PGM-free Fe-N-C Catalysts for Oxygen Reduction Reaction: Catalyst Layer Design

Sarah Stariha^a, Kateryna Artyushkova^a, Michael J. Workman^a, Alexey Serov^a, Sam Mckinney^b,
Barr Halevi^b and Plamen Atanassov^{*,[a]}

^[a] S. Stariha, K. Artyushkova, M.J. Workman, A. Serov, P. Atanassov

Department of Chemical and Biological Engineering and Center for Microengineered Materials
(CMEM)

University of New Mexico

Albuquerque, NM 87131, USA

^[b] S. Mckinney, B. Halevi

Pajarito Powder LLC

317 Commercial St. NE

Albuquerque, NM 87102, USA

E-mail: starihas@unm.edu, kartyush@unm.edu, mworkman@unm.edu, serov@unm.edu,

smckinney@pajaritopowder.com, bhalevi@pajaritopowder.com, plamen@unm.edu

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Abstract

This work studies the morphology of platinum group metal-free (PGM-free) iron-nitrogen-carbon (Fe-N-C) catalyst layers for the oxygen reduction reaction (ORR) and compares catalytic performance via polarization curves. Three different nitrogen-rich organic precursors are used to prepare the catalysts. Using scanning electron microscopy (SEM) and focused ion beam (FIB) tomography, the porosity, Euler number (pore connectivity), overall roughness, solid phase size and pore size are calculated for catalyst surfaces and volumes. Catalytic activity is determined using membrane electrode assembly (MEA) testing. It is found that the dominant factor in MEA performance is transport limitations. Through the 2D and 3D metrics it is concluded that pore connectivity has the biggest effect on transport performance.

1 Introduction

Current commercially available proton exchange membrane fuel cells (PEMFCs) use platinum as both the anode and cathode catalysts. Platinum, which is both expensive and has geopolitical limitations, contributes to over 40% of the total cost of a PEMFC.[1] One way to lower the cost is by replacing platinum on the cathode side with platinum group metal-free (PGM-free) catalysts. In the past few decades, much work has been done to improve PGM-free catalyst activity. One class of PGM-free catalysts that show good promise are nano-structured materials based on transition metal-nitrogen-carbon (M-N-C) networks that facilitate the oxygen reduction reaction (ORR).[2] These materials may be prepared from iron salt and nitrogen-rich organic precursors via high temperature treatments. Other PGM-free catalysts that have been synthesized and results published include M-N-C sheets as support for nickel oxide for the oxygen evolution reaction (OER), zeolitic imidazolate framework (ZIF) derived graphene-based

nitrogen-doped porous carbon sheets for ORR, and M-N-C and Fe₃O₄/N-doped carbon hybrids based on sol-gel chemistry for ORR.[3-5]

It is widely acknowledged that nitrogen from the organic precursors play a crucial role in the ORR mechanism. It has been suggested that the nitrogen helps attach the transition metals to the underlying carbon support creating the ORR active sites. [6-9] A number of different nitrogen-rich organic precursors have been studied and their results published. They include Co-tetramethoxyphenylporphyrin[10], poly(ethyleneimine)[11], 4-aminoantipyrine[1], and carbendazim[12].

For PGM-free catalysts to achieve their highest overall performance, they must have a well-developed pore structure and high density of active sites. For over a decade, the University of New Mexico has been developing an original synthesis method for PGM-free catalysts and other classes of materials, called the Sacrificial Support Method (SSM).[2, 12-15] The SSM produces materials with open-frame hierarchical morphology at the micro- and meso-scale. The SSM is based on the infusion of silica, magnesia or other particles with transition metals and organic precursors. After high temperature pyrolysis in an inert atmosphere, the sacrificial support template is etched away leaving a self-supported M-N-C catalyst with tailored mesoporosity. By using templates with different sizes, the surface area can be tuned, and pore size distribution can be tailored over a range of 10-500 nm.

The use of the SSM for the synthesis of M-N-C catalysts requires precursors that are: (1) carbon rich – the amount of carbon atoms in the molecule of the N-C precursor should be high enough to form a porous, open-frame matrix as mentioned above, (2) nitrogen rich – as synthesis is performed in an inert atmosphere, all the nitrogen-containing moieties must be formed from nitrogen contained in the precursor itself and (3) thermally stable – have low volatility of organic

molecules as the formation of active sites starts at temperatures higher than 700°C and, therefore, volatile N-C precursors cannot be utilized.[16] All three factors are crucial for selecting M-N-C catalyst precursors.

The most realistic method of evaluating catalytic performance of PGM-free catalysts is testing the membrane electrode assemblies (MEAs) in real fuel cell test conditions. This type of testing can be done according to the US Department of Energy (DOE) recommended protocol.[17] Thirteen unpublished nitrogen-rich precursors were used for this study and screened via MEA testing. See Supplementary data Figure S1. Three were selected to study further; nicarbazin (NCB), sulfaguanidine (SGB), and mebendazole (MBZ). See Figure S2 for their structures. The materials selection is based on the performance criteria: NCB was one of the worst performing, MBZ was one of the best performing while SGB has performance in between. It should be noted that previous work involving NCB derived catalysts has been published which shows it to have good performance.[18, 19] Not-optimized poor performing formulation of NCB was purposefully chosen as the worst-performing catalyst to better understand the relationship between performance, chemistry and morphology.

There are many variables that contribute to poor PGM-free MEA performance. Because platinum is expensive, the focus when making catalyst layers is to utilize as little as possible while still maintaining high overall performance. This results in layers that are approximately 10 µm thick. PGM-free catalysts do not have that barrier, therefore, larger amounts of catalyst can be used to increase the number of active sites. This, however, creates much thicker catalyst layers (60-120 µm) leading to loss of performance.[20-23] Reasons for this loss include slow reaction kinetics, poor electronic and/or ionic conductivity, and mass transport limitations.

Previous work has been done studying the effect of PGM-free catalyst layer composition on MEA performance. [10, 19, 24]

The goal of the current study is to examine the chemistry and morphology of both the catalyst and the sprayed catalyst layer and their effects on MEA performance. First the morphology of the catalyst was imaged using a scanning electron microscope (SEM) while chemistry was analyzed by X-ray photoelectron spectrometry (XPS). From the SEM images, 2D metrics were calculated such as overall porosity and measure of connectivity – the Euler number. To evaluate the morphology of the sprayed catalyst layer, first the catalyst was sprayed onto a gas diffusion layer (GDL) to make a gas diffusion electrode (GDE). A FIB-SEM was used to image the sprayed catalyst layer in three dimensions.[25, 26] 3D metrics were calculated from the resulting images such as roughness, connectivity and average solid phase and pore sizes. Lastly, the GDEs were made into MEAs and tested to assess the catalytic performance and relate it to both the catalyst and sprayed catalyst layer morphology.

2 Experimental

2.1 Catalyst Preparation

The catalysts studied in the present work were synthesized by modified SSM.[12] Iron nitrate (2.5 g, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich) was mechanically mixed with 25 g of the nitrogen-rich organic precursor and 10 g of LM150 fumed silica (Cabot, surface area $\sim 150 \text{ m}^2 \text{ g}^{-1}$). The pre-mixed material was loaded into a 100 mL agate ball-mill jar with 16 agate balls (diameter 1 cm). The mixture was subjected to ball-milling at 450 RPM for 1 hour. The homogenous powder was pyrolyzed at $T=950^\circ\text{C}$, $t=30 \text{ min}$ in the flow of Ultra High Purity (UHP) nitrogen, 100 ccm. After heat treatment, silica was removed by 25 wt% HF, followed by

washing with DI water until neutral pH was reached. Obtained powder was dried overnight at $T=85^{\circ}\text{C}$. To remove un-washed H_2SiF_6 , second treatment in a reactive atmosphere (10 wt% NH_3 , 100ccm) was performed at $T=975^{\circ}\text{C}$, $t=30$ min.

2.2 GDE Fabrication

A standard ink was prepared as follows: 500 mg M-N-C non-PGM catalyst and 20.4 g 2:1 IPA/ H_2O solution, while the amount of D2021 Nafion[®] ionomer was adjusted to be 45 wt% of solid residue. The mixture was homogenized using an IKA-18 high energy shear mixer with a S18-19G dispersing element at 18,000 RPM for 60 min. The ink was then sprayed onto a SGL 25BC GDL using a Sono-Tek Exacta-Coat automated spray system delivering 1 mL ink/min through a 25 kHz ultrasonic nozzle. Catalyst loading was $3.0 \pm 0.5 \text{ mg cm}^{-2}$.

2.3 MEA Fabrication and Testing

The MEA was assembled using a 150 μm thick gasket on the anode and 250 μm thick gasket on the cathode. The sandwich of in-house made anode ($0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), membrane (Nafion[®] 211), and the cathode GDE was pressed in a heated Carver press at 500 psi at 130°C for 10 min. The MEA was placed in a 5 cm^2 cell with serpentine flow channels, and bolts were tightened to 4.4 Newton meters. A Fuel Cell Technologies test station was used to obtain H_2/Air polarization curves. The anode and cathode gases were heated and fully humidified at 85°C , and the flow rates were 200 and 250 sccm, respectively. The cell operating temperature was maintained at 80°C . Polarization curves were acquired potentiostatically with a 60 s delay before data acquisition at 12 psi (0.8 bar)_{gauge}, 30 psi (2 bar)_{gauge}, 12 psi (0.8 bar)_{gauge}, 2 psi (0.1 bar)_{gauge} and 60 psi (4 bar)_{gauge} backpressures.

2.4 Catalyst Morphology, Surface Area, and 2D Metrics

Morphology of synthesized materials was determined by SEM. A Hitachi S-5200 Nano SEM with an accelerating voltage of 2.0 kV was used. Each image was processed in Matlab. The details of processing are described in the Results and Discussion section below. 2D metrics; overall porosity, and Euler number, were calculated. Brunauer–Emmett–Teller (BET) Multipoint surface area of each catalyst was measured using a Micrometrics Gemini system.

2.5 Catalyst Layer Morphology and 3D Metrics

The catalyst was sprayed onto a GDL and each catalyst layer was analyzed using an FEI Quanta 3D Dual beam scanning electron microscope equipped with a field emission gun (SEM-FEG). First a protective platinum cap was deposited over the area of interest. Next the FIB, consisting of Ga^+ ions accelerated at 30 kV, was used to dig trenches on three sides of the area of interest in order to get a clean view of the catalyst layer. Finally, the FIB was used to slice through the catalyst layer. 160-180 slices were then taken every 30 nm. Each slice was imaged using the electron beam at 5.0 kV. All the images were combined using an image stack plug-in and processed using ImageJ. The StackReg plugin was used to register images using the “Translation” option. Registered images were saved and processed further in in-house written GUI in Matlab. 3D roughness was calculated with the original gray scale intensity image stack. For the other 3D metrics, each image in image stack was thresholded such that solid phase was assigned an intensity value of 1 (white) and pores an intensity value of 0 (black). In this case, solid phase refers to both the catalyst and ionomer since SEM images do not clearly distinguish between the two phases. See Figure 1.

Figure 1. Steps to process images acquired using FIB-SEM. **(A)** FIB used to clear trenches around the area of interest facilitating a clear view of the catalyst layer. **(B)** FIB used to cut slices through the catalyst layer; SEM imaging of each slice. **(C)** Images are processed in the ImageJ plug-in StackReg. **(D)** A visual of the 3D pore volume was reconstructed.

2.6 XPS

The XPS spectra were acquired using a Kratos AXIS DLD Ultra photoelectron spectrometer using monochromatic Al K α source operating at 225 W. No charge compensation was necessary. Survey spectra were initially acquired at pass energy (PE) of 80 eV, followed by high-resolution spectra of Fe 2p, C 1s, O 1s, S 1s and N 1s at PE of 20 eV. Data analysis and quantification were performed using the CASA XPS software. Curve fitting was performed using a 70 % Gaussian/ 30 % Lorentzian line shape. Quantification was performed using a Shirley background for Fe 2p spectra and a linear background for C 1s, N 1s, S 1s and O 1s spectra.

3 Results and Discussion

3.1 Catalyst Morphology, Surface Area, and 2D Metrics

Morphology of synthesized catalysts was analyzed by SEM. As can be seen from Figure 2, the material has a well-developed porous structure formed by two mechanisms: (1) the removal of silica support and (2) the decomposition of organic molecules. The removal of silica template leaves the catalyst with a surface area between 500 and 650 m² g⁻¹ as measured by BET, with pores of ~50-70 nm. Such porous structure is beneficial for effective transport of oxygen to active sites as well as for water management.

From the SEM images, 2D metrics of overall porosity and Euler number were calculated for each catalyst. Porosity is the ratio of void volume (pores) to total volume. Euler number is the total number of objects (solid phase) minus the total number of pores in those objects. Pore connectivity is determined by the number of connected pixels representing pores.[27] The lower the Euler number, the more connected the pores present within the solid phase. Figure 3 summarizes the 2D metrics for all three catalysts. Fe-NCB has the highest overall porosity while Fe-MBZ has the lowest. However, Fe-MBZ has the lowest Euler number while Fe-NCB has the highest. This indicates that Fe-MBZ has the best pore connectivity.

Figure 2. SEM images of catalysts prepared by Sacrificial Support Method. (A) Fe-NCB (B) Fe-SGB (C) Fe-MBZ

Figure 3. Summary of 2D metrics.

3.2 Catalyst Layer Morphology and 3D Metrics

The morphology of the sprayed catalyst layers was examined using FIB-SEM. A 2D image of a slice from each catalyst layer can be seen in Figure 4. For each image the membrane would be located at the top of the catalyst layer. As discussed in the experimental section, 160-180 slices were acquired for each catalyst layer, which were then combined in image stack, an ImageJ plug-in, and registered to create a 3D volume of the material. First, a 3D visualization of pores in each catalyst layer was reconstructed using volume rendering of image stack in ImageJ (see Figure 5). The pores are indicated in red while solid phase has blue color. Fe-NCB has a higher intensity of red meaning the pores are bigger. However the red is clustered together and not homogeneously spread throughout the catalyst layer, which is consistent with lower pore connectivity. Fe-SGB shows less red intensity indicating smaller pores. However the red is uniformly spread throughout the catalyst layer meaning better pore connectivity. Fe-MBZ has a higher intensity of red spread almost throughout the whole catalyst layer. This means the Fe-MBZ is overall more homogenous and has good pore connectivity.

From the processed images, 3D metrics were calculated (Figure 6). First, 3D roughness or the overall image heterogeneity was calculated. This is based on the greyscale images before thresholding. Here Fe-NCB has the highest roughness followed by Fe-SGB while Fe-MBZ has

the lowest. This means that overall Fe-MBZ is more homogeneous. Next, solid phase size and pore size was calculated from thresholded images. Solid phase size is measured as the average number of consecutive pixels representing the solid phase (pixels with an intensity value of 1) in a given direction. Here, Fe-NCB has the highest solid phase size followed by Fe-SGB while Fe-MBZ has the lowest solid phase size. The metrics representative of pore size are calculated as an average diffusion distance, or the average distance from a solid phase pixel to the nearest void pixel in the image (pore having an intensity value of 0). This measures the closeness of solid phase clusters or the pore size between these clusters. [28, 29] Here again, Fe-NCB has the highest pore size followed by Fe-SGB while Fe-MBZ has the lowest. Lastly, Euler number was calculated from thresholded images. As previously stated, the lower the Euler number, the more connected the pores are throughout the catalyst layer. Here Fe-NCB has an Euler number around 0 while both Fe-SGB and Fe-MBZ have Euler numbers that are negative. This indicates that both Fe-SGB and Fe-MBZ have higher pore connectivity than Fe-NCB. These metrics agree with the conclusions drawn from the 3D reconstructed pore volume in Figure 5.

Figure 4. 2D FIB-SEM images of each of the catalyst layers that were sprayed onto a GDL.

(A) Fe-NCB (B) Fe-SGB (C) Fe-MBZ

Figure 5. 3D reconstruction of catalyst layer pore volume indicated in red. (A) Fe-NCB (B) Fe-SGB (C) Fe-MBZ

Figure 6. Summary of catalyst layer 3D metrics calculated from FIB-SEM images.

3.3 Electrochemical Performance

The catalysts' performance was evaluated using MEAs and compared using polarization curves. There are three important regions within a polarization curve. The kinetic region near 0.8 V indicates the reaction efficiency. The ohmic region around 0.6 V indicates the ionic and electronic resistances in the cell. Lastly, the transport region near 0.4 V represents the mass transport part of the polarization curve. As mentioned above, each MEA was tested at 5 different pressures. Since the focus of this study is the catalyst layer, the interest is in as close to beginning of life performance as possible. In this case, that is the first polarization curve at 12 psi (0.8 bar)_{gauge}. As can be seen in Figure 7, Fe-SGB and Fe-MBZ have the same performance at 0.8 V, the kinetic region, however, Fe-NCB performs significantly worse. At 0.6 V, in the ohmic

region, Fe-SGB is only slightly worse than Fe-MBZ but again Fe-NCB is significantly worse. Finally at 0.4 V, in the transport region, Fe-MBZ has the best performance, followed by Fe-SGB. Fe-NCB's performance is almost an order of magnitude worse than Fe-MBZ. As shown in the above section, one possible reason for Fe-NCB's poor transport performance is the lack of pore connectivity.

In order to compare these results with the state-of-the-art PGM-free M-N-C ORR catalysts reported in the literature power density curves (see Supplementary Material Figure S4) were plotted from the polarization curves in Figure 7. A comprehensive review was recently published in *Chemical Review* by Shao et. al. comparing the initial power density from some of the best PGM-free ORR catalysts to date. It states that in H₂/Air M-N-C catalysts derived from polyaniline and phenanthroline have the best initial power density at 0.41 W cm⁻² and 0.38 W cm⁻² respectively.[30] The best overall performing catalyst from this study, Fe-MBZ, had an initial power density of 0.33 W cm⁻² while Fe-SGB and Fe-NCB had initial power densities of 0.24 W cm⁻² and 0.04 W cm⁻².

There are two types of mass transport losses that can lead to poor MEA performance, gaseous transport, and liquid transport. Liquid transport refers to both water and ionomer that can potentially block pores. One way to determine what type of transport loss is occurring within the catalyst layer was testing the MEA in both air and oxygen. Oxygen has a higher activity than air. If the transport limitation is gaseous, then oxygen will perform better. However, if the transport limitation is liquid, then pores and active sites are being blocked and the performance for both gases will be the same. Figure 8 (A) and (C) are Fe-MBZ and Fe-NCB tested in 12 psi (0.8 bar)_{gauge} backpressure H₂/O₂ and 60 psi (4 bar)_{gauge} backpressure H₂/Air respectively. These pressures were chosen so that the same partial pressure of oxygen was present in each case. For

Fe-MBZ the solid line, O₂, has better overall performance than the dotted line, air. This means that the transport performance is gaseous limited. Fe-SGB follows the same trend and can be seen in Supplementary Material Figure S5 (A). However for Fe-NCB air and oxygen performed the same which indicates liquid transport limited performance.

Another method to determine the type of transport limitation present is to compare the polarization curves of the same MEA tested at different backpressures, in this case in H₂/Air. Figure 8 (B) and (D) are Fe-MBZ and Fe-NCB tested at the five pressures listed above. As can be seen, performance increases as pressure increases for Fe-MBZ. The same trend can be seen for Fe-SGB and is Supplementary Material Figure S5 (B). This means that as more gas is pushed through the catalyst layer the performance improves. This again indicates that performance is gaseous transport limited. If the performance is liquid transport limited all pressures would have had the same performance due to pore and active site blockage as can be seen for Fe-NCB in Figure 8 (D).

Figure 7. First 12 psi (0.8 bar)_{gauge} H₂/Air polarization curves were used to represent beginning of life performance.

Figure 8. (A) Fe-MBZ tested in both 60 psi (4 bar)_{gauge} backpressure H₂/Air and 12 psi (0.8 bar)_{gauge} backpressure H₂/O₂. (B) Fe-MBZ tested in H₂/Air at five different backpressures. (C) Fe-NCB tested in both 60 psi (4 bar)_{gauge} backpressure H₂/Air and 12 psi (0.8 bar)_{gauge} backpressure H₂/O₂. (D) Fe-NCB tested in H₂/Air at five different backpressures.

3.4 Catalyst Chemistry

Table 1 shows elemental composition and nitrogen speciation of catalysts as determined by XPS. Fe-MBZ has the highest amount of Fe detected while Fe-NCB has the lowest amount of both N and Fe detected. Six nitrogen moieties can be discerned from high resolution spectra. See Figure S3. Going from low to high binding energy these types of nitrogen are – imine, pyridinic, nitrogen coordinated to the metal, pyrrolic, quaternary or protonated N and graphitic nitrogen. In previously published reports by our group and by others, higher amounts of nitrogen coordinated

to metal (M-N_x) are correlated with better ORR activity. [31, 32] The species contributing to higher binding energy range such as pyrrolic, protonated and graphitic N results in preferential two electron reduction of oxygen to hydrogen peroxide. [31, 33, 34] Fe-NCB powder has the highest amount of pyrrolic nitrogen and lowest amount of M-N_x. The low amount of M-N_x could indicate a lower number of active sites and possibly explain part of Fe-NCB's poor performance. Fe-MBZ, on the other hand, has the highest amount of beneficial M-N_x centers and lowest amount of pyrrolic nitrogen among the three samples, possibly indicating the highest number of active sites and contributing to its better overall performance.

	C 1s %	O 1s %	N 1s %	S 1s%	Fe 2p
Fe-MBZ powder	92.1	3.9	3.7	0.0	0.30
Fe-SGB powder	90.2	5.6	3.9	0.5	0.27
Fe-NCB powder	92.7	3.8	3.3	0.0	0.15

	Imine	Pyridine	N coordinated to Metal (M-N _x)	N pyrrole	N quaternary	N graphitic
Fe-MBZ powder	10.1	22.6	15.5	29.7	17.7	4.3
Fe-SGB powder	7.7	21.1	13.6	32.3	19.2	6.0
Fe-NCB powder	7.7	24.8	10.4	38.3	11.6	7.0

Table 1. Elemental composition and nitrogen speciation of catalysts as determined by XPS.

4 Conclusion

Catalyst layer morphology plays a key role in MEA performance. However, the relationship between catalyst porosity and pore connectivity and catalyst layer roughness, solid phase size, pore size, and pore connectivity and overall performance is not straightforward. Key conclusions derived from experiments performed in this work are: 1) Fe-MBZ, the best performing catalyst, had the lowest overall porosity, 3D roughness, solid phase size, and pore size. 2) The biggest discrepancy in performance was in the transport region. This loss of performance was due to gaseous transport limitations and not liquid transport limitations. 3) Pore connectivity is the best indicator of performance. Better performing catalysts have greater pore connectivity in both the catalyst and the sprayed catalyst layer.

5 Glossary

PGM-free - platinum group metal-free

ORR- oxygen reduction reaction

OER - oxygen evolution reaction

ZIF - zeolitic imidazolate framework

SEM- scanning electron microscopy

FIB- focused ion beam

MEAs- membrane electrode assemblies

PEMFCs- proton exchange membrane fuel cells

M-N-C- metal-nitrogen-carbon

SSM- Sacrificial Support Method

DOE- Department of Energy

Fe-NCB- iron containing nicarbazin-derived catalyst

Fe-SGB- iron containing sulfaguanidine-derived catalyst

Fe-MBZ- iron containing mebendazole-derived catalyst

XPS- X-ray photoelectron spectrometry

GDL- gas diffusion layer

GDE- gas diffusion electrode

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