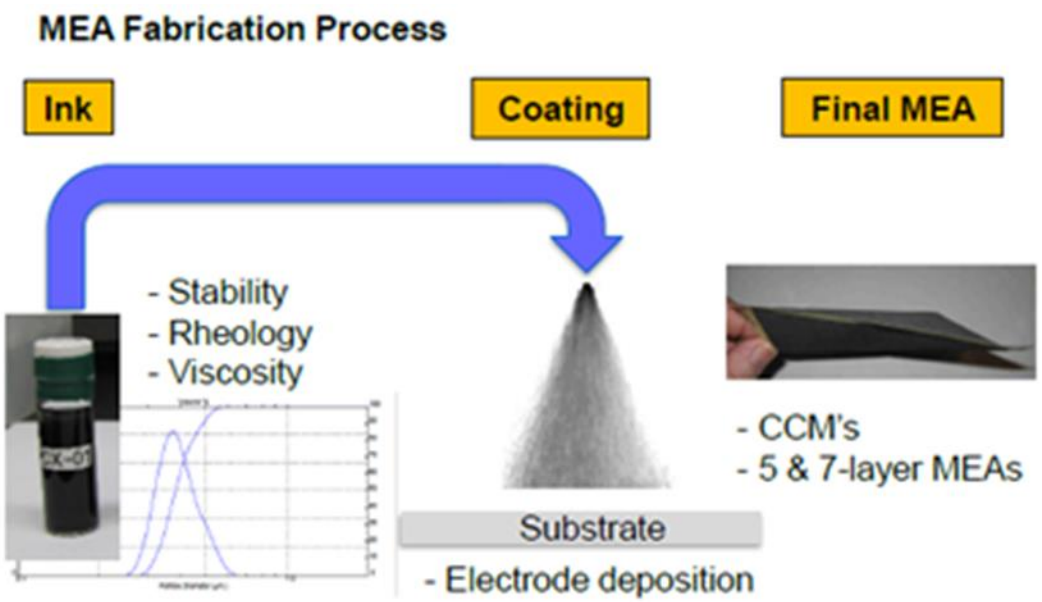
Approach: Catalysts, MEAs and Electrochemistry









Electrochemical evaluation using 25cm^2 MEAs by CV, full pol curve, EIS and EIS modelling.

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Approach: Milestones and Go-no-Go

Milestone Schedule							
Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
2.3	Recommendation to improve catalyst	Milestone	1/31/2020			100%	Surface area of catalysts should be higher than 560 $m^2\ g^{-1}$.
Go/No-Go #1	**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**	**Go/No-Go**	**1/31/2020**			**100%**	**Post-treatment of catalyst in ammonia improved activity.**
3.1	Deliver Gen-2a catalysts (Activity Target in 3.3)	Milestone	4/30/2020			100%	MEAs are under tests at PP and HNEI.
3.1	Deliver Gen-3 catalysts (Activity Target in 3.3)	Milestone	10/31/2020			100%	Accomplished
3.3	Deliver MEAs with Gen-3 catalyst. Activity target: 0.044 A/cm^2 at 0. 85 V	Milestone	1/31/2021			100%	Met
3.4	Estimate mass transfer losses	Milestone	1/31/2021			60%	In progress
3.5	Degradation in performance BoL/EoL MEAs to ElectroCat. Potential hold will be done at 0.65V for 500h (with H_2 /Air at 1.0 bar Air, 100%RH, 80 °C) and degradation rates will be reported. Deliver 10 MEAs 50cm^2 to ElectroCat consortium partners.	Milestone	1/31/2021			25%	In progress

- Team was insignificantly affected by pandemic situation
- All major Milestones are achieved
- Team met Go-no-Go design point
- HNEI moved to new location: installation of FC testing facilities is ongoing. Planning to continue in June 2021.

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Accomplishments: Catalysts Development

NCB (PF-1+PF-2)	1	2	3	Average
C	98.35	98.38	98.38	98.37
N	0.78	0.63	0.67	0.69
O	0.8	0.92	0.88	0.87
Fe	0.07	0.07	0.06	0.07
Zn	0	0	0	0.00
PMF (PF-1)	1	2	3	Average
C	96.97	97.33	96.8	97.03
N	0.81	0.67	0.94	0.81
O	2.17	1.95	2.22	2.11
Fe	0.05	0.05	0.04	0.05
Zn	0	0	0	0.00

Sample	Surface Area, $m^2\ g^{-1}$	Pore size distribution, nm	Particle size (DLS), nm
NCB (PF-1+PF-2)	820	7-8	300-400
PMF (PF-1)	740	~10	600-800

- EDX shows less oxygen in sample. Both samples does not have Zn remained.
- NCB has higher surface area and smaller pore/particles distribution

In order to decrease particle size Zn and 2 proprietary pore formers (PF-1 and PF-2) were used

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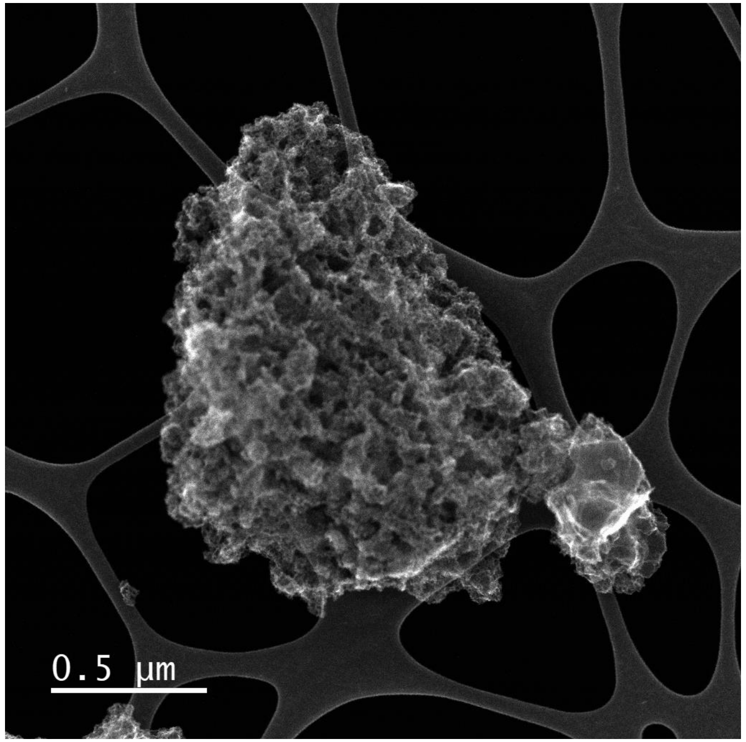
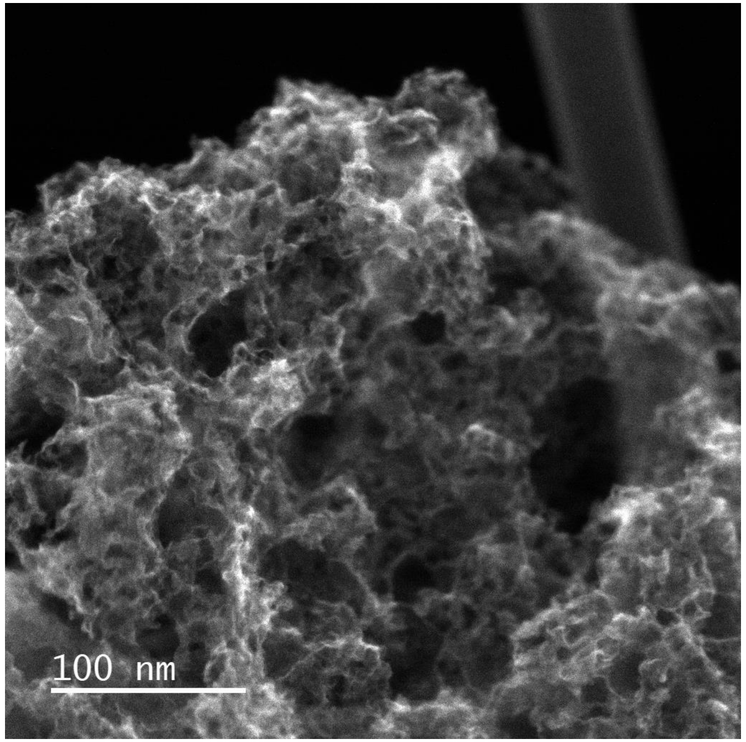
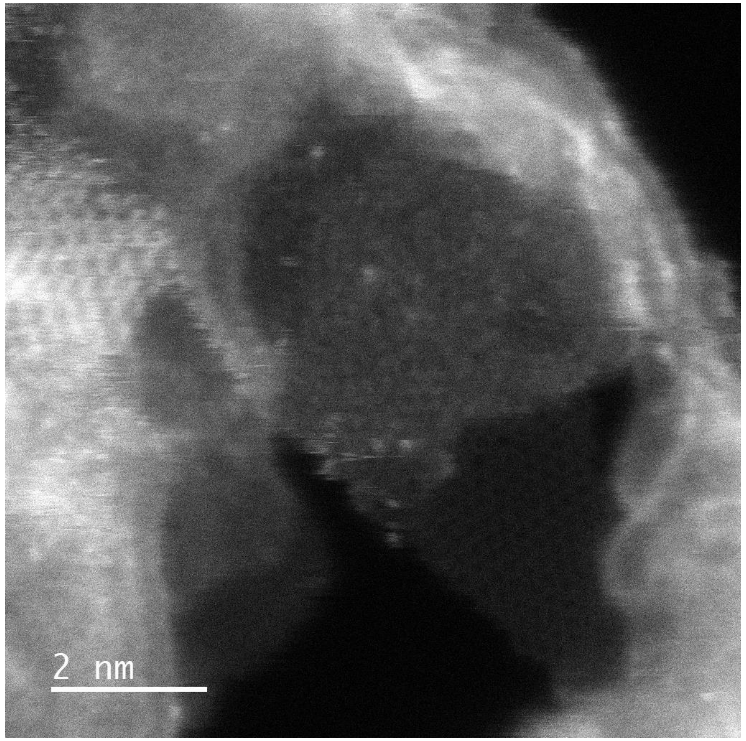
Accomplishments: Catalysts Development (PMF)







Microscopy by Dr. David Cullen (ORNL)

Primary catalysts particles are still large. Atomically dispersed Fe-N_x centers populated the carbon matrix.

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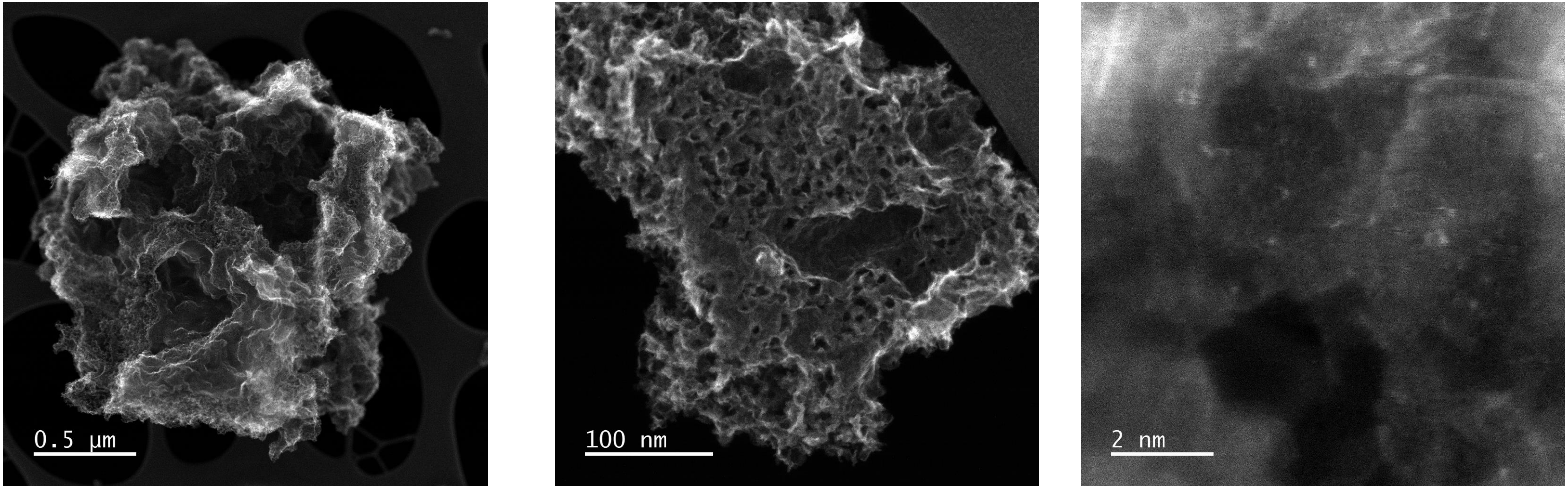
Accomplishments: Catalysts Development (NCB)



Microscopy by Dr. David Cullen (ORNL)

Addition of PF-1 and PF-2 increased porosity and surface area. Very large pores can be seen in material.

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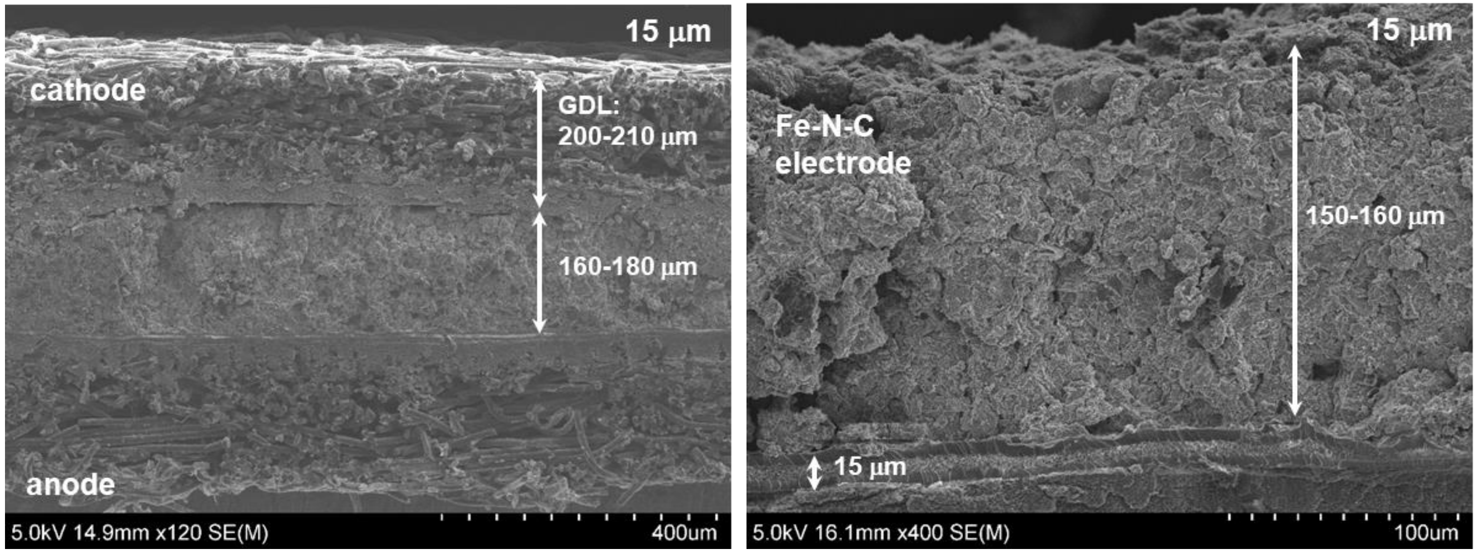
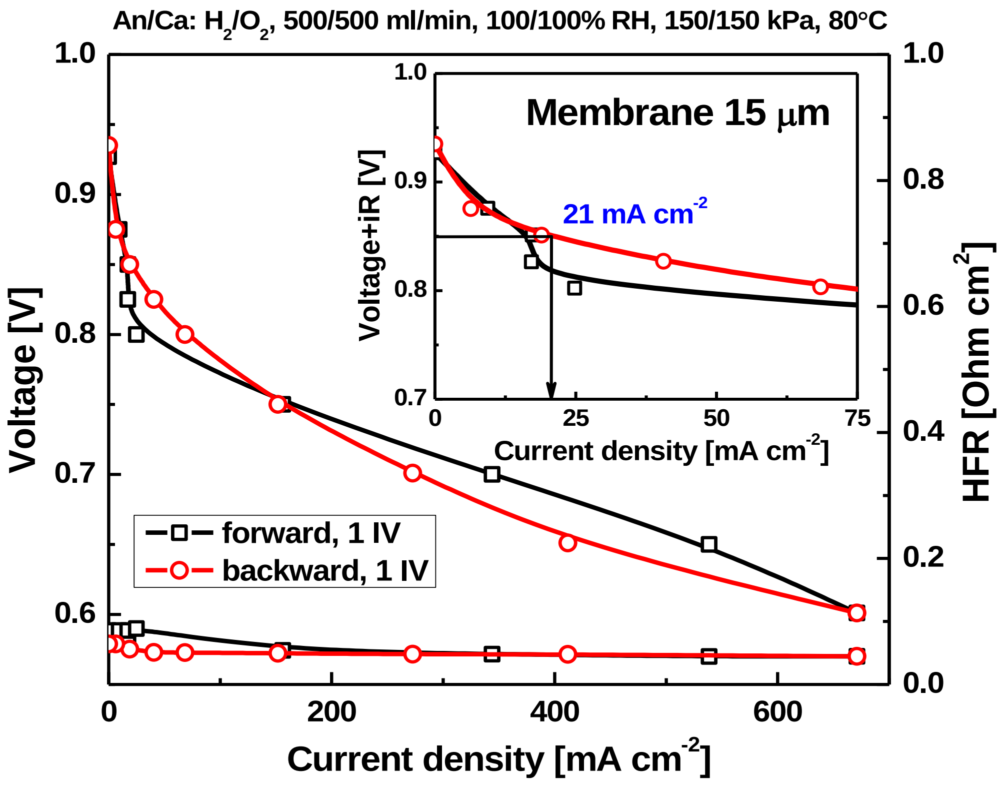
Accomplishments: Electrodes Development

Membrane Thickness Study (15µm)





- OCV ~ 0.927 V
- HFR ~ 45-60 mOhm cm^2
- I=21 mA cm^{-2} @ 0.85 V (iR-corr)
- I=671 mA cm^{-2} @ 0.6 V

Electrode layer thickness (@2.5 mg loading) is ~150µm.
Issues to be solved: O_2 and H^+ transport, flooding.

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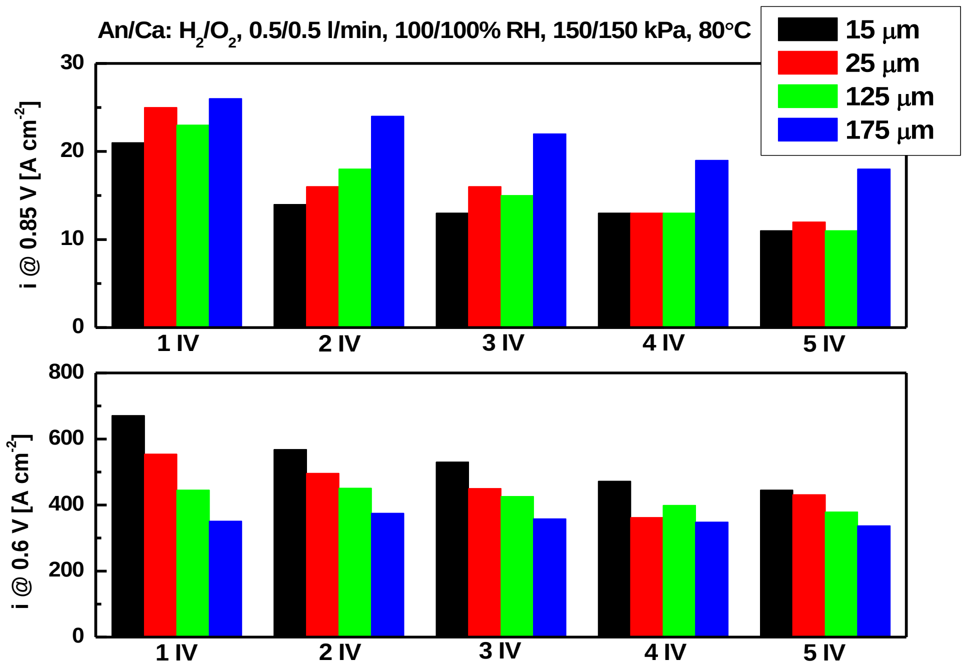
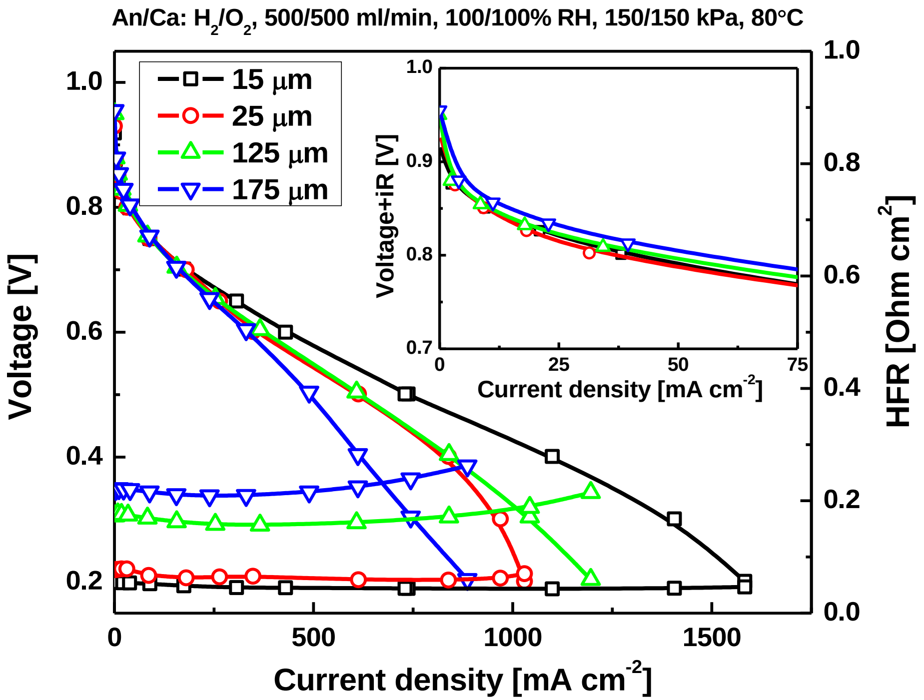
Accomplishments: Electrodes Development

Membrane Thickness Study (15, 25, 125 and 175µm)





The membrane with thickness of 15µm was downselected for further electrode optimization.

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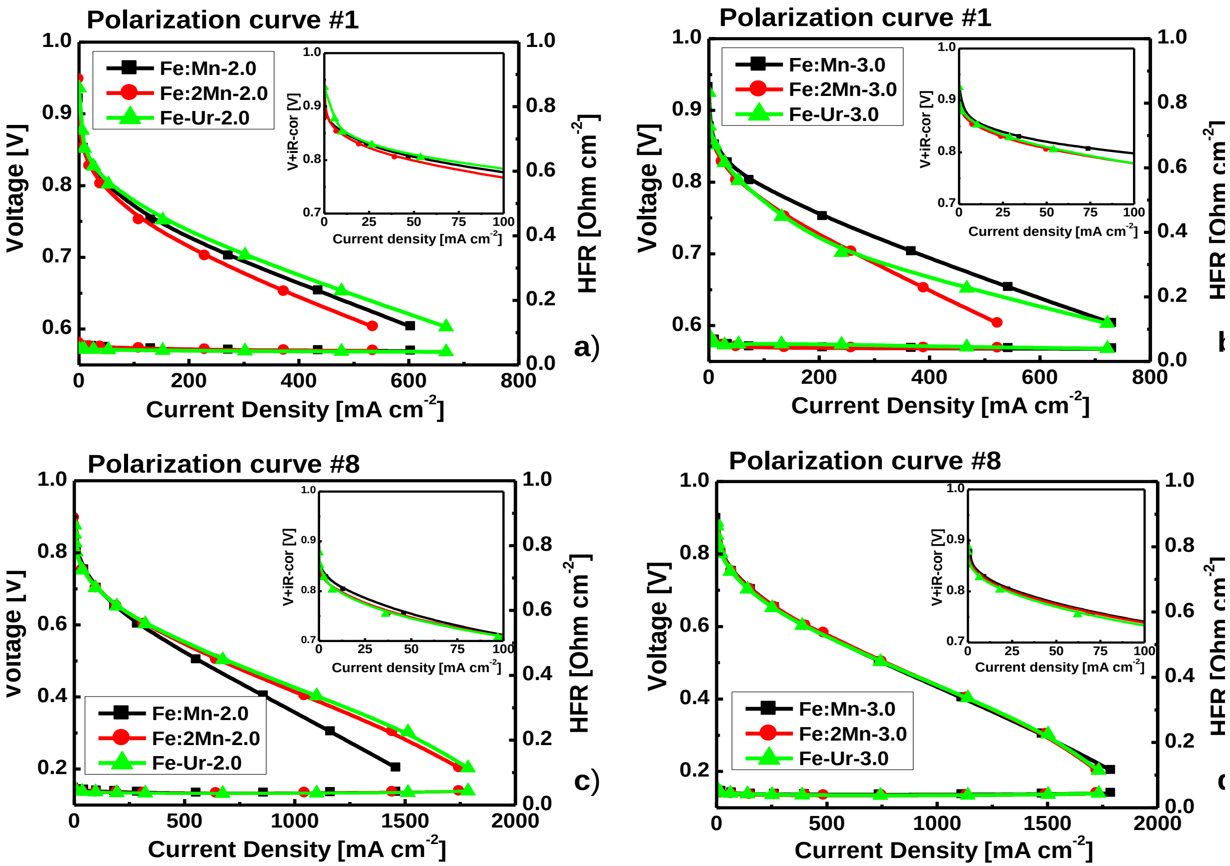
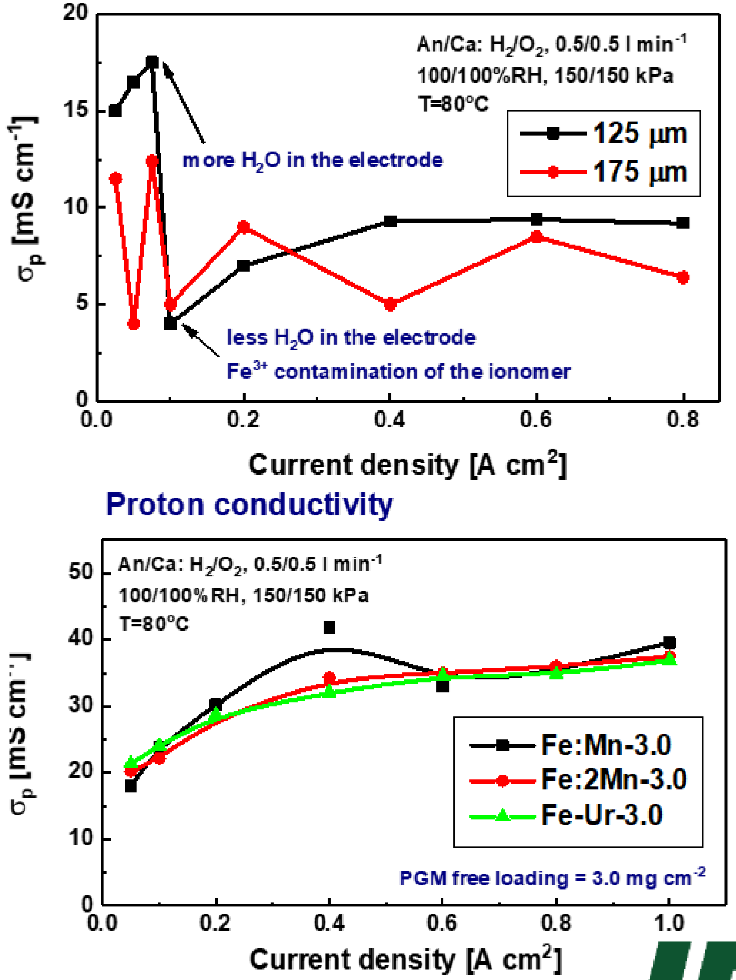
Accomplishments: Electrodes Development

Low EW=720 and Electrode Additives Study



Proton conductivity



Proton conductivity was improved 4 times

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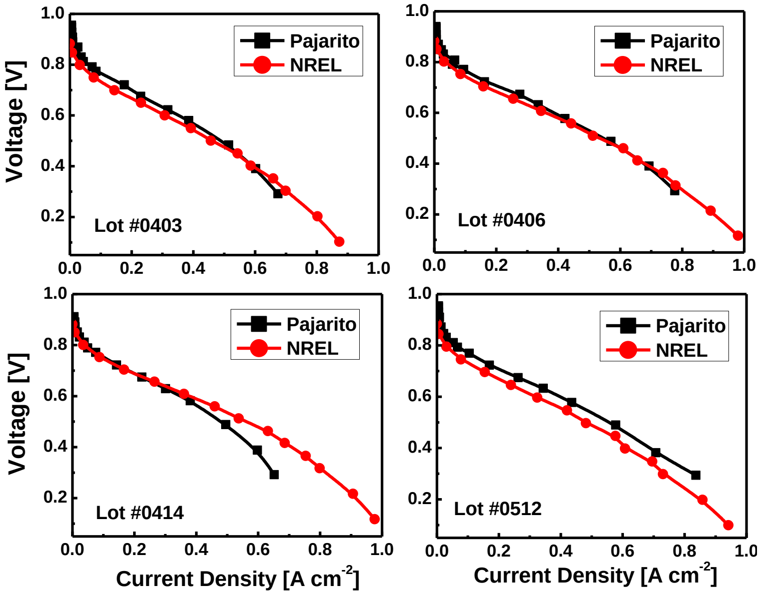
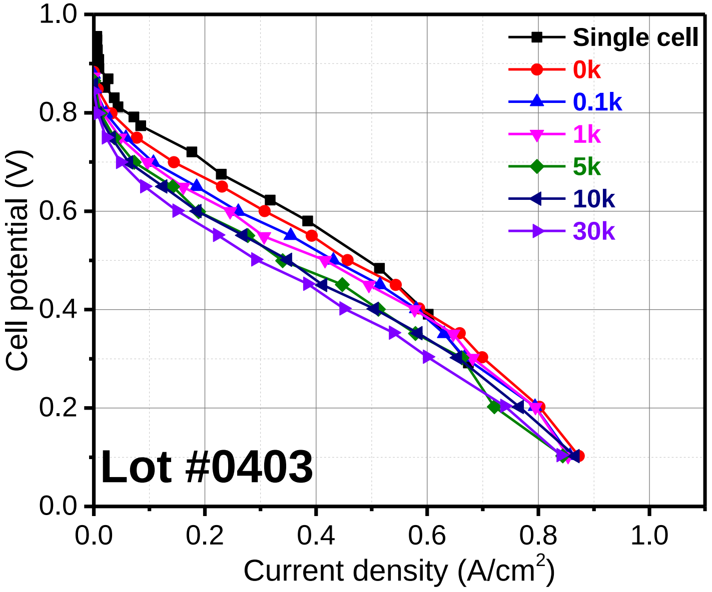
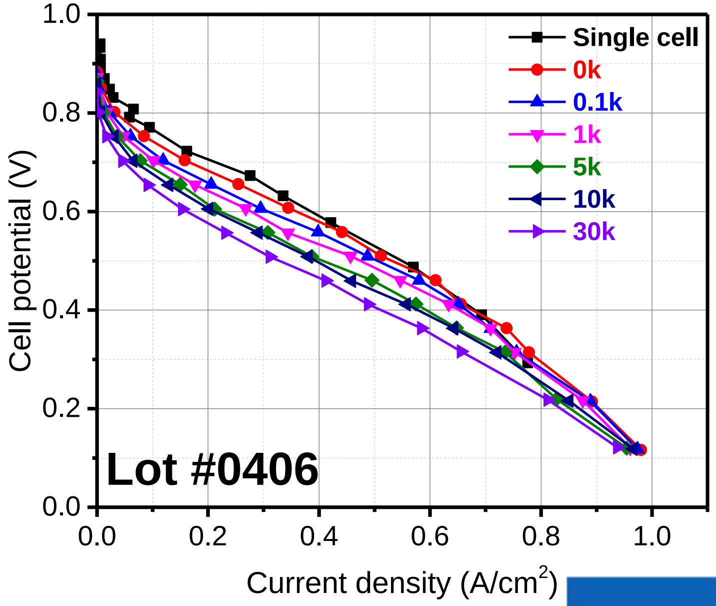
Accomplishments: MEAs Durability



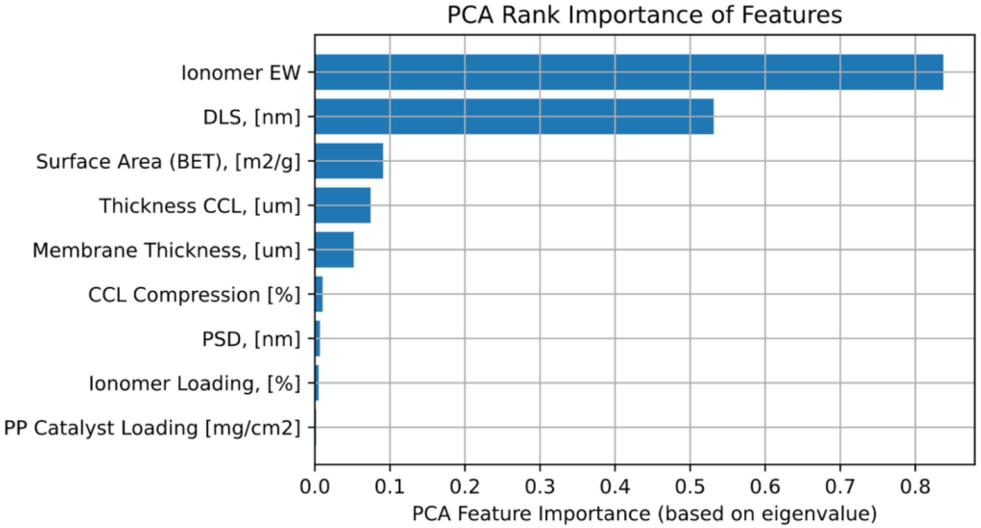




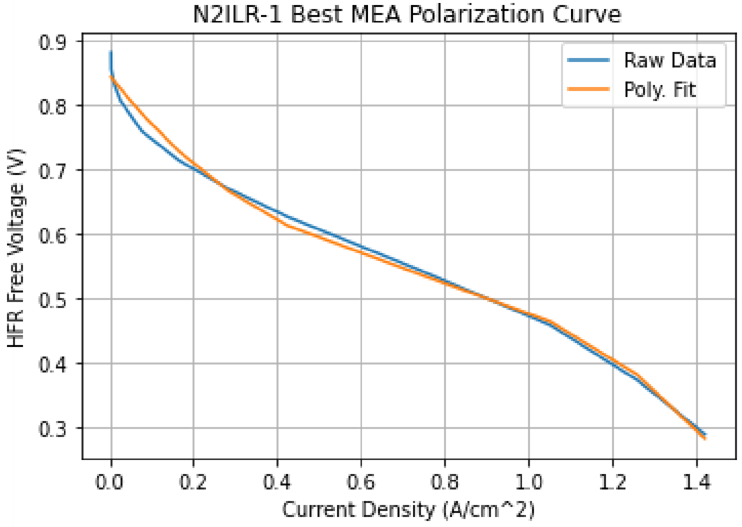
Sample (Lot#)	Cycling between OCV and 0.60 V						Cycling between 0.95 V and 0.60 V			
	Current density (A/cm^2) @0.80V			Potential (V) @0.80A/cm^2			Current density @0.80V		Potential @0.80A/cm^2	
	0k	30k	DOE target	0k	30k	DOE target	0k	30k	0k	30k
0403	0.032	0.007	0.300 A/cm^2 at beginning of test (BOT)	0.204	0.144	≤ 30 mV loss at 0.80 A/cm^2 after 30k cycles	0.035	0.002	0.150	N/A
0406	0.034	0.003		0.295	0.226		0.036	0.002	0.266	0.142
0414	0.036	0.004		0.316	0.197		0.034	0.002	0.235	N/A
0512-1	0.028	0.002		0.244	0.163		0.027	0.002	0.263	0.121
0512-3	0.020	0.002		0.230	0.130		0.023	0.002	0.205	N/A

Accomplishments: Machine Learning

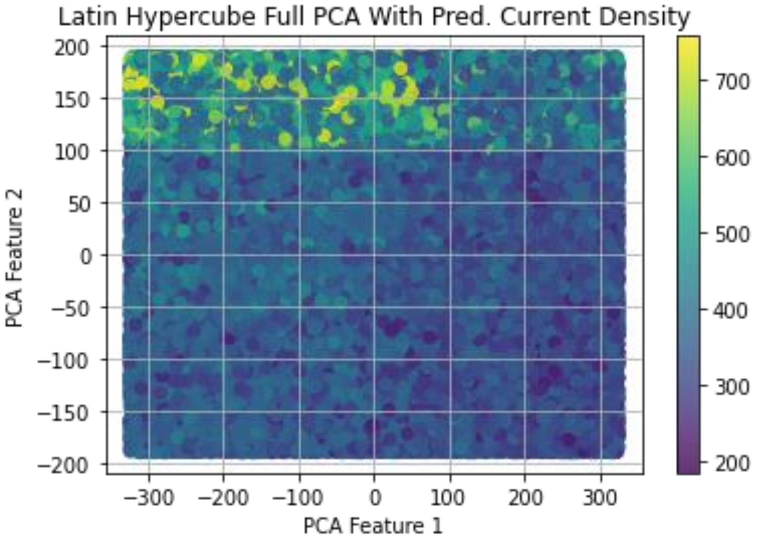
Principal Component Analysis



Polynomial Coefficient Fitting



Latin Hypercube Predictions



	Ionomer EW	DLS, [nm]	Surface Area (BET), [m2/g]	Thickness CCL, [um]	Membrane Thickness, [um]	CCL Compression [%]	PSD, [nm]	Ionomer Loading, [%]	PP Catalyst Loading [mg/cm2]	Pred_Poly3	Pred_Poly2	Pred_Poly1	Pred_Poly0	Sum_R	Pt_R
80550	723.586540	530.931285	774.424124	157.327318	110.517880	22.404926	7.601255	41.454840	2.291655	-1.147173	1.644636	-0.957938	0.880424	-3.749747	757.183970
67269	747.462225	575.612991	632.633339	141.383552	140.699609	22.041109	10.661745	38.279177	2.435398	-1.220943	1.752500	-1.002289	0.882903	-3.975731	754.296294
87863	754.451274	676.999365	576.229852	134.416701	140.241656	22.427478	8.109015	30.977924	2.079642	-1.225835	1.760211	-1.005488	0.882713	-3.991534	753.581301

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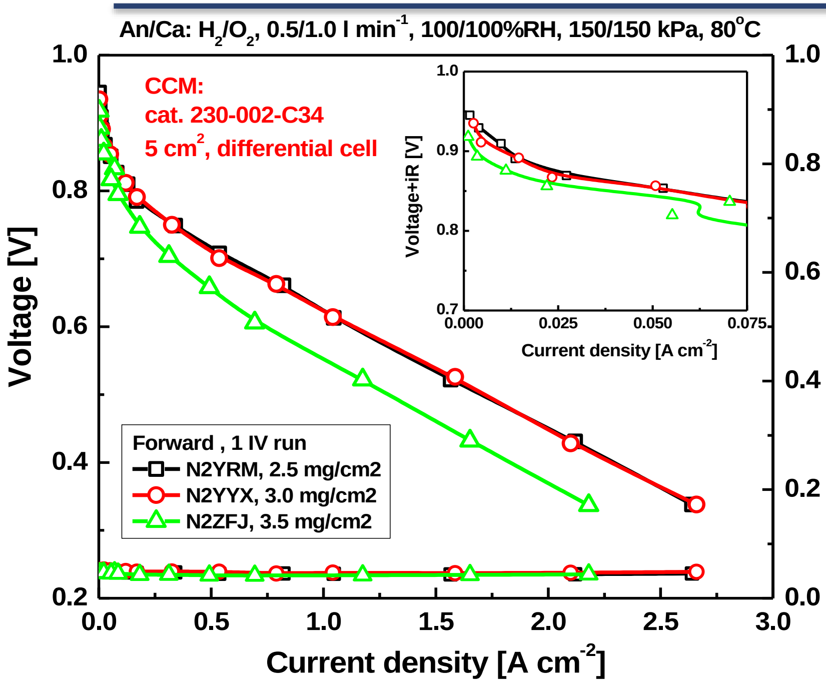
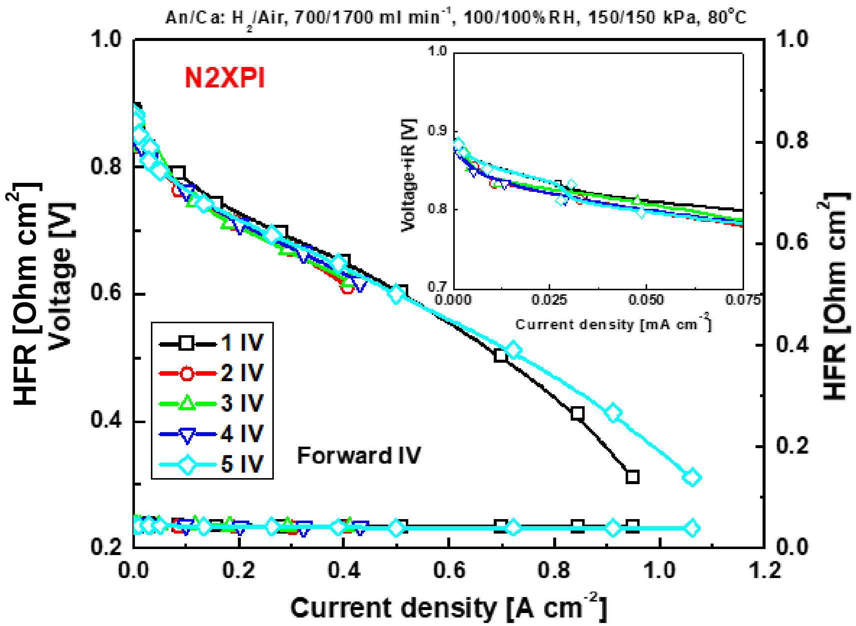
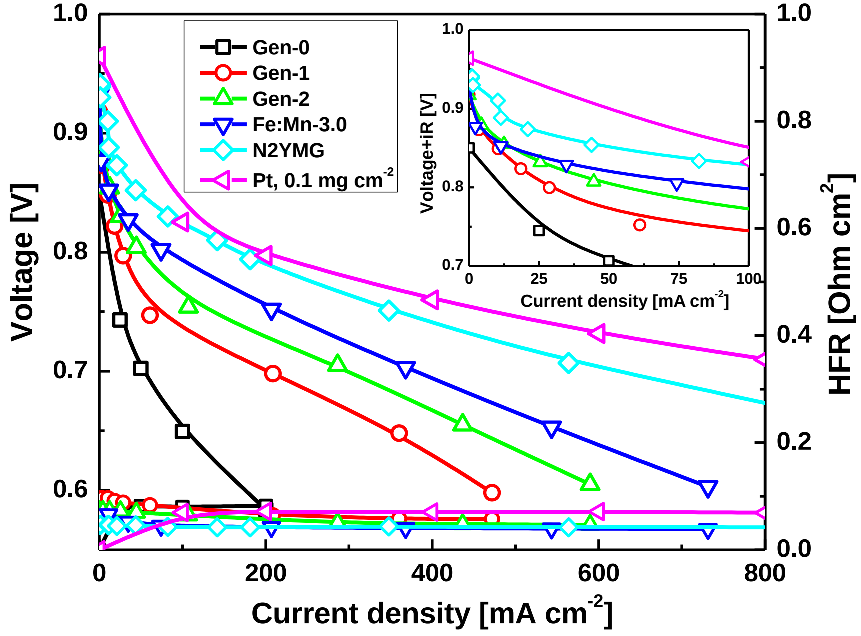
Accomplishments: Overall Project Progress







V, mV	C_{dl}	D_{ox}	2e vs 4e
N2KYZ			
50	10.6982	3.108733	7.63E-07
100	9.42928	6.392552	4.29E-07
200	9.39129	10.941709	1.04E-05
400	9.41978	15.988991	0.00013311
800	13.45351	4063.99204	0.02162464

Fe-N-C catalysts selective towards 4e$^-$ ORR mechanism. 0.8 A/cm^2 at 0.675V (H_2/O_2)

C_{dl} – double layer capacitance; D_{ox} – oxygen diffusivity (CL); 2e vs 4e – 2e$^-$ contribution

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Responses to Reviewers' Comments

- The critical Reviewers' comments project obtained in 2019 were fully addressed in AMR presentation 2020 (https://www.hydrogen.energy.gov/pdfs/review20/fc305_serov_2020_o.pdf)
- Project **was not reviewed** in 2020

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Collaboration and Coordination

- ANL (ElectroCat)
  - High Throughput Synthesis
  - Characterization (USAXS, XAFS)
  - Machine Learning
- NREL (ElectroCat)
  - Durability Studies
- ORNL (ElectroCat)
  - Microscopy
- LANL (ElectroCat)
  - Evaluation the Density of Active Sites
- Juelich Research Center (Germany)
  - EIS modelling (Dr. Kulikovsky)
  - Benchmark PGM-free catalysts (Dr. Cherevko)
- U South Carolina
  - Study Fe-N-C in AEMFC
- Tartu University (Estonia)
  - Study Fe-N-C in AEMFC
- Technion (Israel)
  - Benchmark PGM-free catalysts
- CNR (Italy)
  - Study Fe-N-C in DMFC
- PEGASUS (EU)
  - Benchmark PGM-free catalysts
- CRESCENDO (EU)
  - Benchmark PGM-free catalysts
- U Szeged (Hungary)
  - Evaluation of Fe-N-C in CO2RR
- INL (Portugal)
  - Study PGM-free in HER
- Kyushu University (Japan)
  - Study Fe-N-C in AEMFC
- New Mexico Tech
  - Alternative usage of PGM-free materials

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Remaining Challenges and Barriers

- Increase the density of active sites in final catalyst.
- Understand and resolve the issue with shelf stability.
- Improve catalyst stability and MEA durability in FC tests.
- Increase size of dataset for the usage in Machine Learning applications.

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Proposed Future Work

- Synthesis: optimize Fe content (tune amount of Fe precursors initially added to N-C compound).
- Electrodes: “half-MEAs” – partially Catalyst Coated Membrane (CCM) and partially Catalyst Coated Substrate (CCS).
- Electrochemical: durability of new Fe-N-C:MEA configurations.
- Characterization: post-AST XPS, EDX and microscopy.
- Machine Learning: evaluate new Catalyst/MEA combinations, based on ML predictions/prescriptions (Active Machine Learning – ANL Group).

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Summary

- During the project Team synthesized and characterized more than 30 different PGM-free catalysts. Batch size was **increased** from 25 to ~50g.
- The electrode optimization (IRD Fuel Cells) resulted in improvement of performance from **150 to 950 mA/cm^2 @ 0.65V** (H_2/O_2 ElectroCat conditions, Differential Cell). MEAs were reproducibly manufactured in 25cm^2 form-factor (>300 CCMs total, during the project).
- HNEI's thorough electrochemical analysis allowed to understand main drawbacks in catalysts (too large primary particles and insufficient number of pores >50nm) and mitigate them.
- Team accumulated a dataset sufficiently large enough for using in ML/AI and performed first modelling of full polarization curves.
- Team published for less than 2 years **7 peer-reviewed articles** (one is in an advanced draft stage).

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- Technical Backup and Additional Information

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Technology Transfer Activity

- Pajarito Powder launched new generation of commercial PGM-free catalysts (will substitute previous PMF-011904) **based on the results** of this project.
- Pajarito and IRD Fuel Cells, LLC looking for enhancing joint provisional application with novel electrode structure (**USPTO examination stage**).
- Pajarito exploring possibilities for alternative commercial application of Fe-N-C catalysts (**several companies are approached**).

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Progress toward DOE Targets or Milestones

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (50 cm^2 cell, differential conditions)
MEA performance	mA/cm^2 @ 900 mV (H_2/O_2; iR-free)	30	27
MEA degradation	Potential (V) @0.80A/cm^2	<30	60

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Special Recognitions and Awards

- PI Alexey Serov is in the list of Top 2% Most Cited Scientists by Stanford research: “Updated science-wide author databases of standardized citation indicators” (https://doi.org/10.1371/journal.pbio.3000918)

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Publications and Presentations

Publications:

[7] J. Lilloja, M. Mooste, E. Kibena-Põldsepp, A. Sarapuu, B. Zulevi, A. Kikas, H.-M. Piirsoo, A. Tamm, V. Kisand, S. Holdcroft, **A. Serov**, K. Tammeveski "Mesoporous iron-nitrogen co-doped carbon material as cathode catalyst for the anion exchange membrane fuel cell" J. of Power Sources Advances 8 (2021) 100052.

[6] A. Serov, K. Kovnir, M. Shatruk, Y. V. Kolen'ko "Critical Review of Earth-Abundant Borides and Phosphides for Water Electrolysis: Transition from the Lab to the Market" Johnson Matthey Technol. Rev., 65, (2) (2021).

[5] T. Reshetenko, **A. Serov**, **M. Odgaard**, G. Randolf, L. Osmieri, A. Kulikovsky "Electron and proton conductivity of Fe-N-C cathodes for PEM fuel cells: A Model-based electrochemical impedance spectroscopy measurement" Electrochem. Comm. (2020) DOI: doi.org/10.1016/j.elecom.2020.106795.

[4] M. J. Dzara, K. Artyushkova, M. T. Sougrati, C. Ngo, M. A. Fitzgerald, **A. Serov**, B. Zulevi, P. Atanassov, F. Jaouen, S. Pylypenko "Characterizing Complex Gas-Solid Interfaces with in Situ Spectroscopy: Oxygen Adsorption Behavior on Fe-N-C Catalysts" J. of Physical Chemistry C (2020) DOI: 10.1021/acs.jpcc.0c05244.

[3] T. Reshetenko, G. Randolf, **M. Odgaard**, B. Zulevi, **A. Serov***, A. Kulikovsky "The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance" Journal of The Electrochemical Society 167 (2020) 084501.

[2] C.L. Vecchio, **A. Serov***, H. Romero, A. Lubers, B. Zulevi, A.S. Aricò, V. Baglio "Commercial platinum group metal-free cathodic electrocatalysts for highly performed direct methanol fuel cell applications" J. of Power Sources 437 (2019) 226948.

[1] T. Reshetenko, **A. Serov**, A. Kulikovsky, P. Atanassov "Impedance Spectroscopy Characterization of PEM Fuel Cells with Fe-NC-Based Cathodes" J. of The Electrochemical Society 166 (2019) F653-F660.

Presentations:

[1] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, **M. Odgaard**, **T. V. Reshetenko**, B. Zulevi "*PGM-Free Oxygen Reduction Reaction Electrocatalyst: From the Design to Manufacturing*", ECS Meeting 235, Dallas, TX (2019).

[2] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, **M. Odgaard**, **T. V. Reshetenko**, B. Zulevi "*Are PGM-free Fuel Cell Catalysts Ready for Prime-Time?*", EFCD2019, La Grand Motte, France (2019). **Invited.**

[3] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, **M. Odgaard**, **T. V. Reshetenko**, B. Zulevi "VariPore™: A Powerful Manufacturing Platform for Fuel Cell and Electrolyzer Applications", ECS Meeting 236, Atlanta, GA (2019).

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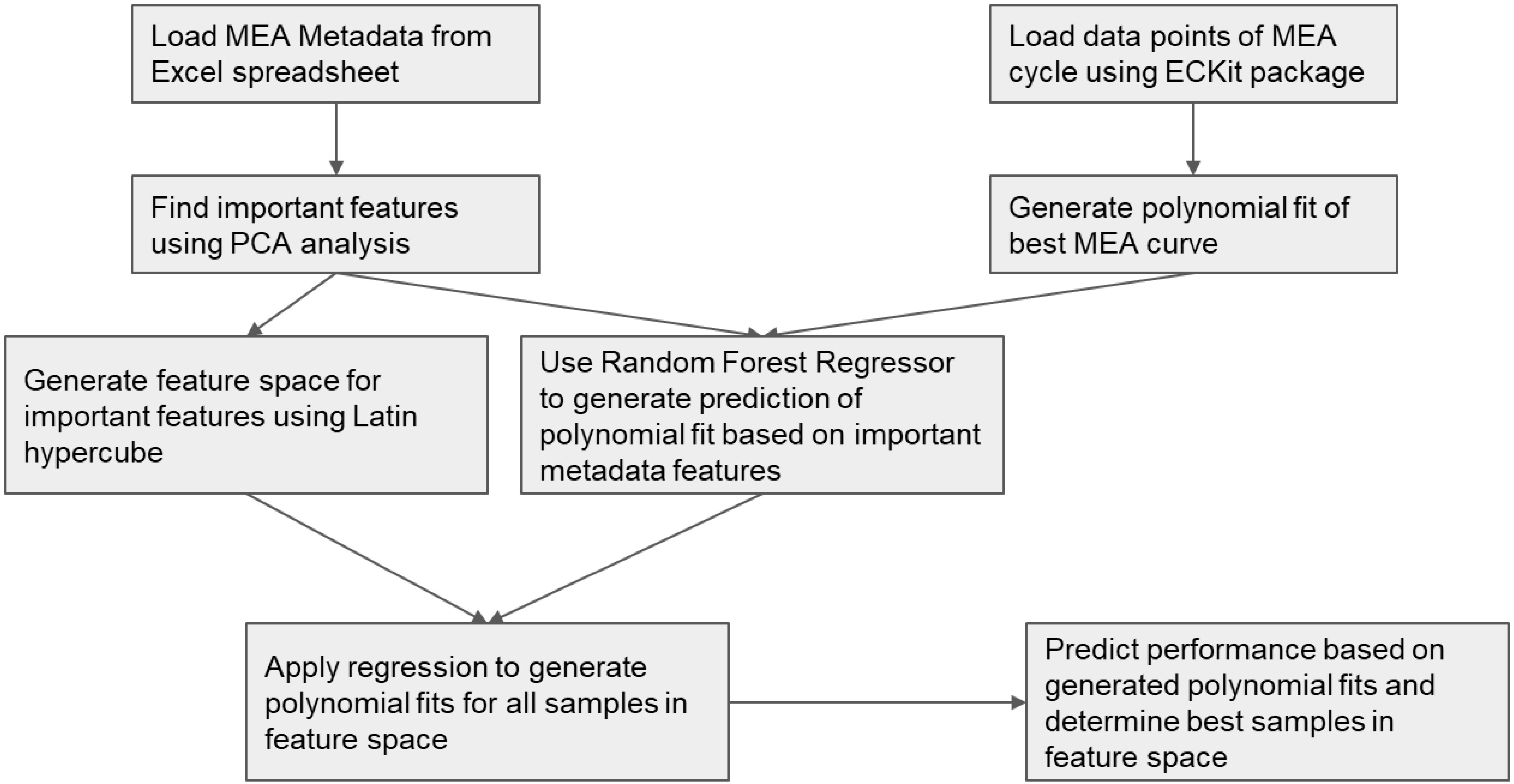
Machine Learning: Workflow



- Dataset of 64 full polarization curves
- 9 parameters (ionomer EW, ionomer loading, surface area etc)

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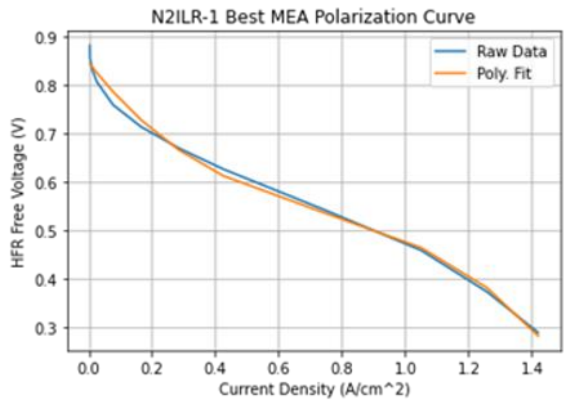
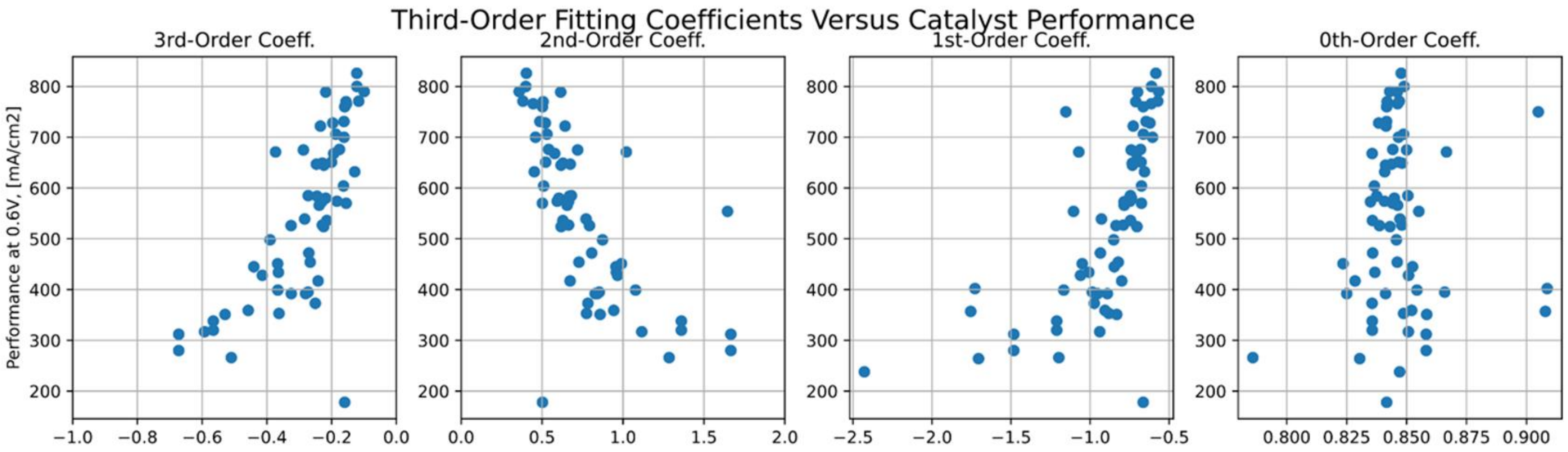
Machine Learning: Polynomial Fitting

Right: an example MEA polarization curve with third-order polynomial fitting. Bottom: Polynomial coefficients compared with current density (at 0.6 V). We therefore use the polynomial coefficients as a proxy for catalyst performance.





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Machine Learning: PCA Analysis

PCA = Principal Component Analysis

Provides a decomposition based on the importance of each feature. We then select the top features for further predictive analysis.

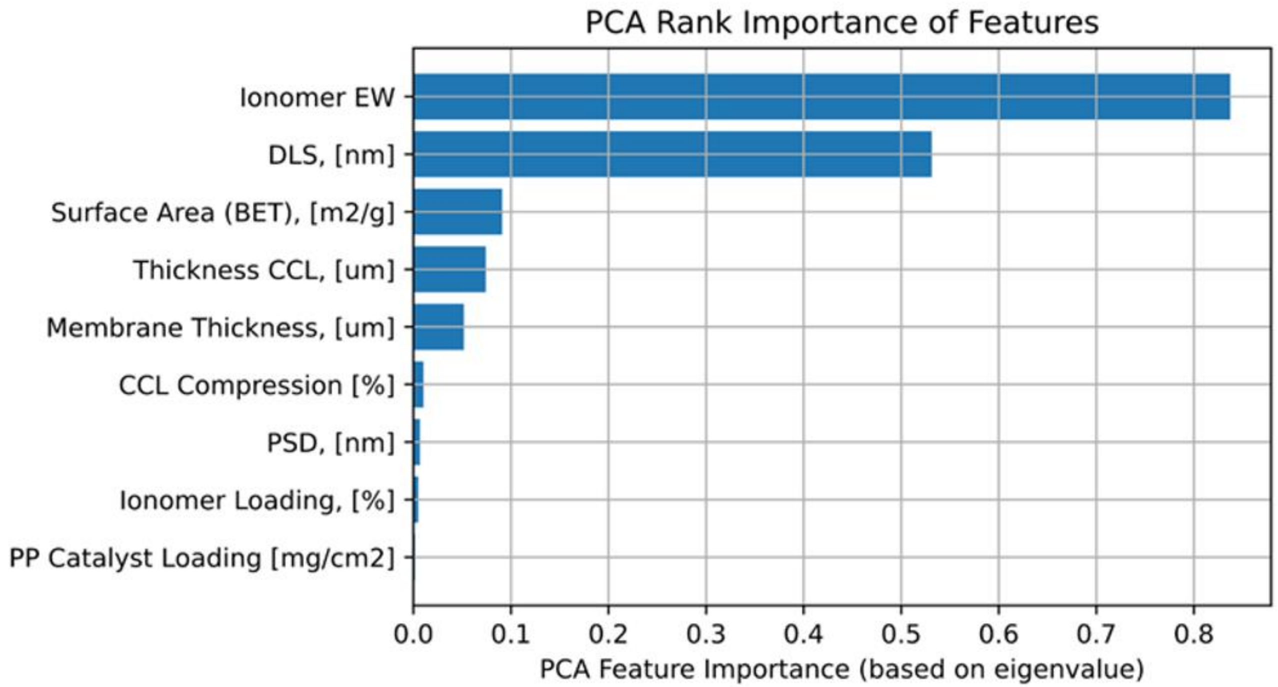
Top important features include:

1) Ionomer EW

2) DLS [nm]

3) Surface Area (BET) [m2/g]

…and others



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Machine Learning: Random Forest Regressor

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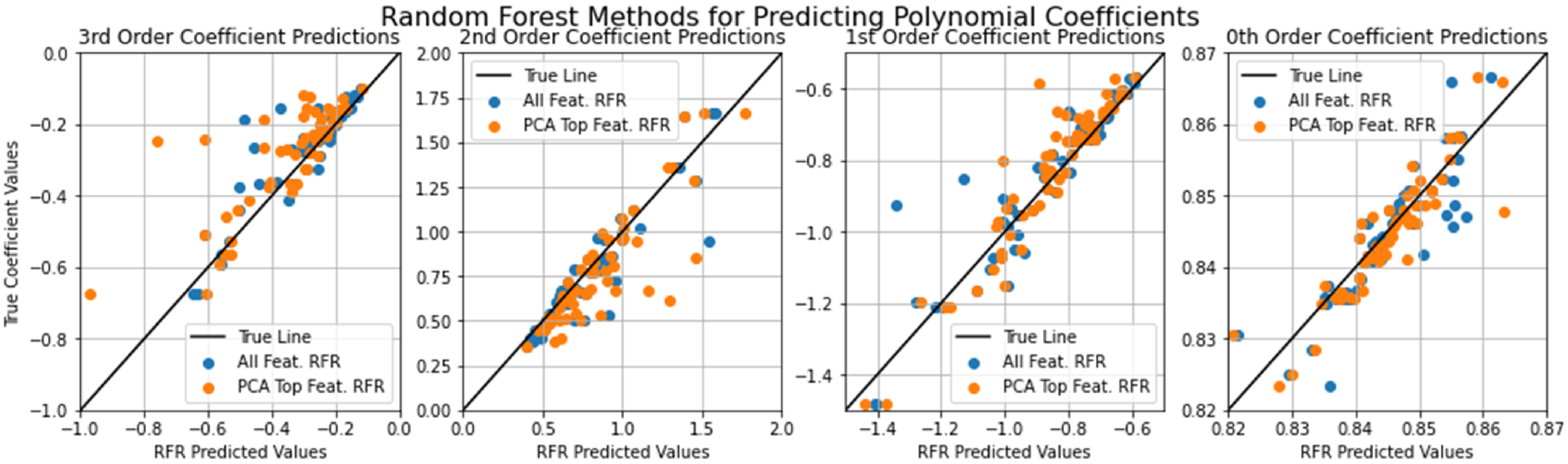
RFR = Random Forest Regressor (special property: cannot overfit)

RFR provides predictions of the polynomial coefficients in the case of using all features or using the top five features derived from PCA importance.



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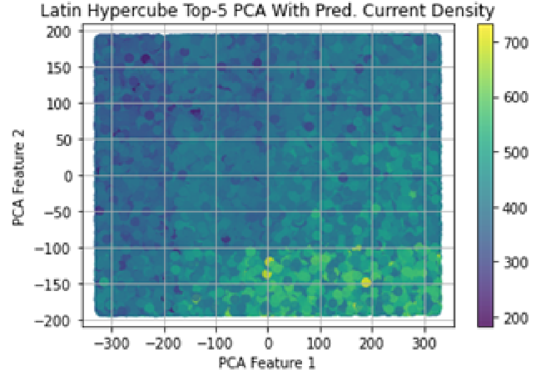
Machine Learning: Latin Hypercube

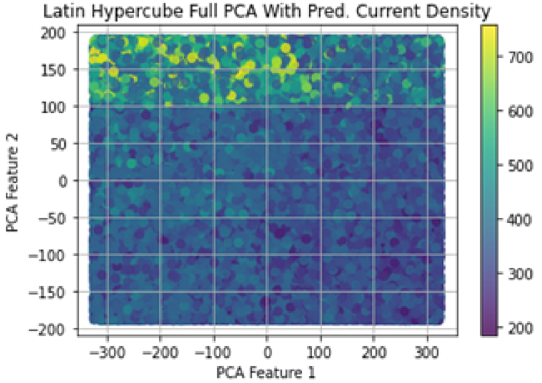
Sampling within our bounded feature space allows us to find areas where current density appears to be the highest. Top predicted results shown below.

Further validation with experiments can now be performed.

	Ionomer EW	DLS, [nm]	Surface Area (BET), [m2/g]	Thickness CCL, [um]	Membrane Thickness, [um]	Pred_Poly3	Pred_Poly2	Pred_Poly1	Pred_Poly0	Sum_R	Pt_R
41732	771.383652	449.705351	643.271874	107.152503	152.154928	-1.195516	1.726819	-1.007528	0.881145	-3.929864	731.991461
27055	765.039157	499.971256	547.813695	109.824221	28.556029	-1.098347	1.606545	-0.967129	0.877848	-3.672022	731.835627
764	733.080848	646.422333	602.617073	107.164870	20.723627	-1.070622	1.572565	-0.956398	0.877003	-3.599586	730.971700
64795	735.318089	562.819309	572.932874	106.047107	101.054473	-1.081795	1.591718	-0.965110	0.877381	-3.638622	730.648497
71162	741.650690	583.788107	572.743000	107.956172	77.154926	-1.085204	1.596641	-0.966879	0.877366	-3.648724	730.623179



	Ionomer EW	DLS, [nm]	Surface Area (BET), [m2/g]	Thickness CCL, [um]	Membrane Thickness, [um]	CCL Compression [%]	PSD, [nm]	Ionomer Loading, [%]	PP Catalyst Loading [mg/cm2]	Pred_Poly3	Pred_Poly2	Pred_Poly1	Pred_Poly0	Sum_R	Pt_R
80550	723.586540	530.931285	774.424124	157.327318	110.517880	22.404926	7.601255	41.454840	2.291655	-1.147173	1.644636	-0.957938	0.880424	-3.749747	757.183970
67269	747.462225	575.612991	632.633339	141.383552	140.699609	22.041109	10.661745	38.279177	2.435398	-1.220943	1.752500	-1.002289	0.882903	-3.975731	754.296294
87863	754.451274	676.999365	576.229852	134.416701	140.241656	22.427478	8.109015	30.977924	2.079642	-1.225835	1.760211	-1.005488	0.882713	-3.991534	753.581301
63714	758.639484	658.791375	750.697818	220.799759	65.405977	22.011020	7.032086	47.463725	4.666276	-1.122016	1.617802	-0.952522	0.879152	-3.692339	753.372712
32933	772.614116	729.299563	582.995462	159.837631	164.891570	22.217694	14.126197	41.255299	2.514343	-1.212857	1.742312	-0.999357	0.882602	-3.954526	753.350715



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