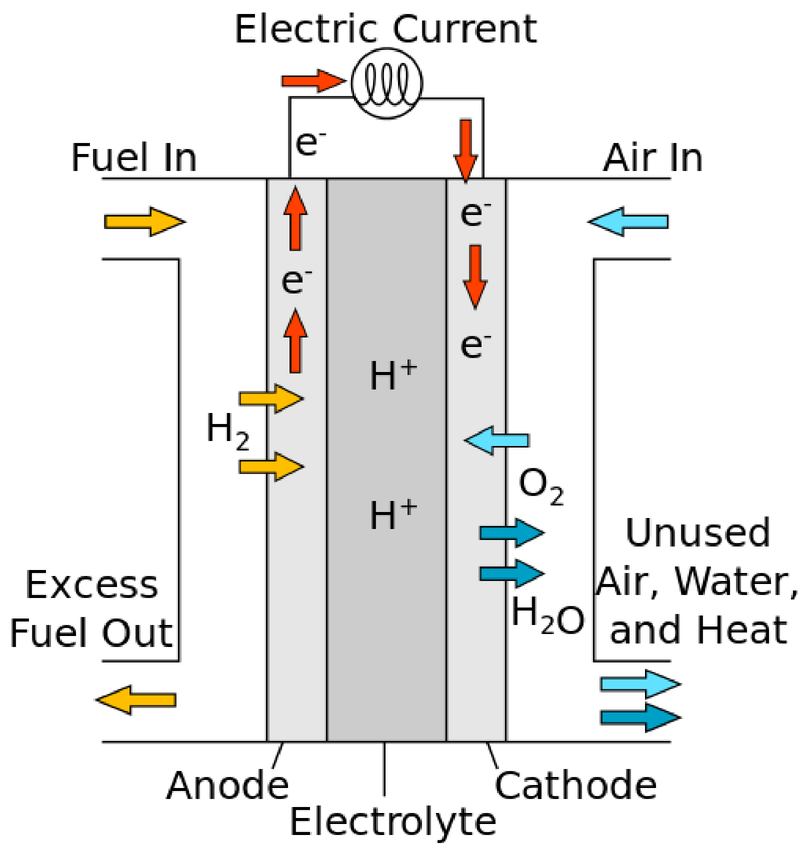
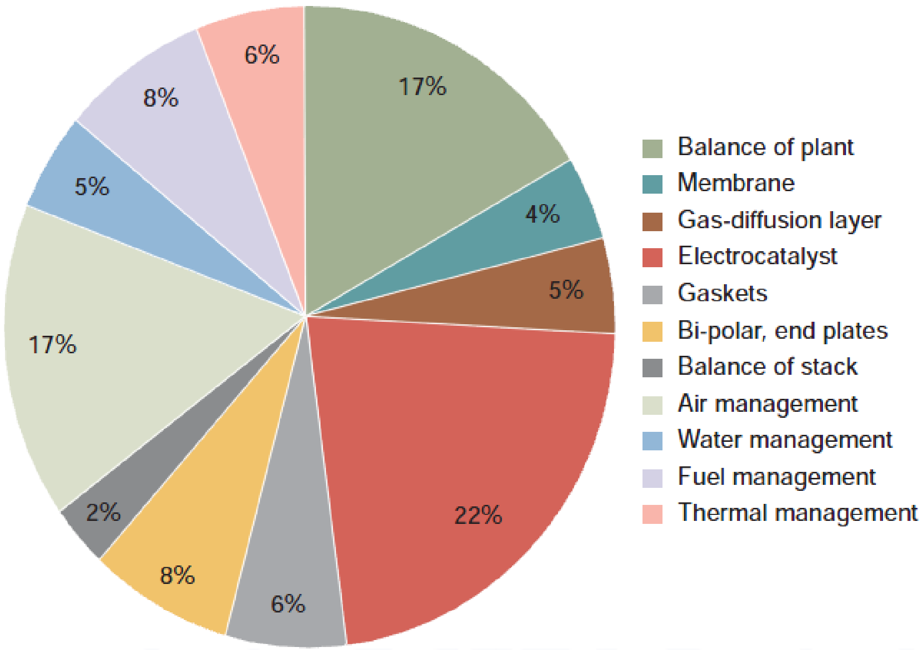
COLORADO SCHOOL OF MINES

Elucidating performance-property trends in Pt-group metal free oxygen reduction reaction catalysts

Michael J. Dzara, Chilan Ngo, Michael Workman, Plamen Atanassov, Kateryna Artyushkova, Svitlana Pylypenko

Polymer electrolyte membrane fuel cells (PEMFCs)





- Catalysts required for cathode and anode reactions

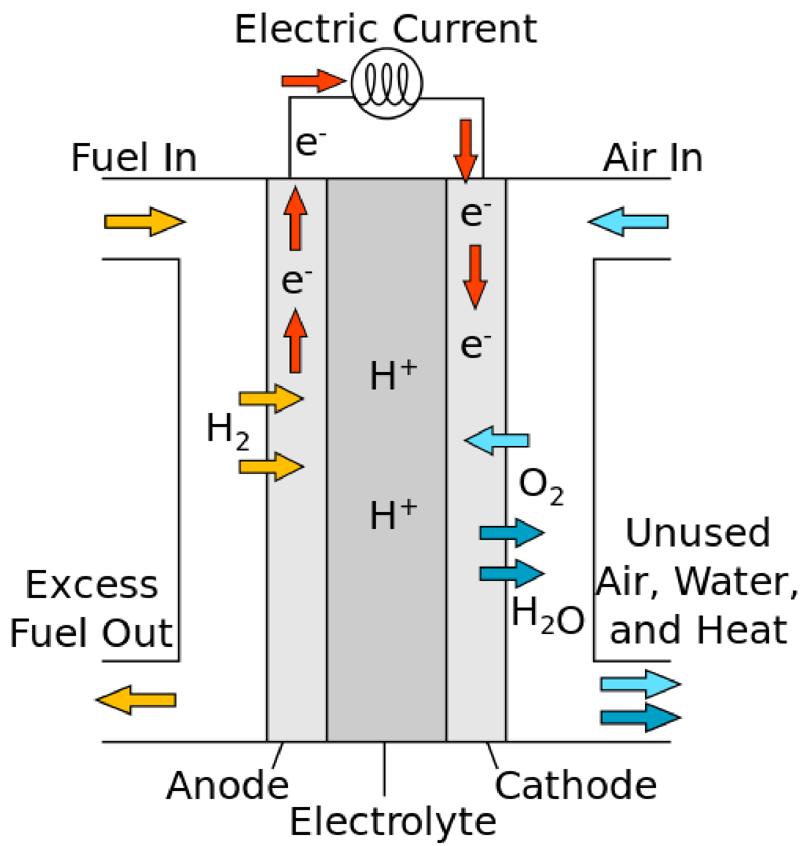
Half-reactions

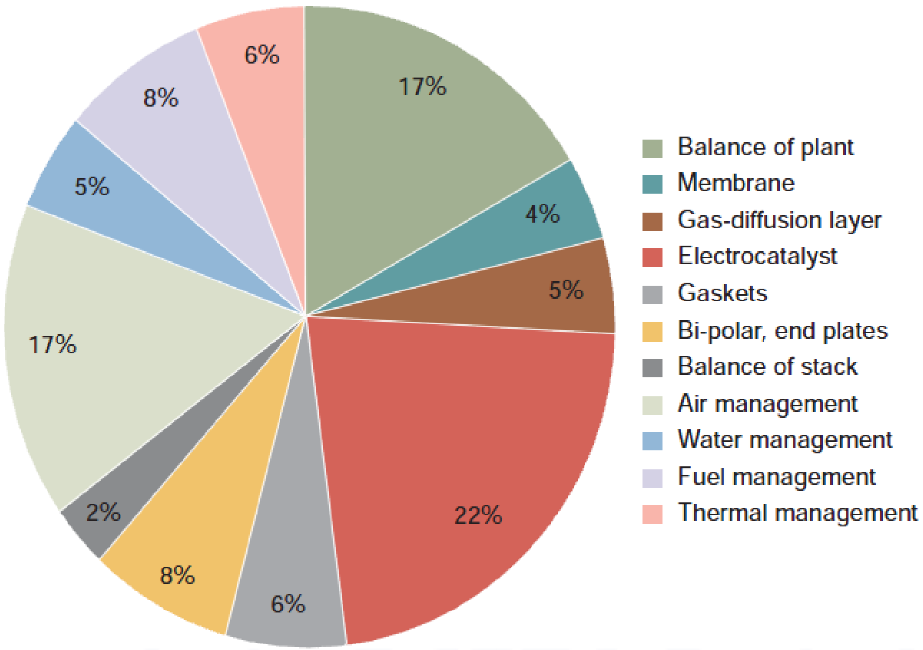
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Shyam Kocha, Bryan Pivovar, and Thomas Gennett , Fuel Cells, 46, 2012

Polymer electrolyte membrane fuel cells (PEMFCs)





- Catalysts required for cathode and anode reactions
- State-of-the art Pt-based catalysts are expensive

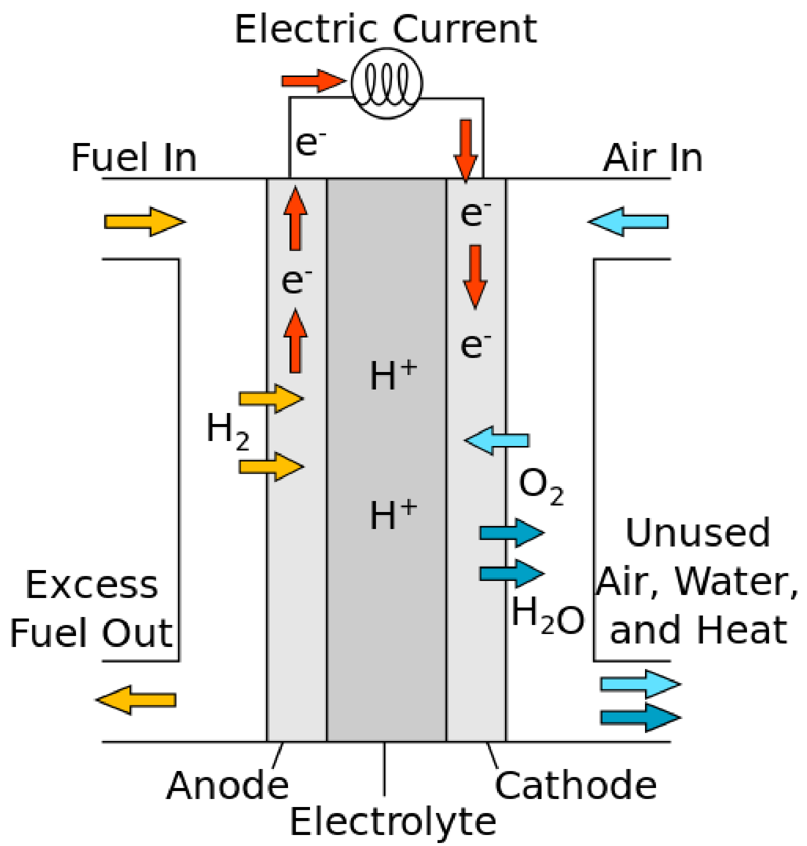
<u>Half-reactions</u>

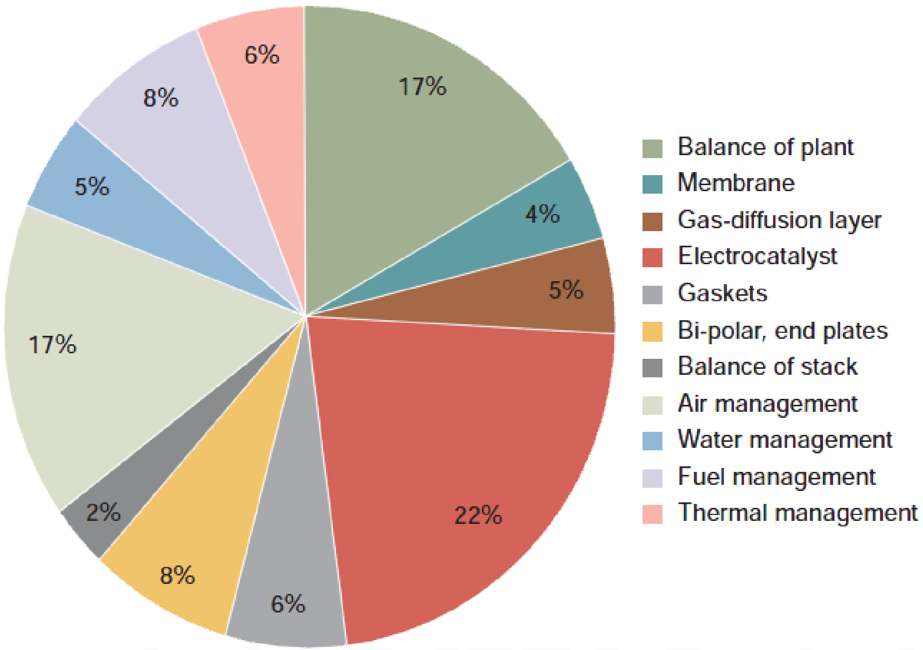
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Shyam Kocha, Bryan Pivovar, and Thomas Gennett , Fuel Cells, 46, 2012

Polymer electrolyte membrane fuel cells (PEMFCs)





- Catalysts required for cathode and anode reactions
- State-of-the art Pt-based catalysts are expensive
- Replacing Pt with earth abundant catalysts is desired in order to reduce PEMFC cost

<u>Half-reactions</u>

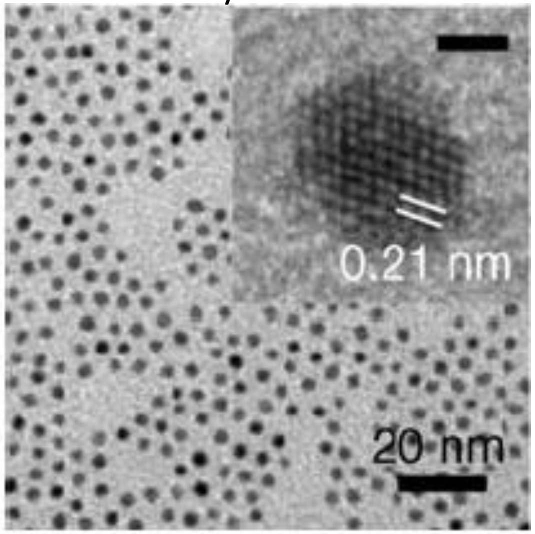
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Shyam Kocha, Bryan Pivovar, and Thomas Gennett , Fuel Cells, 46, 2012

Oxygen reduction reaction (ORR) catalysts

Pt/Carbon

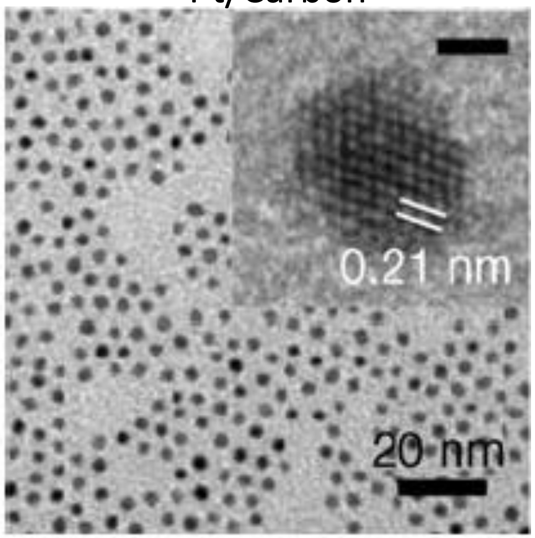


State-of-the art is Pt nanoparticles (NPs) supported on carbon

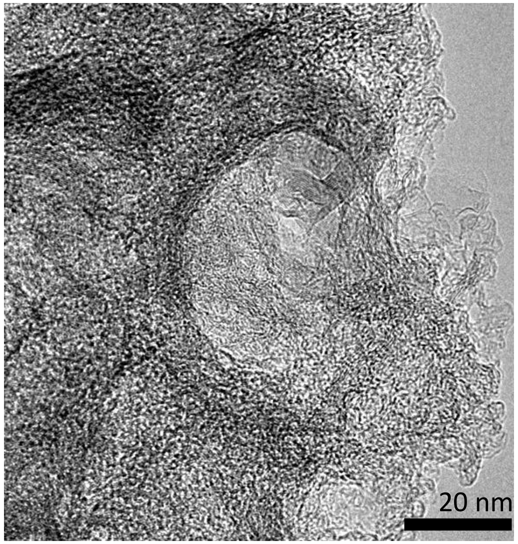
1. Wang, C., Daimon, H., Onodera, T., Koda, T. & Sun, S. A General Approach to the Size- and Shape-Controlled Synthesis of Platinum Nanoparticles and Their Catalytic Reduction of Oxygen, *Angew. Chem. Int. Ed.,* 3588–3591 (2008).

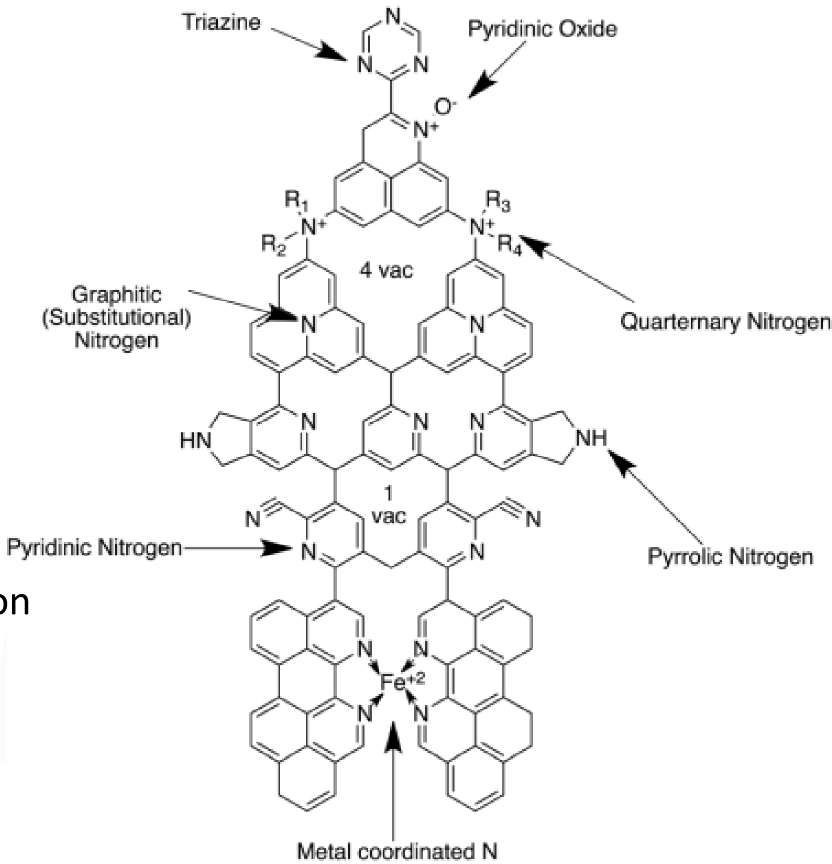
Oxygen reduction reaction (ORR) catalysts

Pt/Carbon



Fe-N-C





State-of-the art is Pt nanoparticles (NPs) supported on carbon

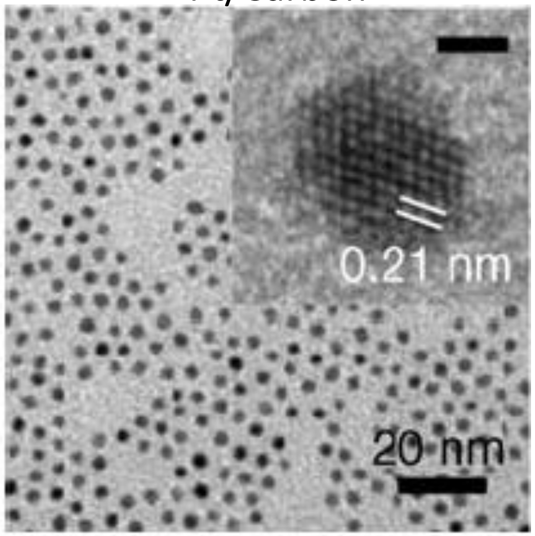
Fe-N-C-based catalysts:

- Significantly more heterogeneous

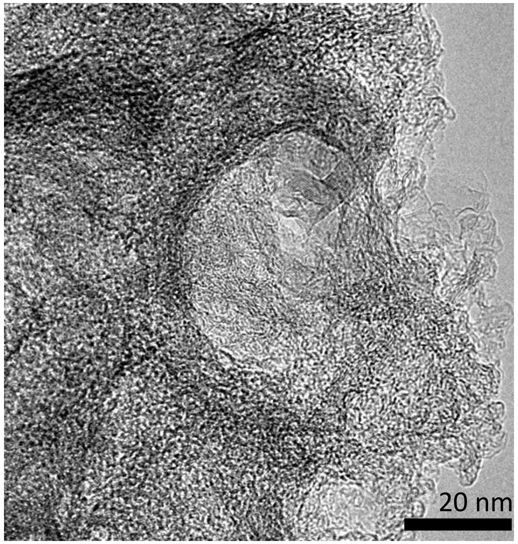
1. Wang, C., Daimon, H., Onodera, T., Koda, T. & Sun, S. A General Approach to the Size- and Shape-Controlled Synthesis of Platinum Nanoparticles and Their Catalytic Reduction of Oxygen, *Angew. Chem. Int. Ed.*, 3588–3591 (2008).
2. K. Wood, R. O'Hayre and S. Pylypenko, Recent progress on nitrogen/carbon structures designed for use in energy and sustainability applications, *Energy Environ. Sci.*, 7, 1212-1249, (2014).

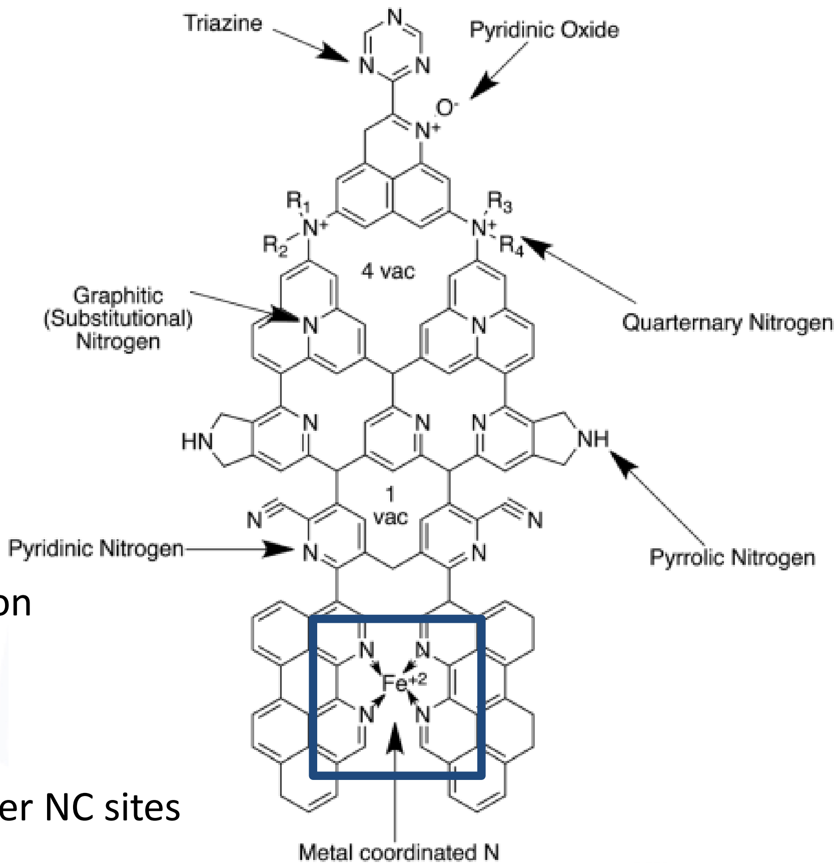
Oxygen reduction reaction (ORR) catalysts

Pt/Carbon



Fe-N-C





State-of-the art is Pt nanoparticles (NPs) supported on carbon

Fe-N-C-based catalysts:

- Significantly more heterogeneous
- FeN_x centers proposed to be most active sites; some other NC sites also contribute to ORR activity
- Fe NPs are thought to be detrimental to performance

1. Wang, C., Daimon, H., Onodera, T., Koda, T. & Sun, S. A General Approach to the Size- and Shape-Controlled Synthesis of Platinum Nanoparticles and Their Catalytic Reduction of Oxygen, *Angew. Chem. Int. Ed.*, 3588–3591 (2008).
2. K. Wood, R. O'Hayre and S. Pylypenko, Recent progress on nitrogen/carbon structures designed for use in energy and sustainability applications, *Energy Environ. Sci.*, 7, 1212-1249, (2014).

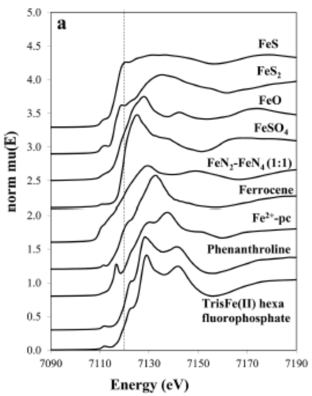
Fe–N–C electrocatalysts
Challenges and our approach

Complexity of the catalysts necessitates
multi-technique approach to characterize
chemistry and morphology at multiple scales

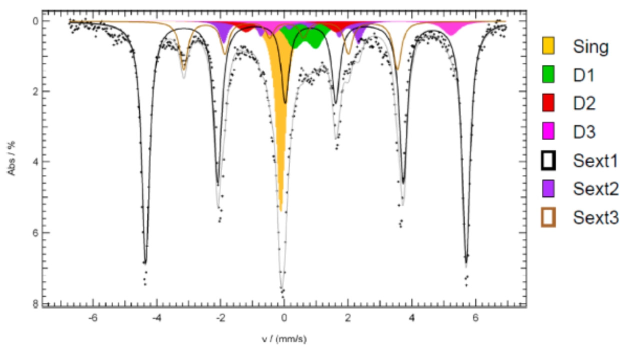
Fe–N–C electrocatalysts
Challenges and our approach

Complexity of the catalysts necessitates ***multi-technique approach*** to characterize ***chemistry and morphology at multiple scales***

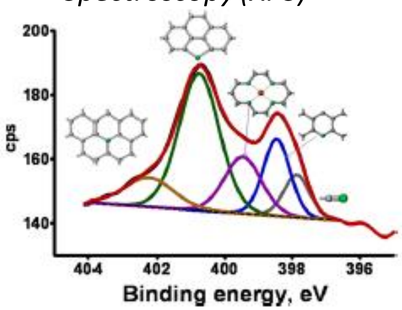
X-ray Absorption Spectroscopy (XAS)



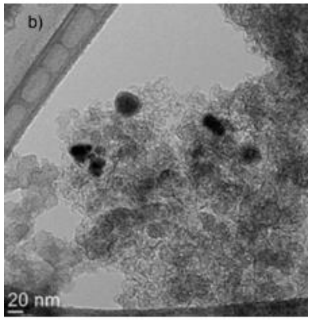
[57]Fe Mossbauer Spectroscopy



X-ray Photoelectron Spectroscopy (XPS)



Transmission Electron Microscopy (TEM)



- Kramm, U. I. *et al.* Structure of the catalytic sites in Fe/N/C-catalysts for O2-reduction in PEM fuel cells. *Phys. Chem. Chem. Phys.* **14,** 11673–88 (2012).
- Ferrandon, M. *et al.* Multitechnique Characterization of a Polyaniline – Iron – Carbon Oxygen Reduction Catalyst. *J. Phys. Chem. C* **116,** 16001–16013 (2012).
- Kramm, U. I. *et al*. Correlations between mass activity…via 57 Fe Möβbauer spectroscopy and other techniques. *J. Am. Chem. Soc.* **136,** 978–985 (2014).

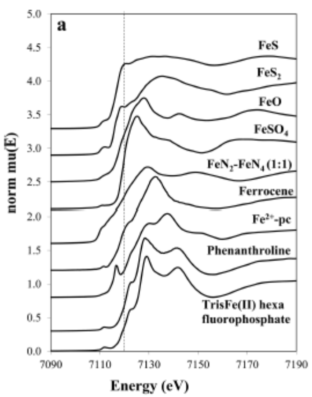
Fe–N–C electrocatalysts
Challenges and our approach

Complexity of the catalysts necessitates ***multi-technique approach*** to characterize ***chemistry and morphology at multiple scales***

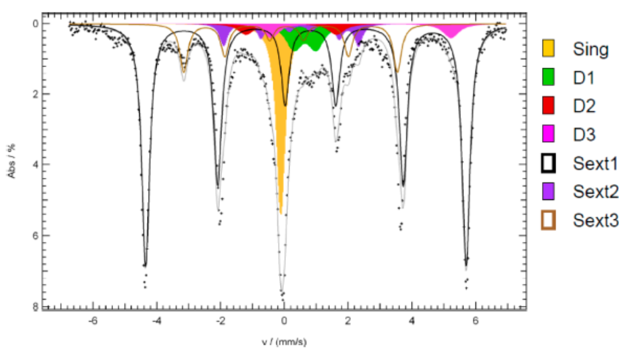
Challenge:

- Puzzle… 3D …with atomic resolution
- Evolution under realistic conditions

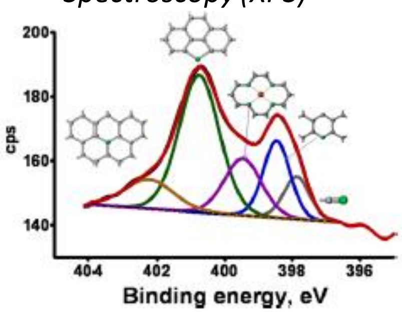
X-ray Absorption Spectroscopy (XAS)



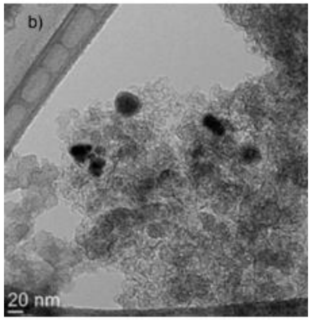
^{57}Fe Mossbauer Spectroscopy



X-ray Photoelectron Spectroscopy (XPS)



Transmission Electron Microscopy (TEM)

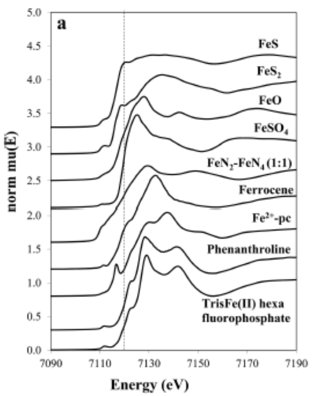


- Kramm, U. I. *et al.* Structure of the catalytic sites in Fe/N/C-catalysts for O2-reduction in PEM fuel cells. *Phys. Chem. Chem. Phys.* **14,** 11673–88 (2012).
- Ferrandon, M. *et al.* Multitechnique Characterization of a Polyaniline – Iron – Carbon Oxygen Reduction Catalyst. *J. Phys. Chem. C* **116,** 16001–16013 (2012).
- Kramm, U. I. *et al.* Correlations between mass activity…via 57 Fe Möβbauer spectroscopy and other techniques. *J. Am. Chem. Soc.* **136,** 978–985 (2014).

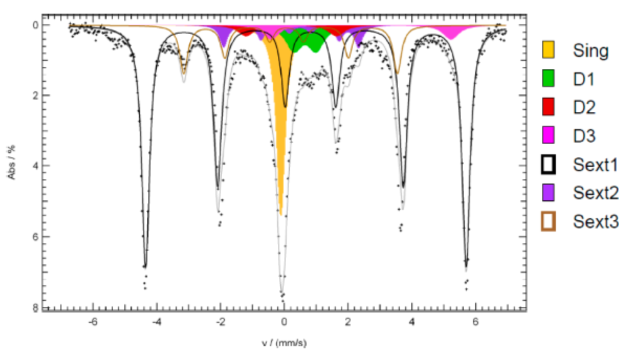
Fe–N–C electrocatalysts
Challenges and our approach

Complexity of the catalysts necessitates ***multi-technique approach*** to characterize ***chemistry and morphology at multiple scales***

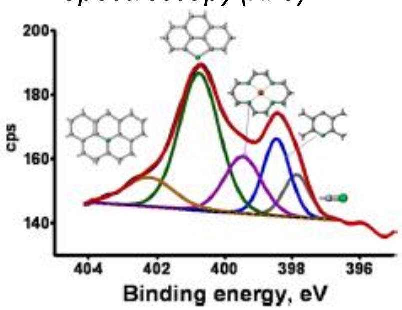
X-ray Absorption Spectroscopy (XAS)



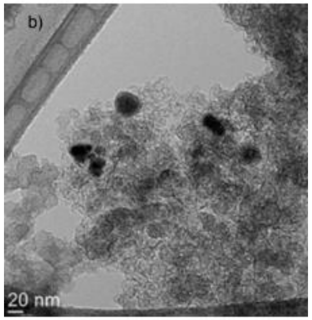
[57]Fe Mossbauer Spectroscopy



X-ray Photoelectron Spectroscopy (XPS)



Transmission Electron Microscopy (TEM)



Challenge:

- Puzzle… 3D …with atomic resolution
- Evolution under realistic conditions

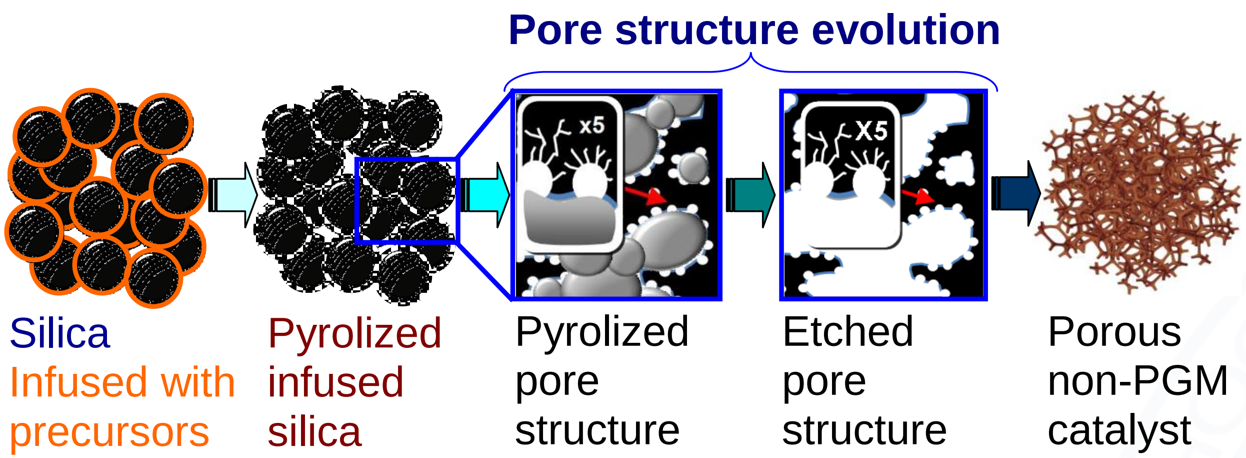
Our approach:

- ***TEM/energy dispersive x-ray spectroscopy (EDS) to address heterogeneity of active sites at the nanoscale and better understand active site density***
- *Atom probe tomography for 3D elemental distribution with atomic resolution*
- *Mossbauer spectroscopy for identification of Fe species*
- *In situ TEM and in situ/in operando XPS and XAS for evolution of active sites under realistic operating conditions*

- Kramm, U. I. *et al.* Structure of the catalytic sites in Fe/N/C-catalysts for O2-reduction in PEM fuel cells. *Phys. Chem. Chem. Phys.* **14,** 11673–88 (2012).
- Ferrandon, M. *et al.* Multitechnique Characterization of a Polyaniline – Iron – Carbon Oxygen Reduction Catalyst. *J. Phys. Chem. C* **116,** 16001–16013 (2012).
- Kramm, U. I. *et al.* Correlations between mass activity…via 57 Fe Möβbauer spectroscopy and other techniques. *J. Am. Chem. Soc.* **136,** 978–985 (2014).

Fe–N–C electrocatalysts
Synthesis methods

THE UNIVERSITY of NEW MEXICO

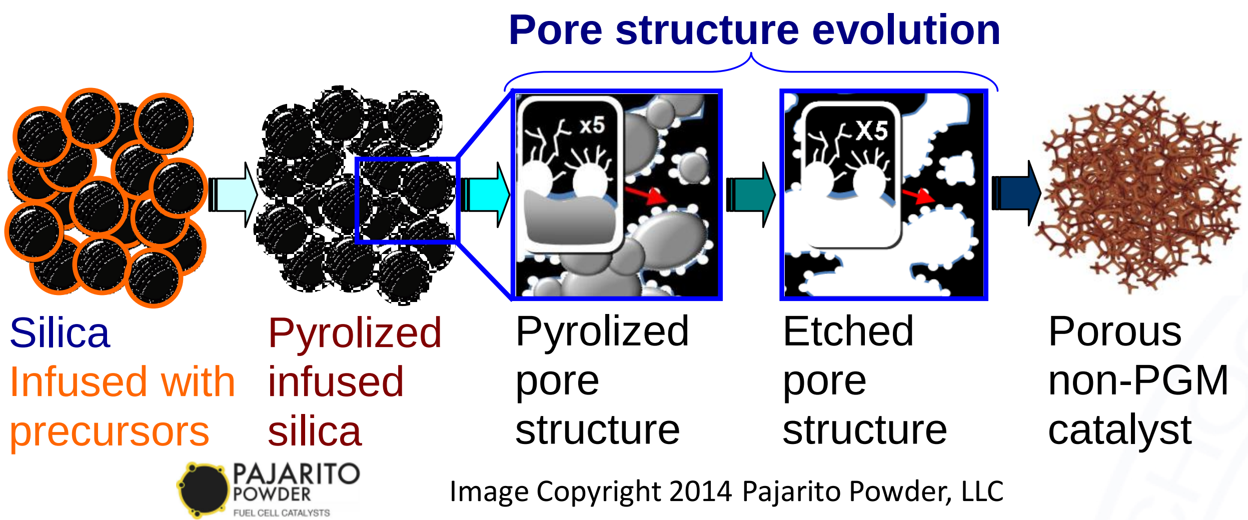


PAJARITO POWDER FUEL CELL CATALYSTS

- Synthesis performed at UNM via sacrificial support method using iron (III) nitrate nonahydrate and nicarbazin precursors

Fe–N–C electrocatalysts

Synthesis methods

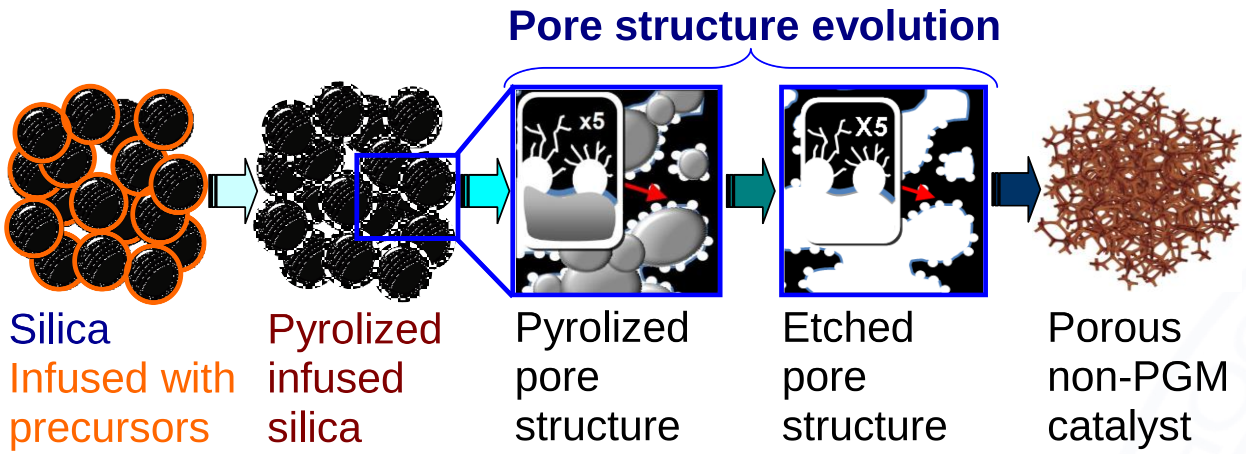


- Synthesis performed at UNM via sacrificial support method using iron (III) nitrate nonahydrate and nicarbazin precursors
- Set of catalysts synthesized with controlled variation in parameters, resulting in a diverse set of materials

Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	NH_3/N_2

Fe–N–C electrocatalysts
Synthesis methods



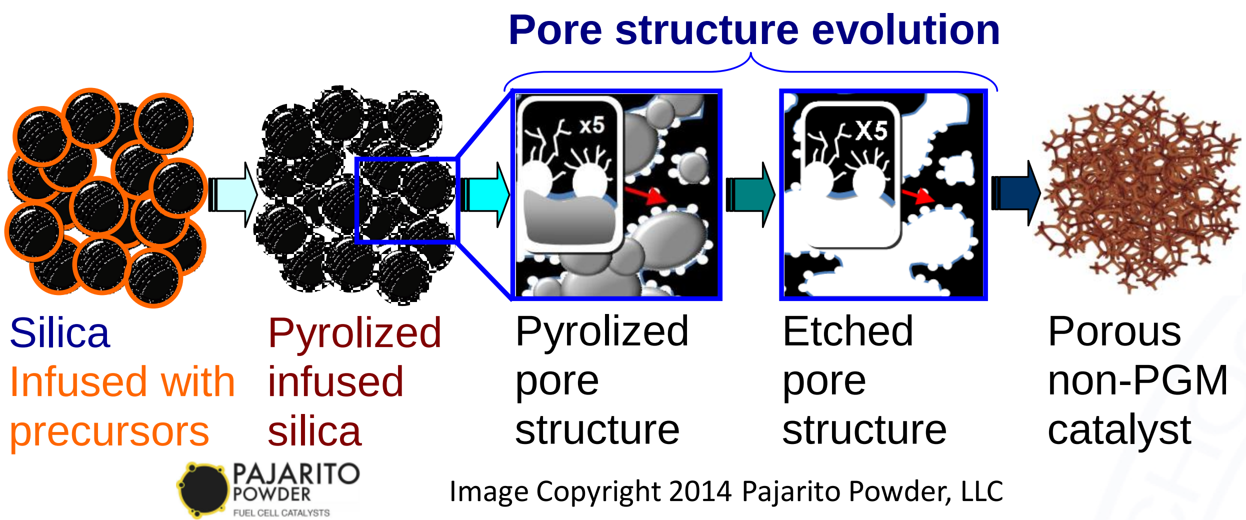
PAJARITO POWDER FUEL CELL CATALYSTS

Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	NH_3/N_2

- Synthesis performed at UNM via sacrificial support method using iron (III) nitrate nonahydrate and nicarbazin precursors
- Set of catalysts synthesized with controlled variation in parameters, resulting in a diverse set of materials
- Silica etching results in high surface area materials with multi-scale porosity,

Fe–N–C electrocatalysts
Synthesis methods



- Synthesis performed at UNM via sacrificial support method using iron (III) nitrate nonahydrate and nicarbazin precursors
- Set of catalysts synthesized with controlled variation in parameters, resulting in a diverse set of materials
- Silica etching results in high surface area materials with multi-scale porosity,
- Heat treatments are necessary to form active FeN_x moieties

Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	NH_3/N_2

Fe–N–C electrocatalysts
Synthesis methods

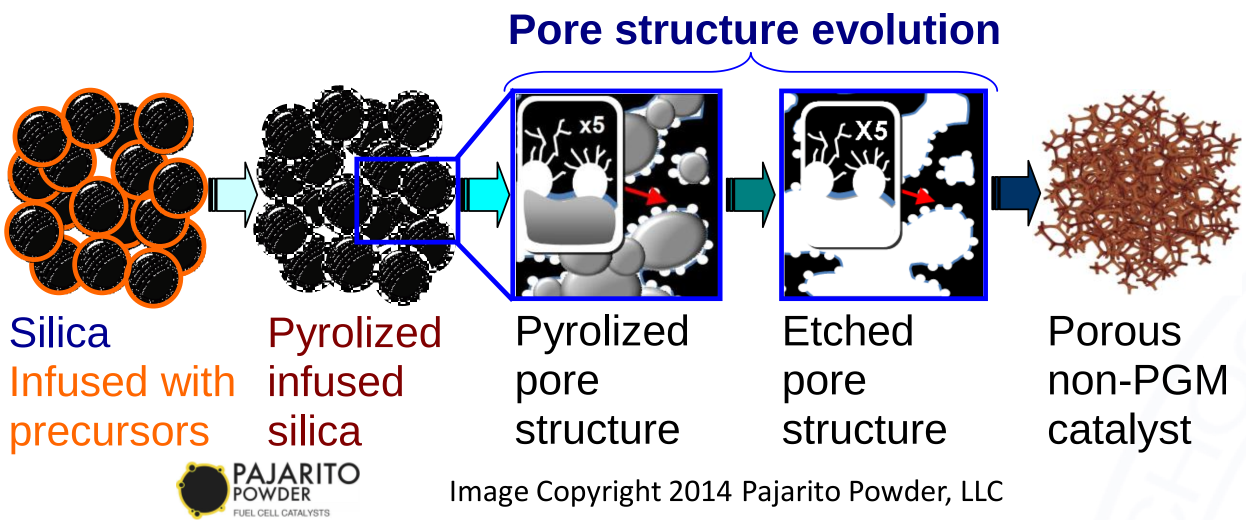


Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

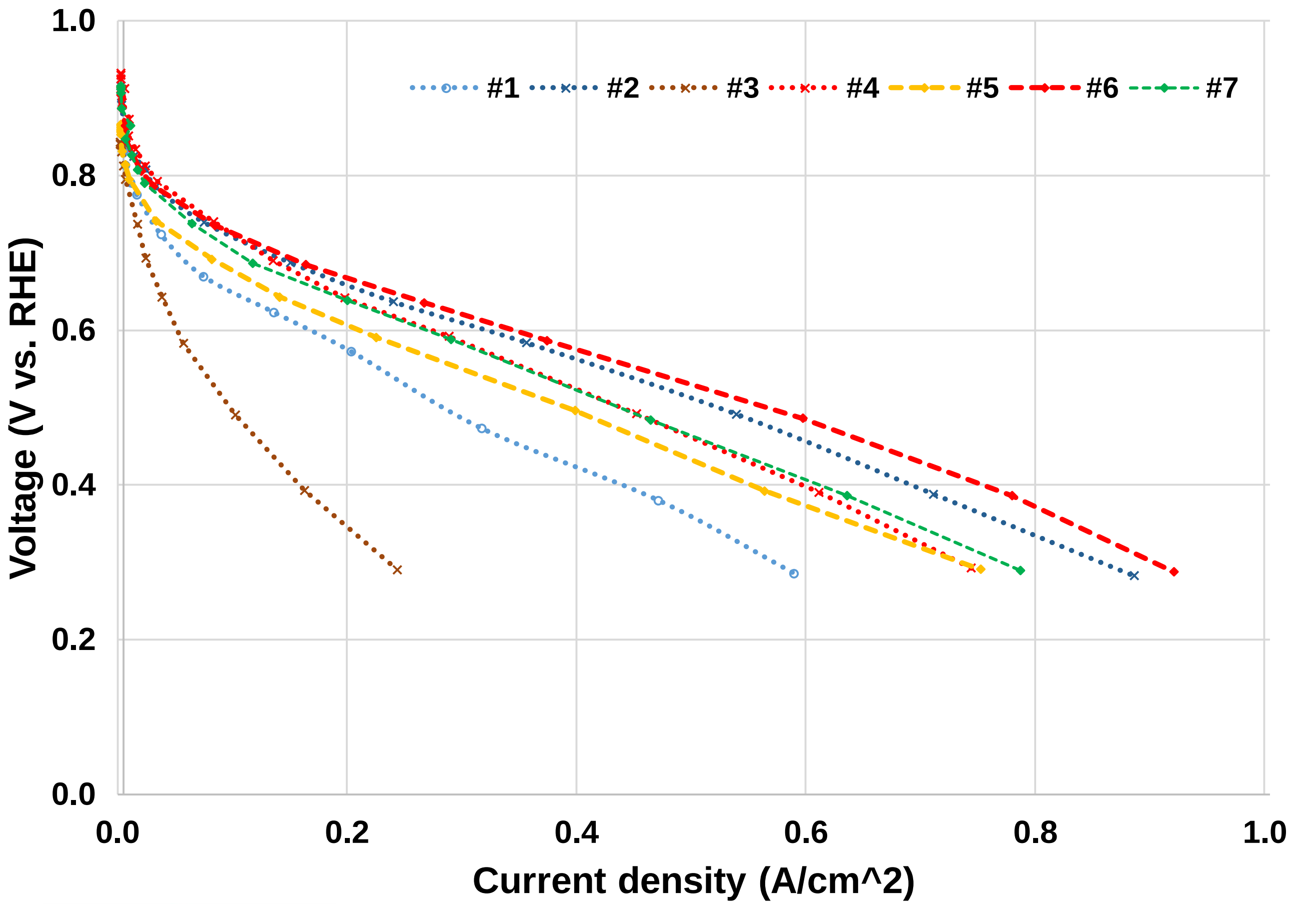
Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	NH_3/N_2

- Synthesis performed at UNM via sacrificial support method using iron (III) nitrate nonahydrate and nicarbazin precursors
- Set of catalysts synthesized with controlled variation in parameters, resulting in a diverse set of materials
- Silica etching results in high surface area materials with multi-scale porosity,
- Heat treatments are necessary to form active FeN_x moieties

This set of catalysts is used to derive property-performance correlations

Fe–N–C electrocatalysts

Membrane electrode assembly (MEA) performance



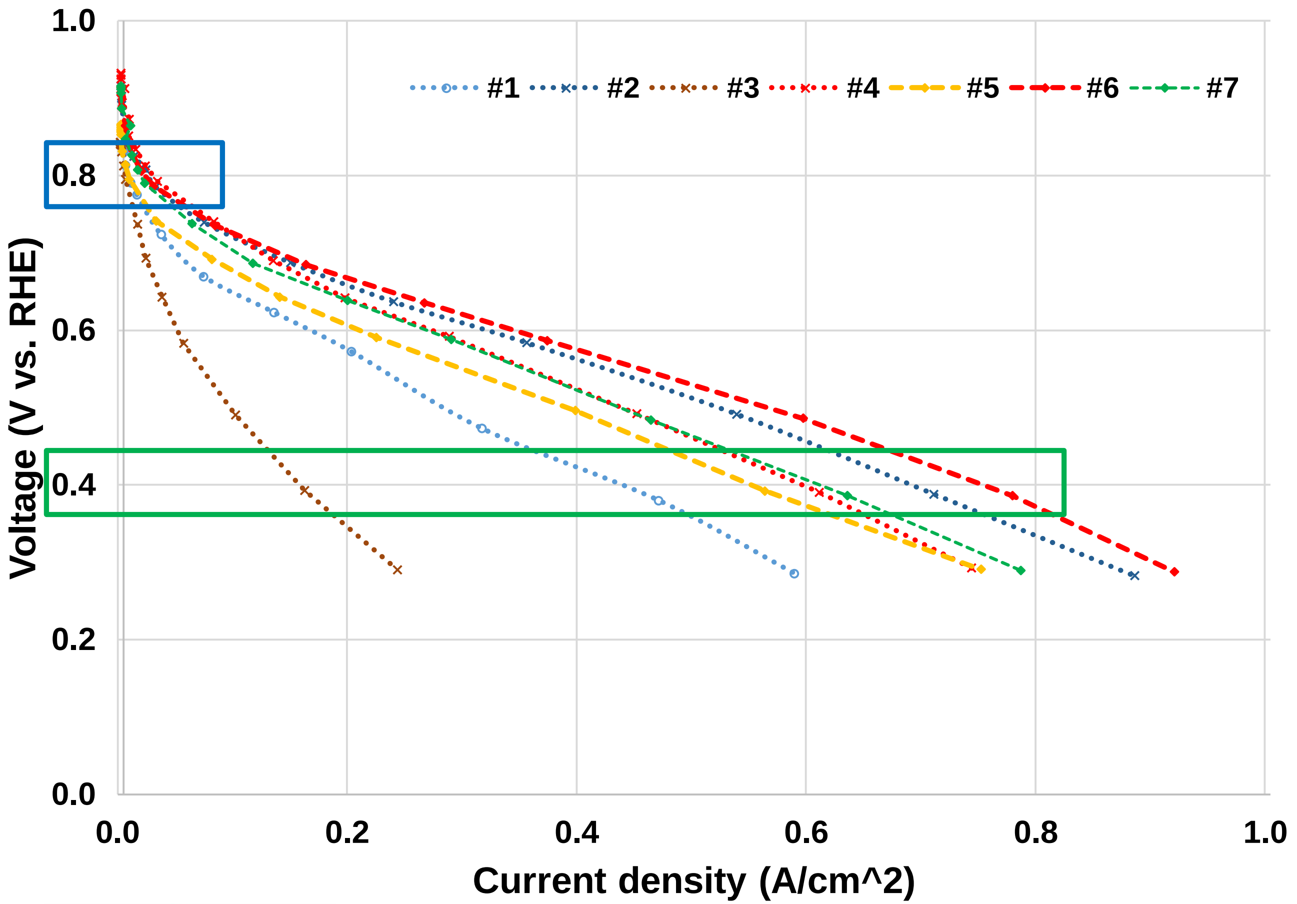
- Polarization curves show significant distribution of performance

THE UNIVERSITY of NEW MEXICO

PAJARITO POWDER FUEL CELL CATALYSTS

Fe–N–C electrocatalysts

Membrane electrode assembly (MEA) performance



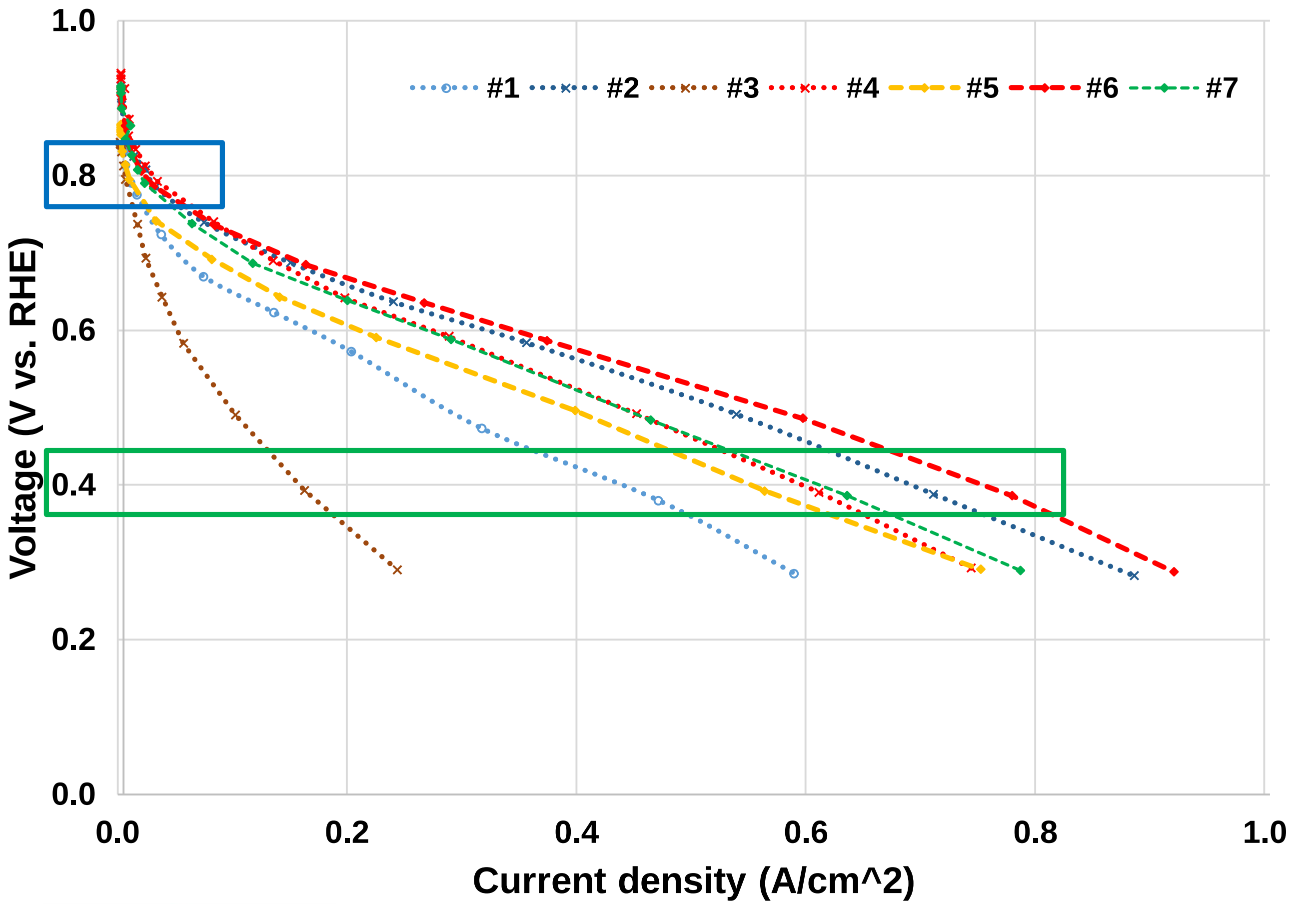
- Polarization curves show significant distribution of performance
- Focus is on two performance metrics, current density at:
  - 0.8 V (Kinetic limited region)
  - 0.4 V (Transport limited region)

THE UNIVERSITY *of* NEW MEXICO

PAJARITO POWDER FUEL CELL CATALYSTS

Fe–N–C electrocatalysts

Membrane electrode assembly (MEA) performance



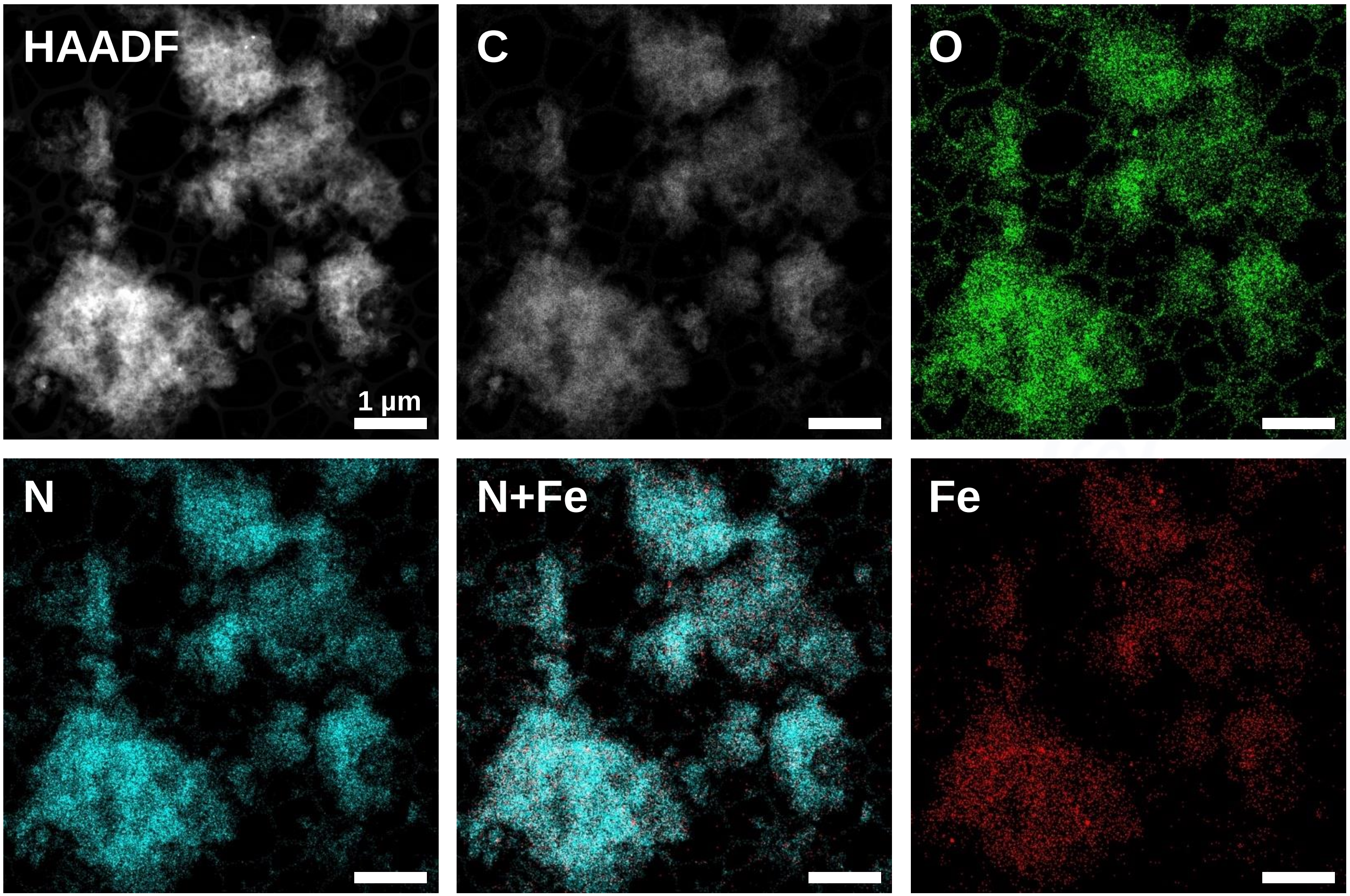
- Polarization curves show significant distribution of performance
- Focus is on two performance metrics, current density at:
  - 0.8 V (Kinetic limited region)
  - 0.4 V (Transport limited region)
- Our approach – explain performance differences using scanning TEM (STEM) and EDS by evaluating heterogeneity of active sites at the nanoscale

THE UNIVERSITY of NEW MEXICO

PAJARITO POWDER FUEL CELL CATALYSTS

STEM–EDS
Elemental distribution

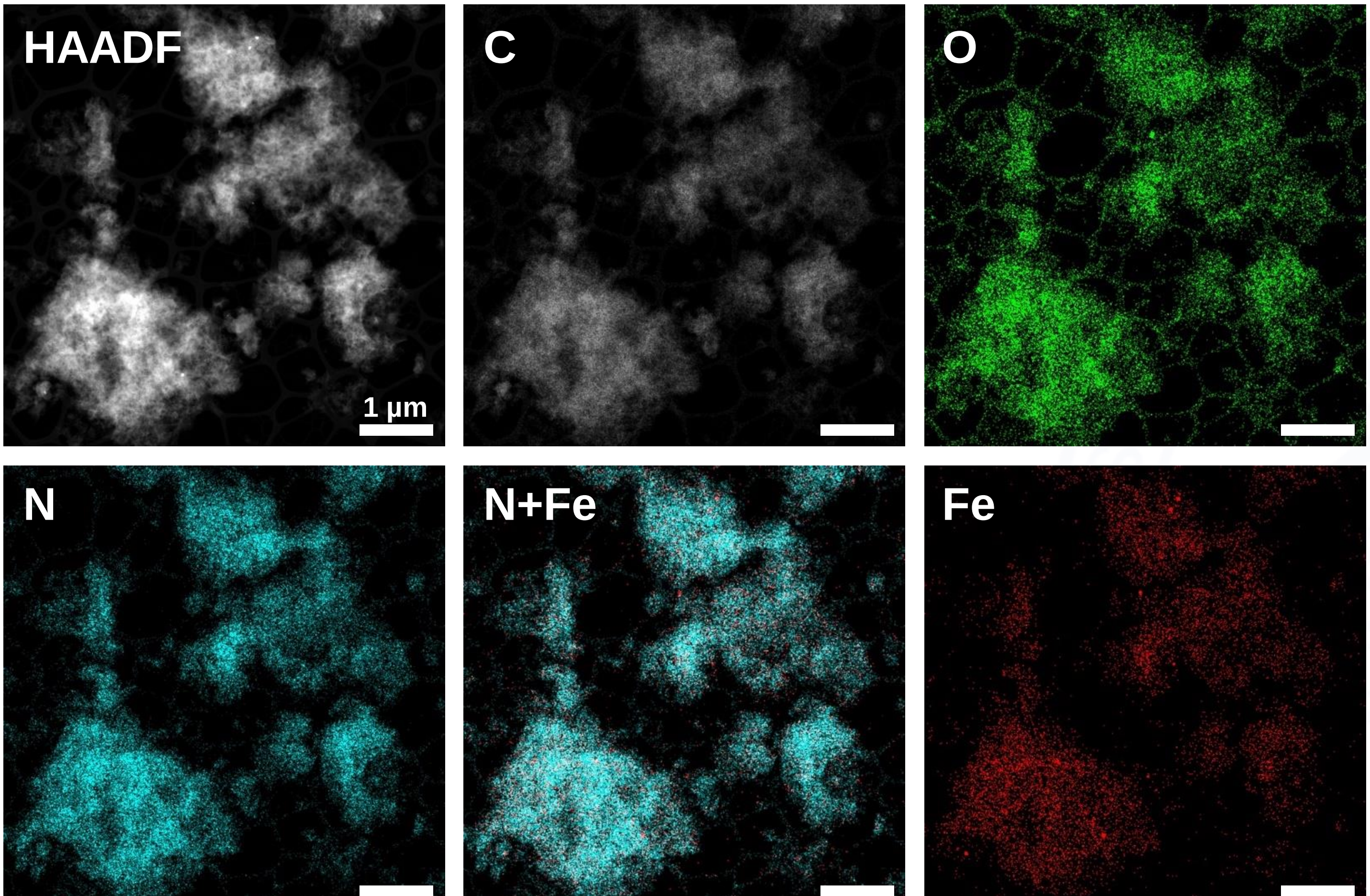
High angle annular dark field (HAADF) STEM-mode image shows elemental contrast



- C, O, and N EDS maps show these elements homogenously distributed throughout the sample

STEM–EDS
Elemental distribution

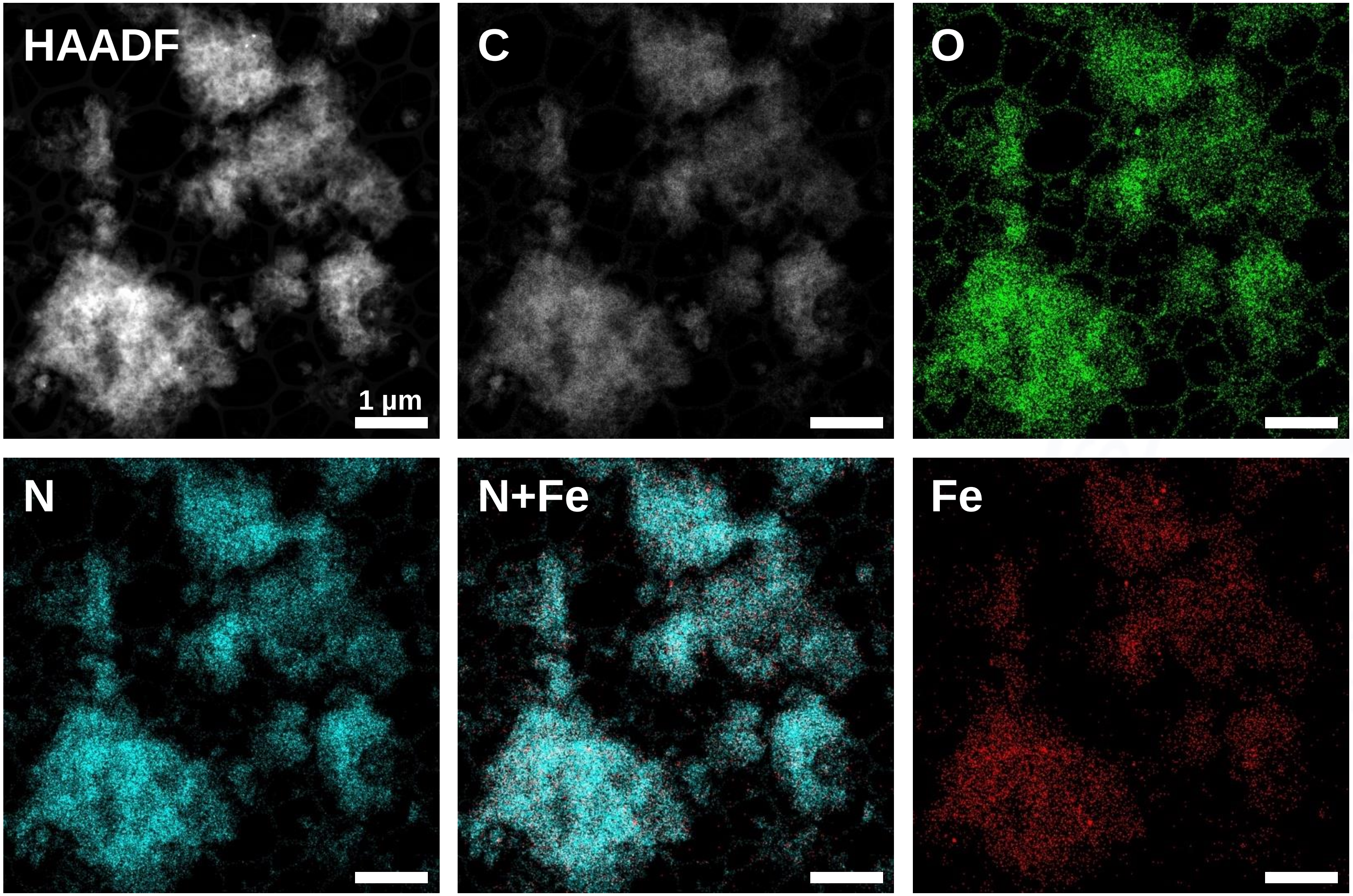
High angle annular dark field (HAADF) STEM-mode image shows elemental contrast



- C, O, and N EDS maps show these elements homogenously distributed throughout the sample
- Fe distribution is more varied from area to area

STEM–EDS
Elemental distribution

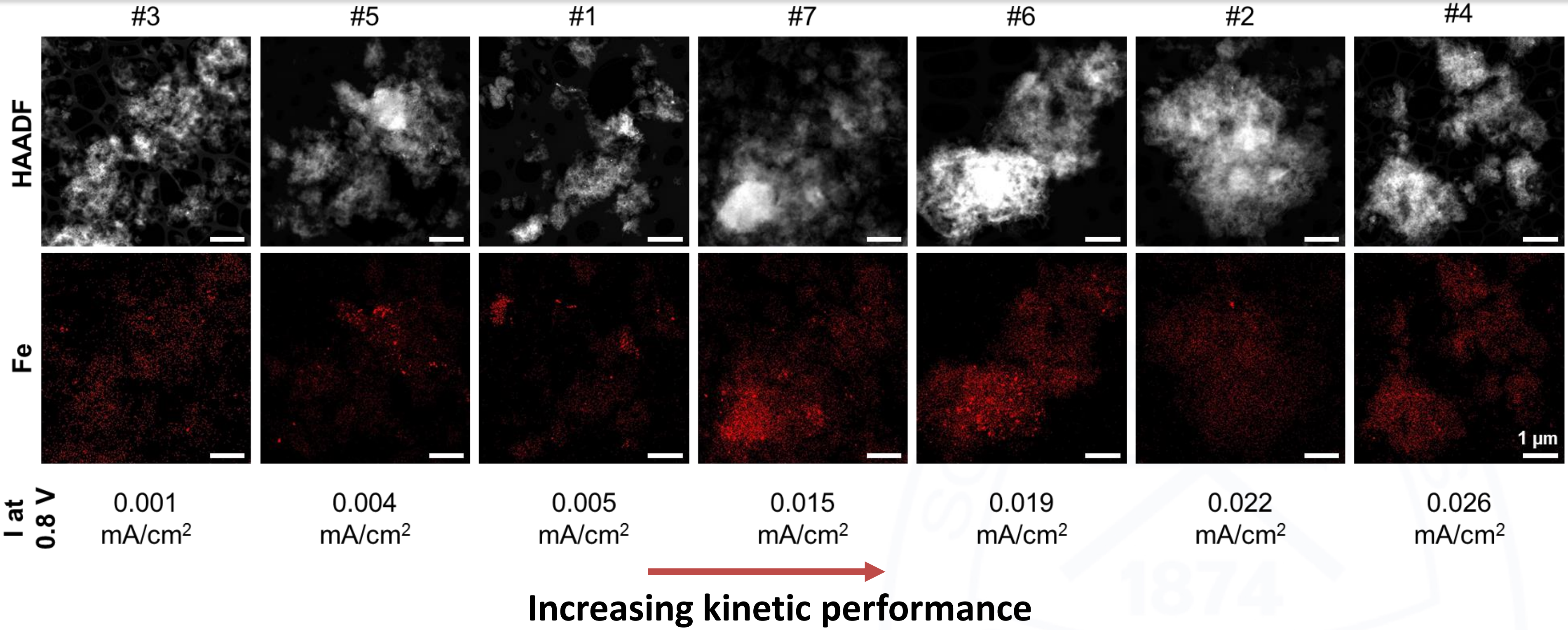
High angle annular dark field (HAADF) STEM-mode image shows elemental contrast



- C, O, and N EDS maps show these elements homogenously distributed throughout the sample
- Fe distribution is more varied from area to area
- Two types of iron species present: Fe NPs, which can detrimental to performance, and what is referred to in literature as ORR active atomically-dispersed Fe species ($Fe_{at\text{-}dsp}$)

STEM-EDS

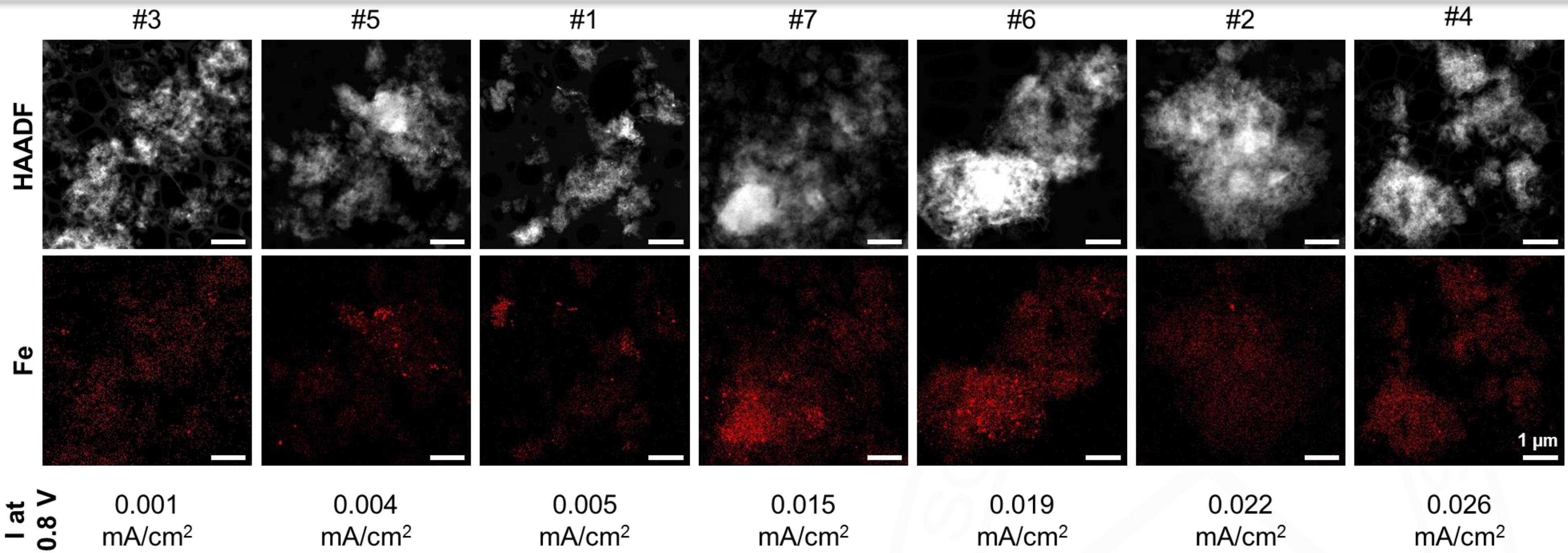
Atomically dispersed Fe content



- Best performers show less Fe heterogeneity

STEM-EDS

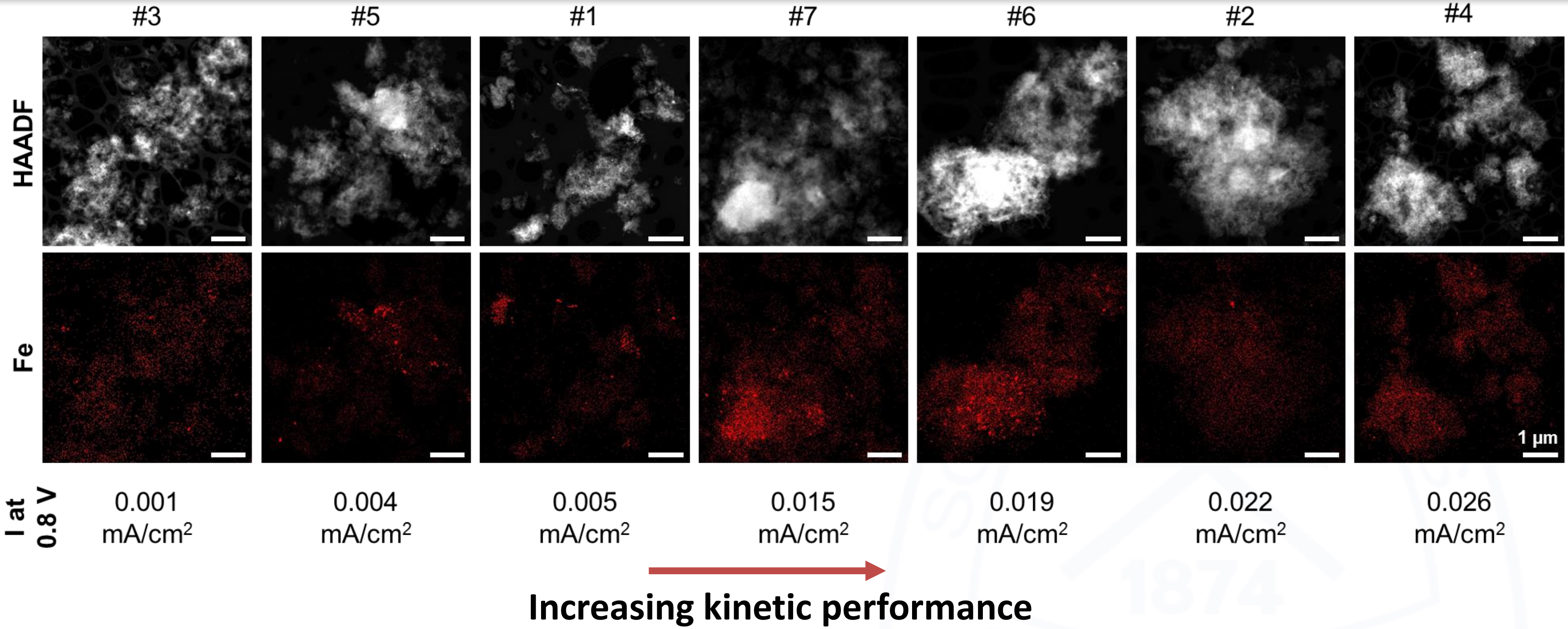
Atomically dispersed Fe content



Increasing kinetic performance

- Best performers show less Fe heterogeneity
- To quantify active Fe species, higher magnification maps were acquired for areas with no Fe-NPs

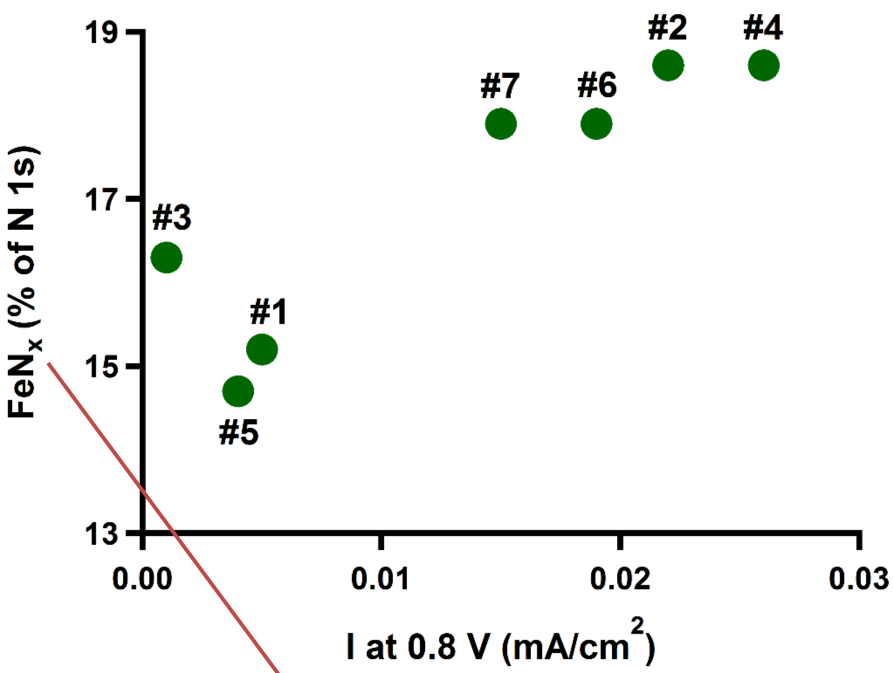
STEM-EDS
Atomically dispersed Fe content

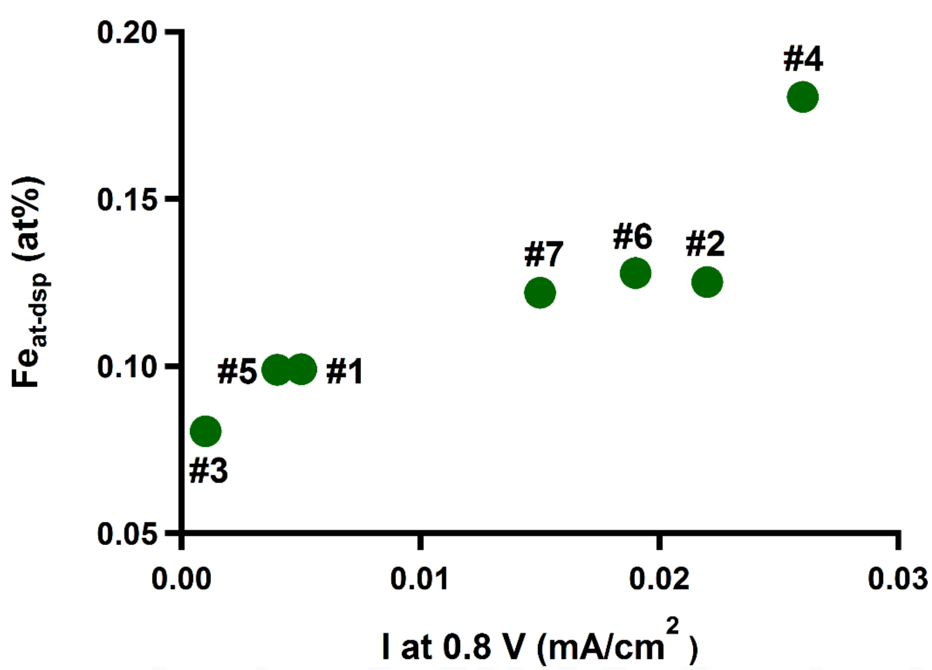


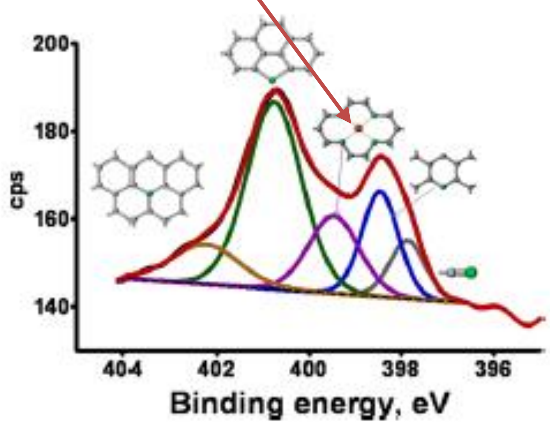
- Best performers show less Fe heterogeneity
- To quantify active Fe species, higher magnification maps were acquired for areas with no Fe-NPs
- $Fe_{at\text{-}dsp}$ is quantified, along with N to estimate coordination and to understand performance trends

Correlations

Property–performance trends



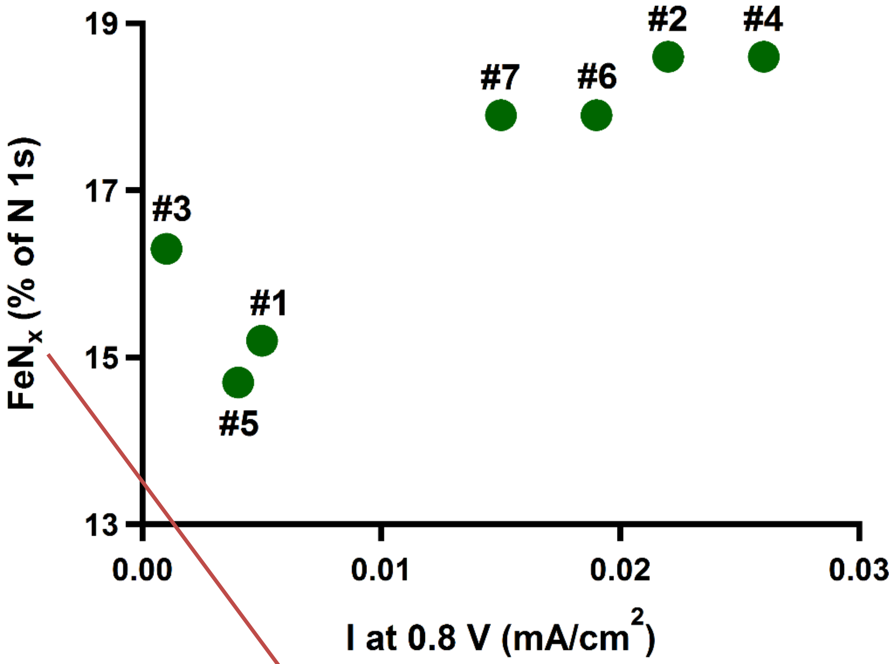


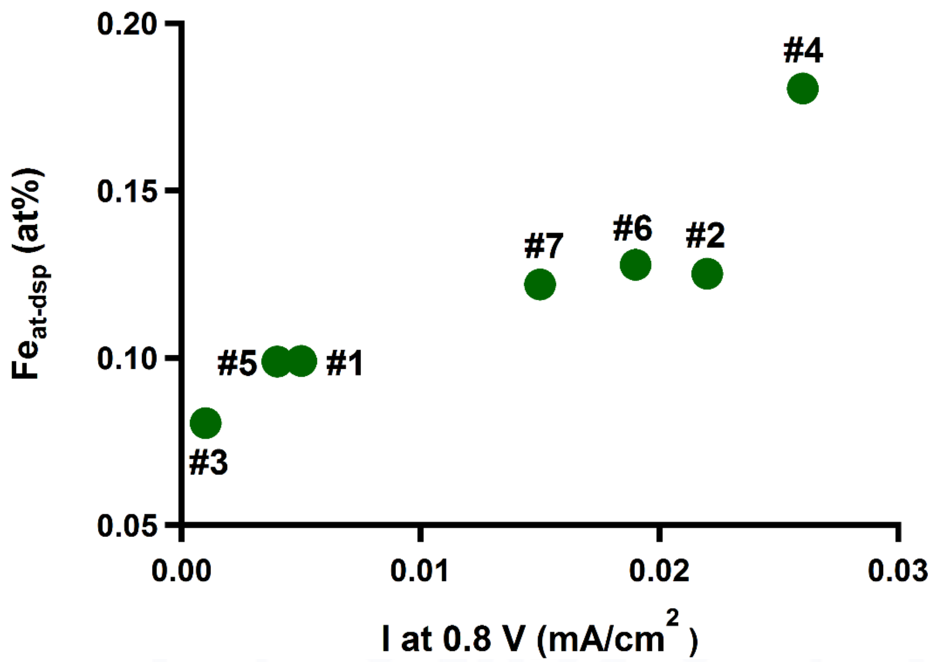


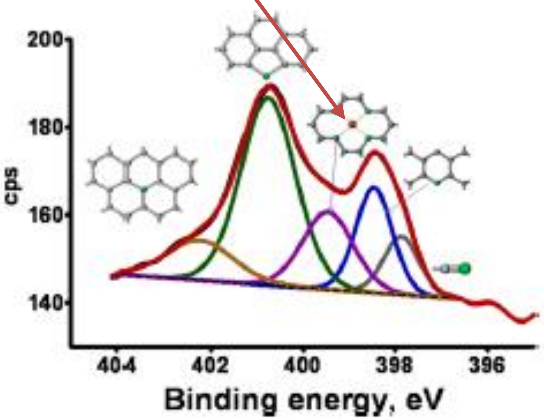
- Kinetic current is plotted versus two structural properties – % FeN_x (proposed active site) from XPS, and $Fe_{at\text{-}dsp}$ content from EDS

Correlations

Property–performance trends



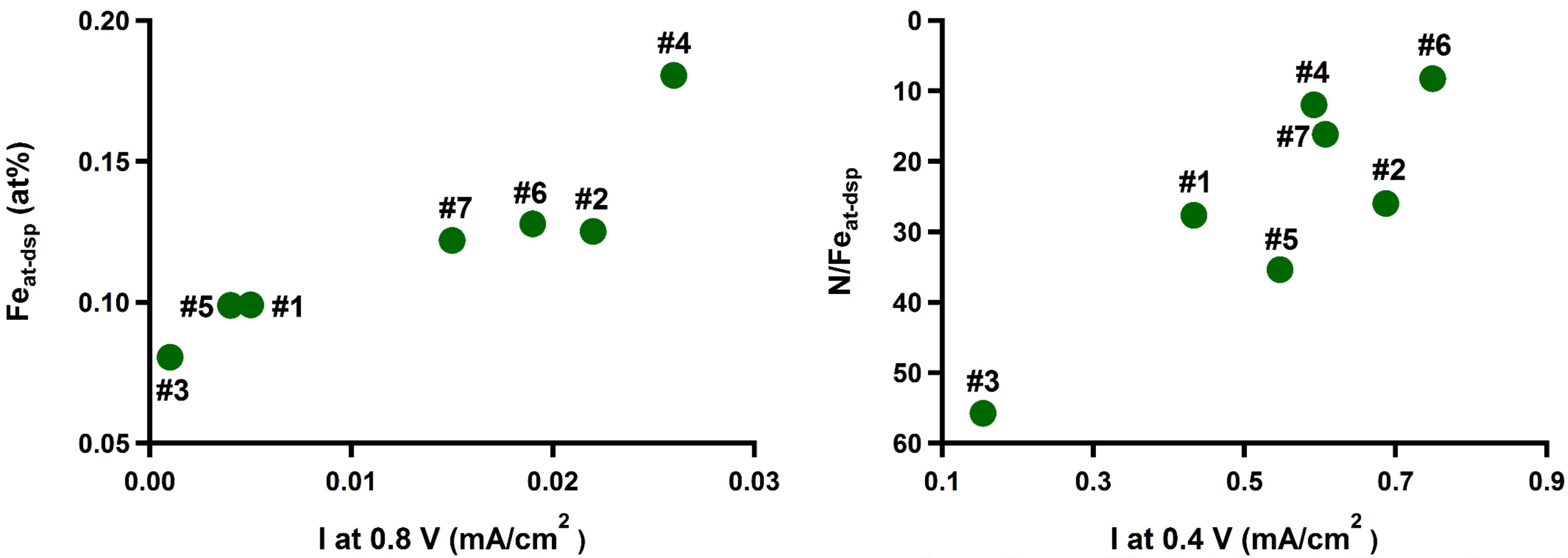




- Kinetic current is plotted versus two structural properties – % FeN_x (proposed active site) from XPS, and $Fe_{at\text{-}dsp}$ content from EDS
- Both properties show a positive linear trend with kinetic current, indicating that both are measuring active sites – $Fe_{at\text{-}dsp}$ is most likely FeN_x

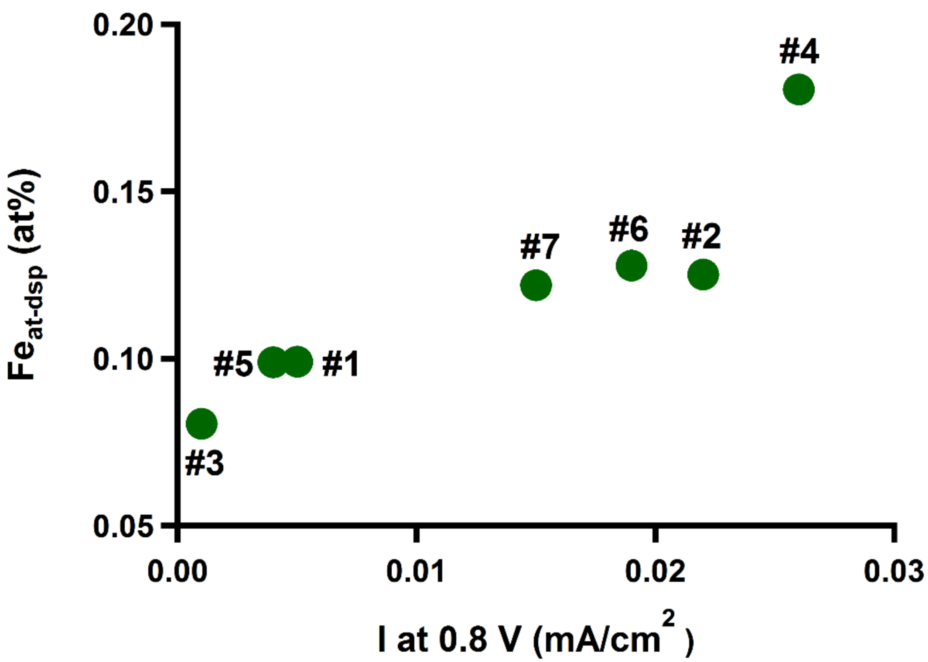
Correlations

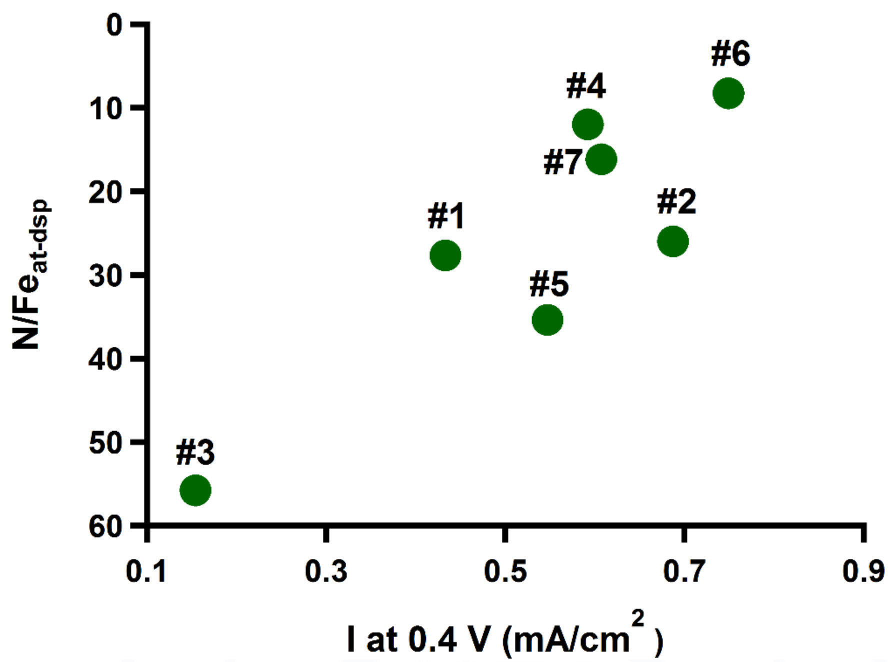
Fe_{at-dsp} trends



- Kinetic performance trends with Fe_{at-dsp} content, but a different descriptor is needed to best explain transport performance

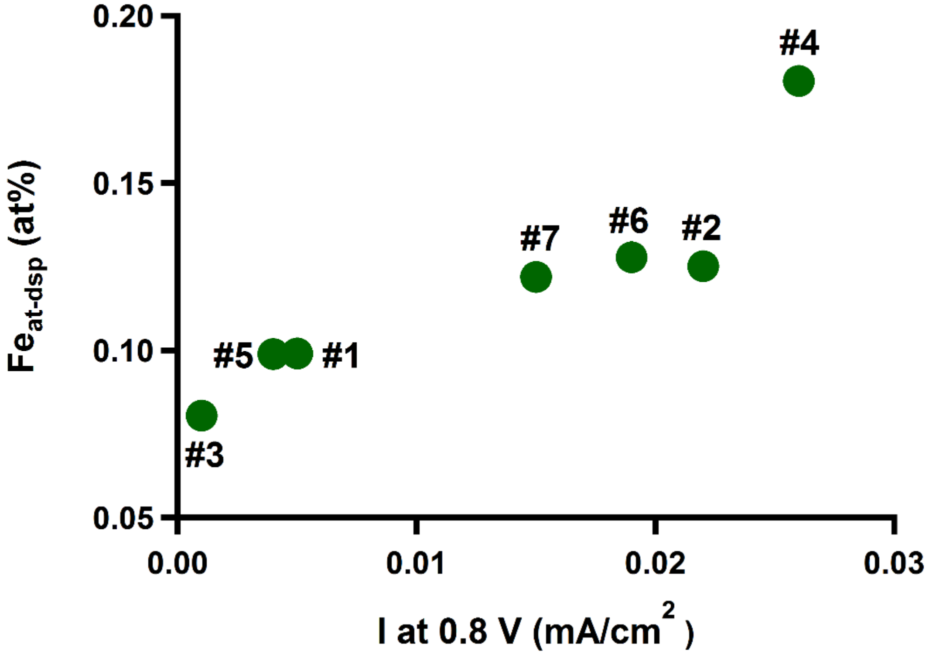
Correlations
Fe_{at-dsp} trends

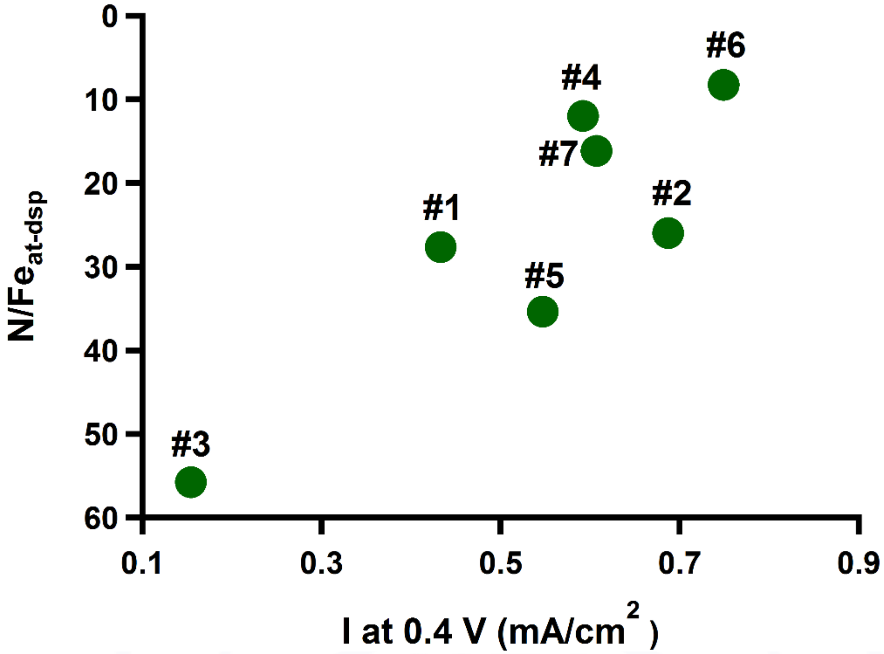




- Kinetic performance trends with Fe_{at-dsp} content, but a different descriptor is needed to best explain transport performance
- Ratio of total N content from EDS to Fe_{at-dsp} was found to trend with transport performance – indicative of coordination of Fe and N, and amount of N species other than FeN_x

Correlations
Fe_{at-dsp} trends





- Kinetic performance trends with $Fe_{at\text{-}dsp}$ content, but a different descriptor is needed to best explain transport performance
- Ratio of total N content from EDS to $Fe_{at\text{-}dsp}$ was found to trend with transport performance – indicative of coordination of Fe and N, and amount of N species other than FeN_x
- When related back to synthesis parameters, gives an indication of which variables can be tuned to increase performance

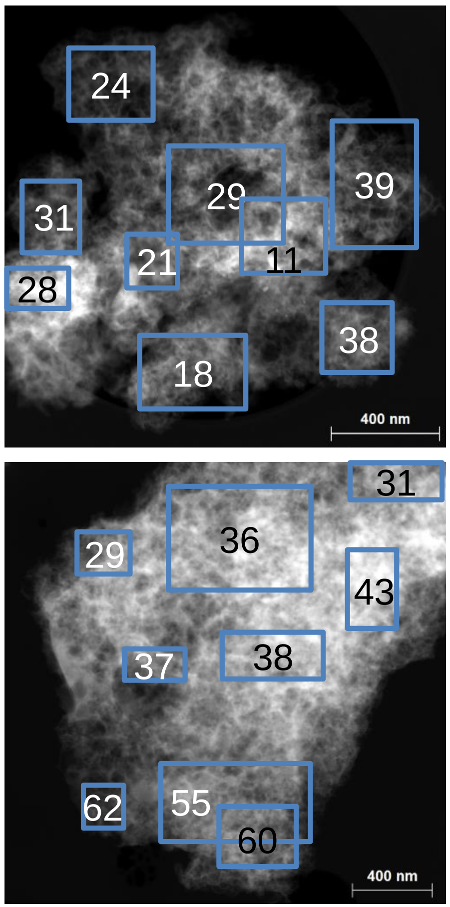
Integration into MEAs and durability

Tracking active sites and ionomer distribution in MEAs

EDS: N/Fe_{atom} ratio of indicated areas

BOL

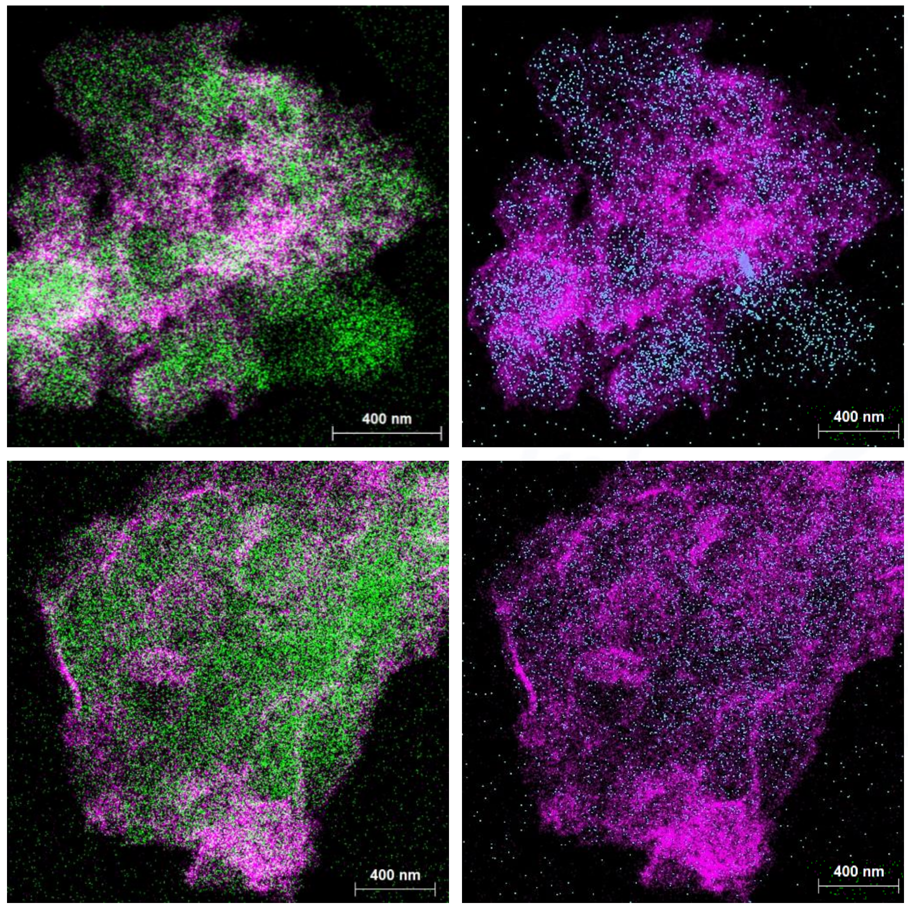
EOL



EDS: Ionomer distribution (F, purple) relative to catalyst (N, green & Fe, blue)

BOL

EOL



- Track changes in the catalyst in the presence of proton conductor (Nafion® ionomer, fluorinated polymer)

Increase in N/Fe_{atom} indicates decrease in coordinated $Fe-N_x$ species

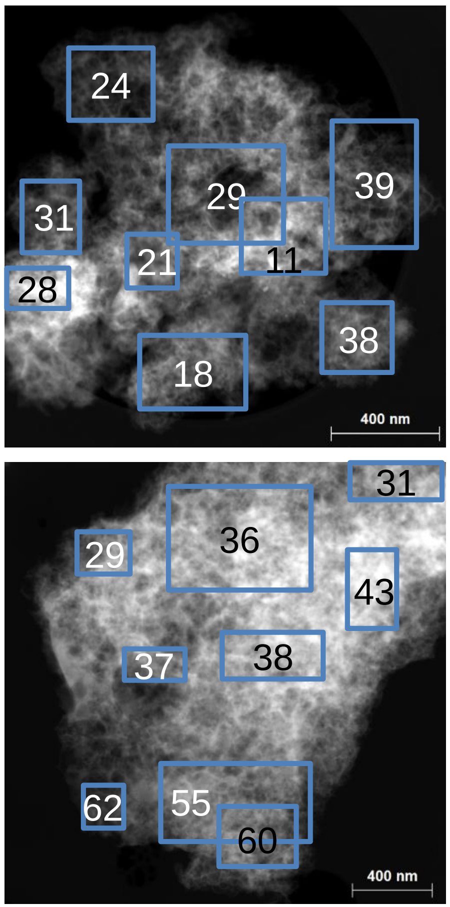
Integration into MEAs and durability

Tracking active sites and ionomer distribution in MEAs

EDS: N/Fe$_{atom}$ ratio of indicated areas

BOL

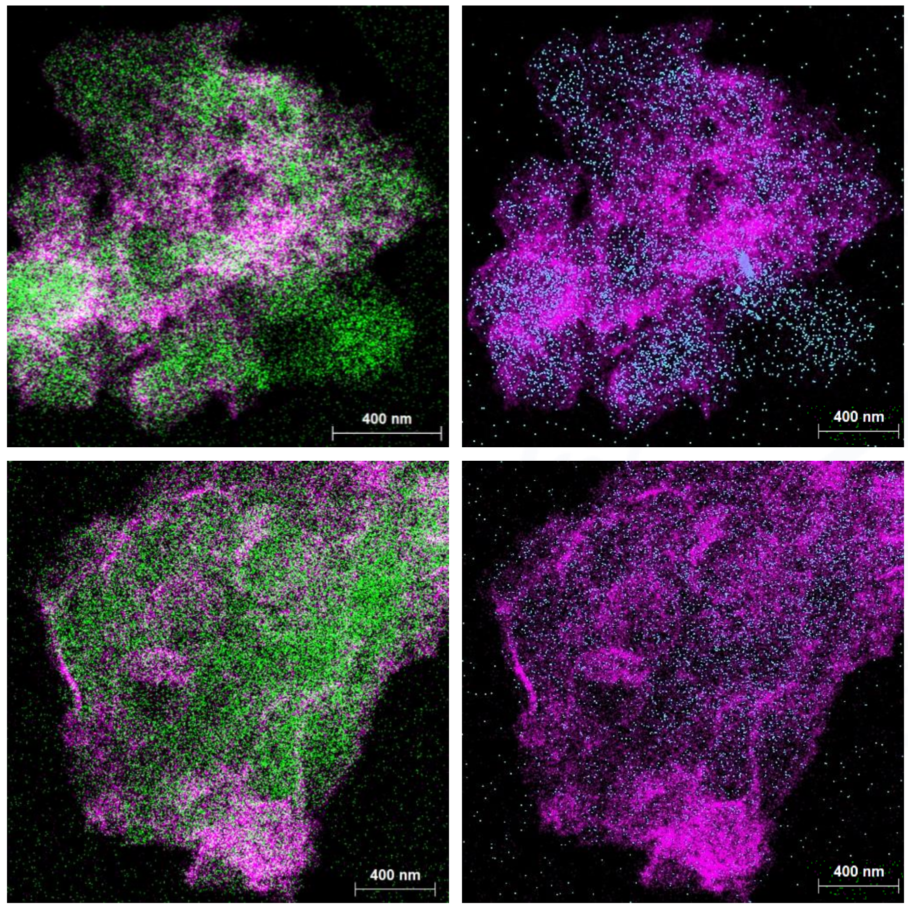
EOL



EDS: Ionomer distribution (F, purple) relative to catalyst (N, green & Fe, blue)

BOL

EOL



- Track changes in the catalyst in the presence of proton conductor (Nafion® ionomer, fluorinated polymer)
- Distribution of F shows how well ionomer is integrated with catalyst within the MEA electrode structure

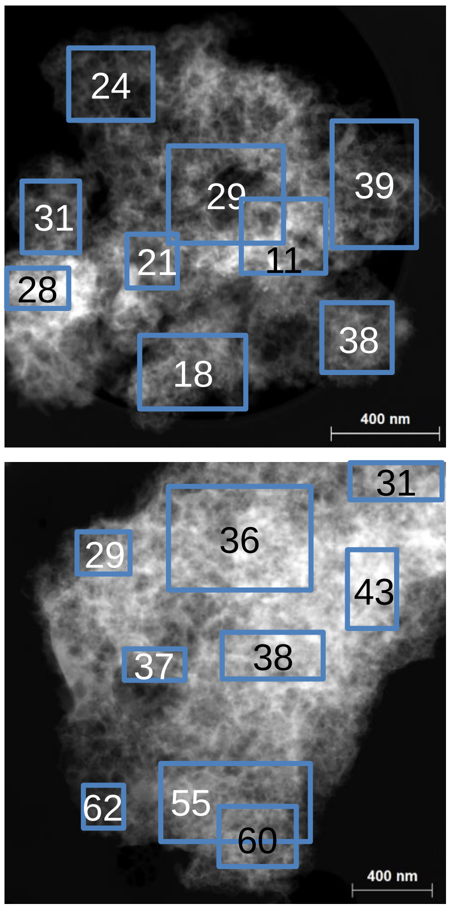
Increase in N/Fe$_{atom}$ indicates decrease in coordinated Fe-N$_x$ species

Tracking active sites and ionomer distribution in MEAs

EDS: N/Fe$_{atom}$ ratio of indicated areas

BOL

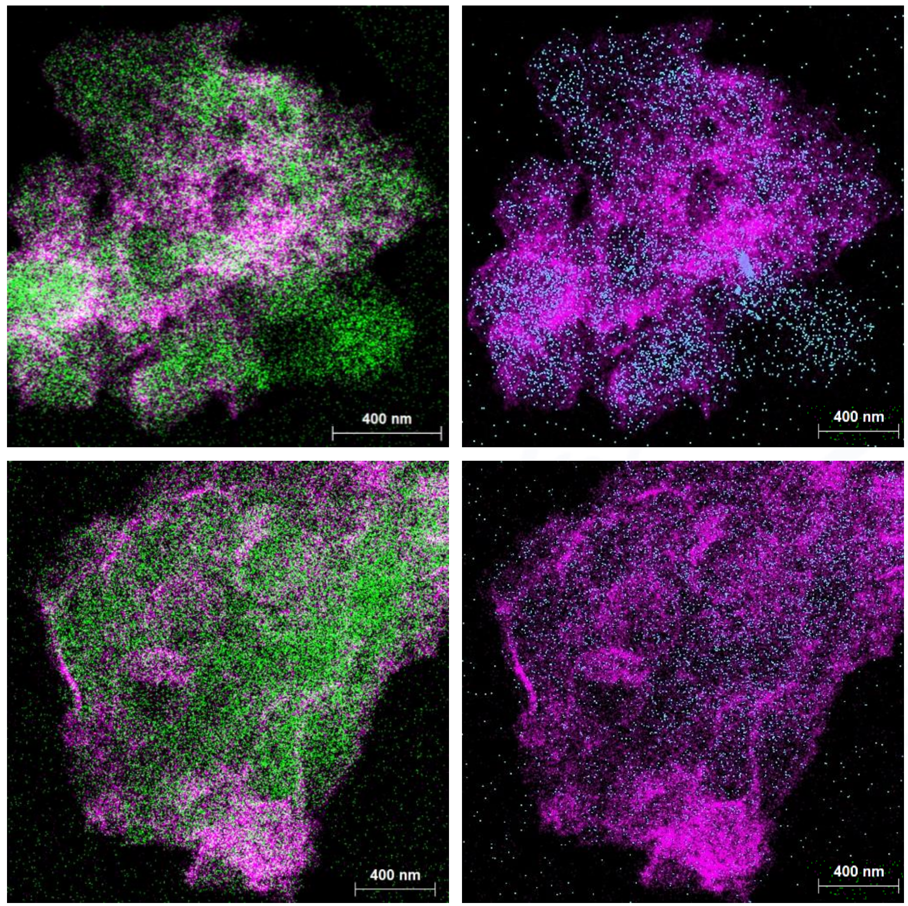
EOL



EDS: Ionomer distribution (F, purple) relative to catalyst (N, green & Fe, blue)

BOL

EOL



Increase in N/Fe$_{atom}$ indicates decrease in coordinated Fe-N$_x$ species

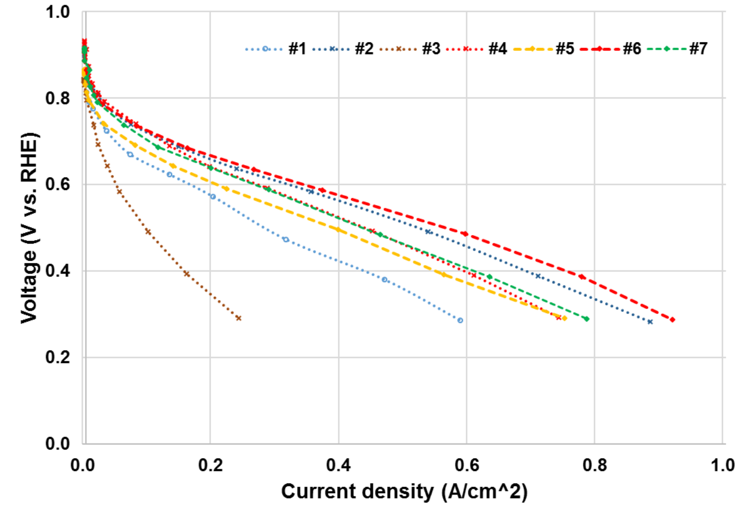
- Track changes in the catalyst in the presence of proton conductor (Nafion® ionomer, fluorinated polymer)
- Distribution of F shows how well ionomer is integrated with catalyst within the MEA electrode structure
- Characterizing before and after MEA testing is used to evaluate the stability of active sites and electrode quality

Summary

- Characterized a series of Fe-N-C electrocatalysts with different performance characteristics

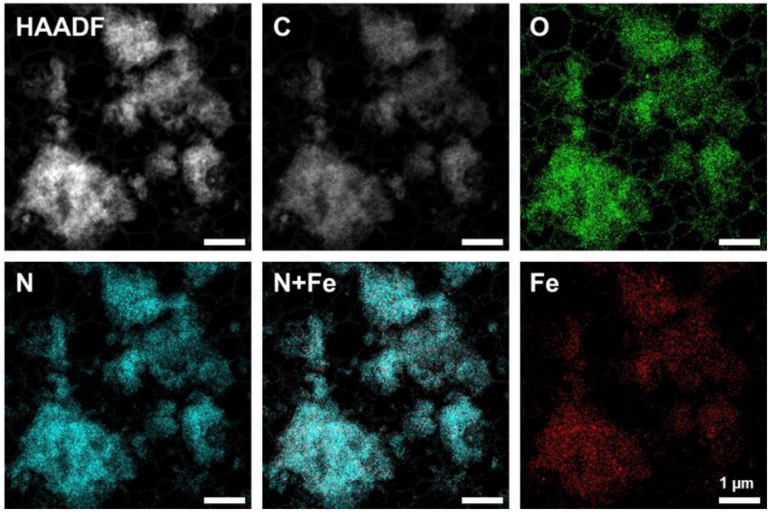
Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO 3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO 3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO 3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO 3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO 3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO 3	**950 ^{0}C 45 min, quench**	NH_3/N_2



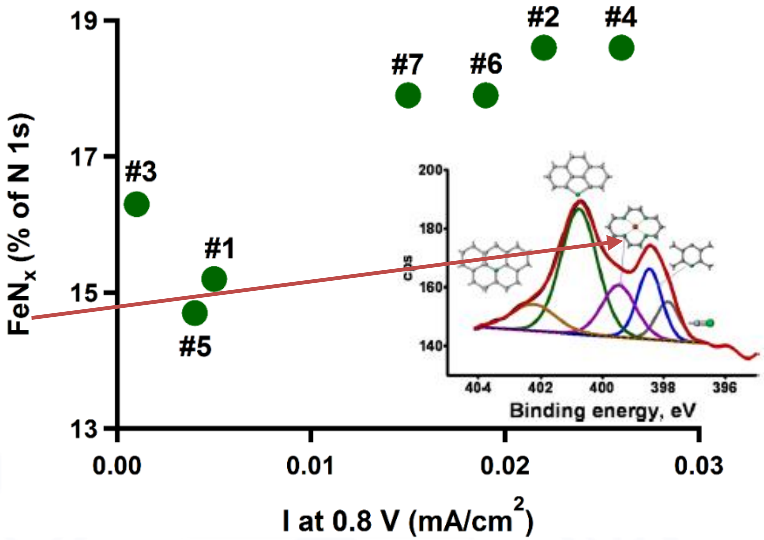
Summary

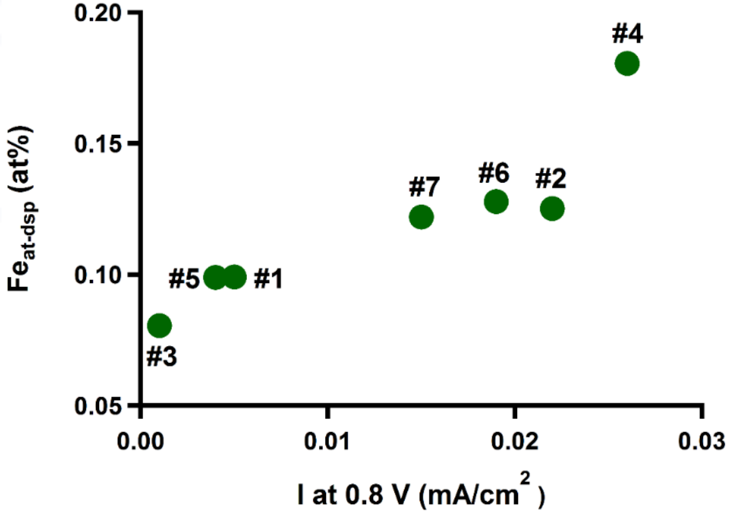
- Characterized a series of Fe-N-C electrocatalysts with different performance characteristics
- Demonstrated that EDS is an effective technique for evaluating elemental distribution of iron species



Summary

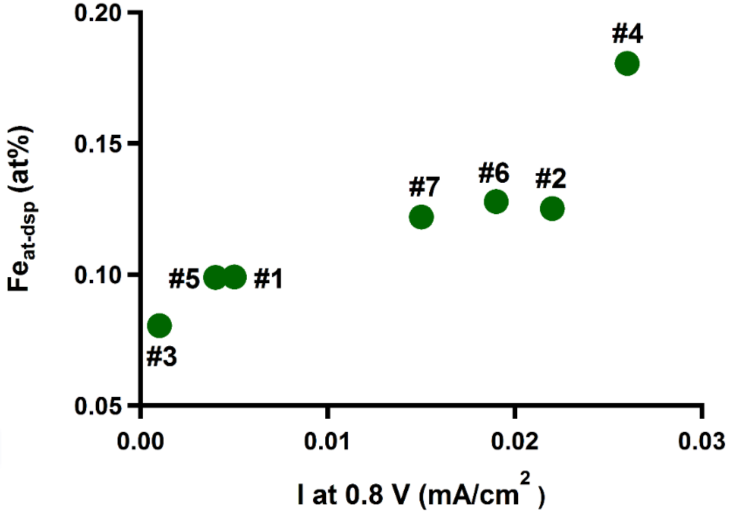
- Characterized a series of Fe-N-C electrocatalysts with different performance characteristics
- Demonstrated that EDS is an effective technique for evaluating elemental distribution of iron species
- Showed corroboration between XPS and EDS data, indicating that EDS is able to map active sites

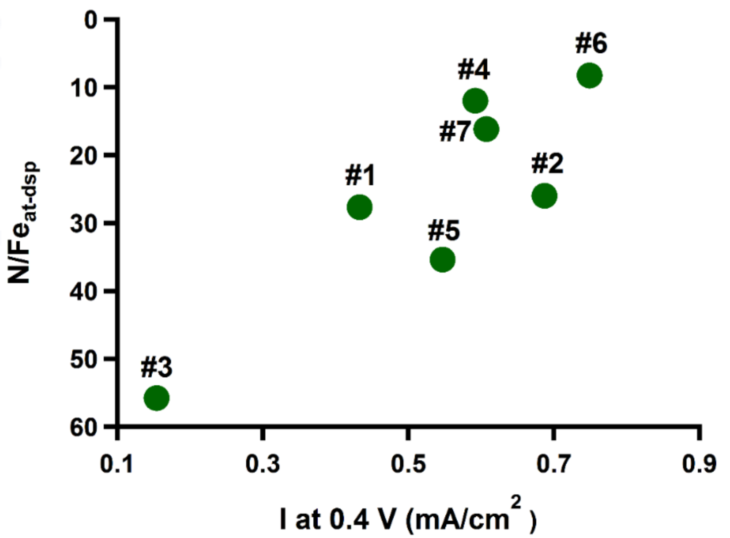




Summary

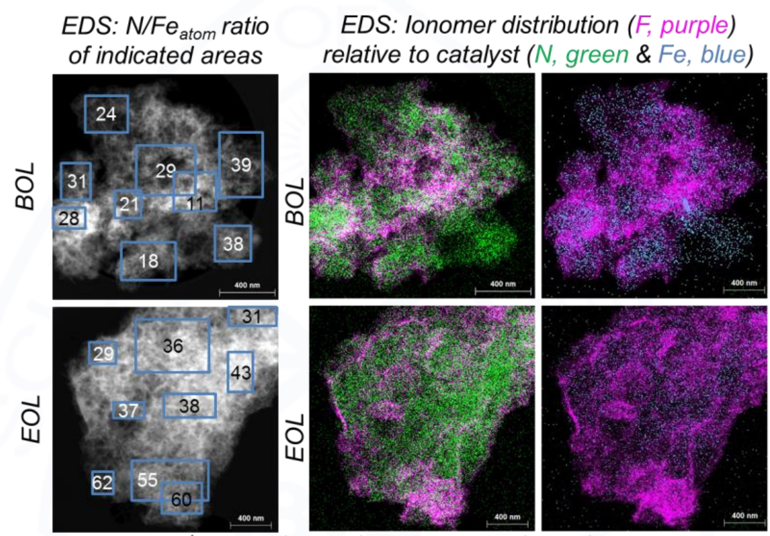
- Characterized a series of Fe-N-C electrocatalysts with different performance characteristics
- Demonstrated that EDS is an effective technique for evaluating elemental distribution of iron species
- Showed corroboration between XPS and EDS data, indicating that EDS is able to map active sites
- Explained performance trends by quantifying $Fe_{at\text{-}dsp}$ content and $N/Fe_{at\text{-}dsp}$ ratio





Summary

- Characterized a series of Fe-N-C electrocatalysts with different performance characteristics
- Demonstrated that EDS is an effective technique for evaluating elemental distribution of iron species
- Showed corroboration between XPS and EDS data, indicating that EDS is able to map active sites
- Explained performance trends by quantifying $Fe_{at\text{-}dsp}$ content and $N/Fe_{at\text{-}dsp}$ ratio
- Showed feasibility to use EDS to evaluate ionomer distribution and active site stability



Increase in N/Fe_{atom} indicates decrease in coordinated $Fe\text{-}N_x$ species

Acknowledgements

Trefny I² Center
Innovative Instruction

THE UNIVERSITY of NEW MEXICO

PAJARITO POWDER
FUEL CELL CATALYSTS

DEPARTMENT OF CHEMISTRY
COLORADO SCHOOL OF MINES

John M. Poate Doctoral First-Year Fellowship

Pylypenko Group:
Chilan Ngo
Sarah Shulda
Sam Gage
Matthew Strand
Caleb Stetson
Natalie Sietzman
Jamie Hagen
Matthew Curtis

Former members:
Prabhuram Joghee
Jason Christ
Tim Batson

Fe–N–C catalysts

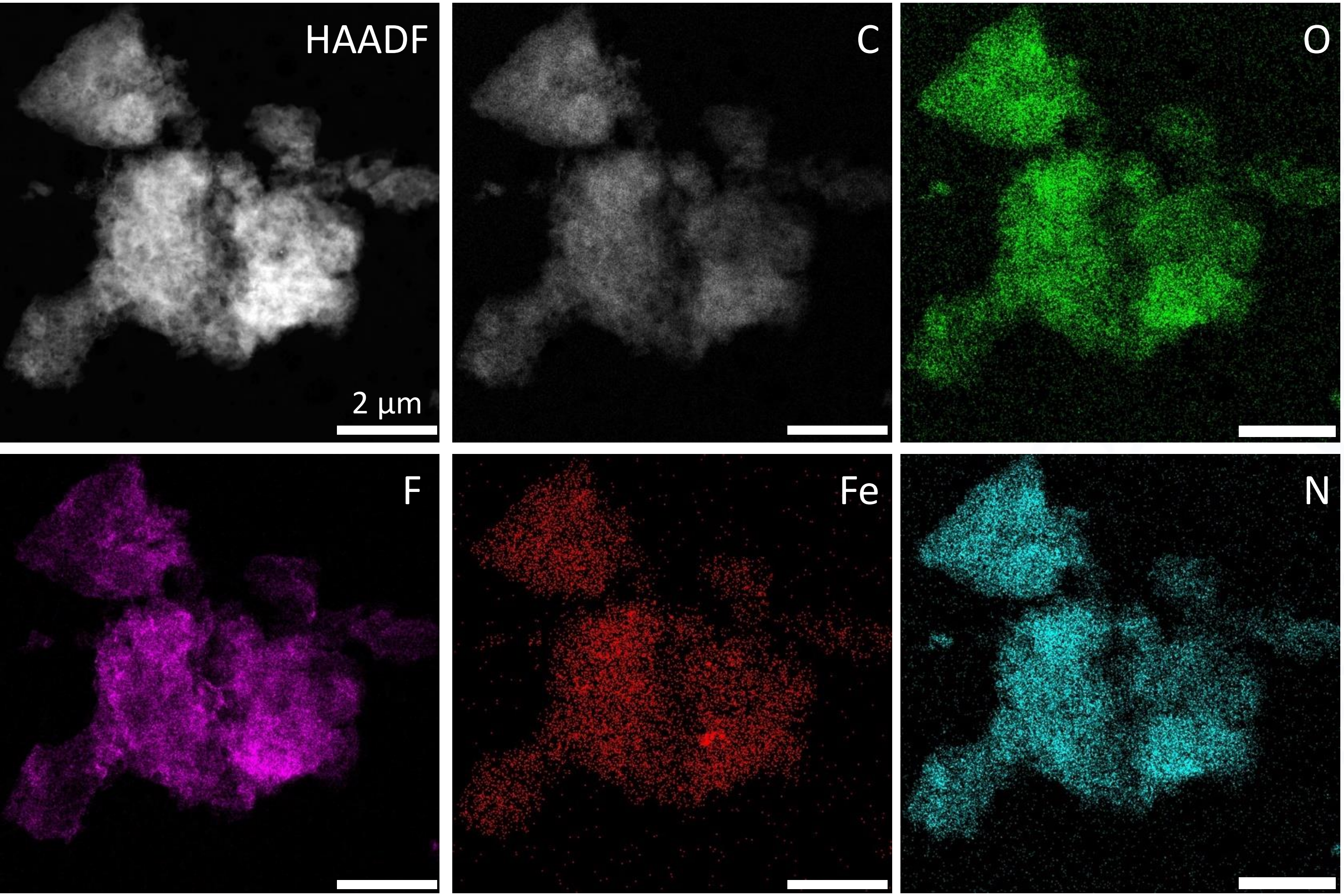
Synthesis methods – variations

Table 1. Table of varied synthesis parameters. Amounts of Stöber glass and CNT are in grams. All samples used 12.5 g nicarbazin and 1.2 g iron nitrate nonahydrate.

Sample	Stöber	CNT	Etch Prep	Etch	HT2 method	HT2 gas
1	1.0	1.0	**Mortar & Pestle**	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
2	1.0	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
3	**5.0**	1.0	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
4	1.0	**-**	Ball mill	HF/HNO_3	950 ^{0}C 30 min, quench	NH_3/N_2
5	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	**H_2/N_2**
6	1.0	1.0	Ball mill	**HF**	950 ^{0}C 30 min, quench	NH_3/N_2
7	1.0	1.0	Ball mill	HF/HNO_3	**950 ^{0}C 45 min, quench**	NH_3/N_2

Work-in-progress

Tracking active sites and ionomer distribution in MEAs



- Next step is to evaluate changes in the catalyst in the presence of proton conductor (Nafion® ionomer, fluorinated polymer)
- Tracking F distribution shows how well ionomer is integrated with catalyst within the MEA electrode structure
- Characterizing after MEA testing is used to evaluate the durability of catalysts