Non-PGM Membrane Electrode Assemblies: Optimization for Performance

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Abstract

The performance of non-platinum group metals (non-PGM) iron-nitrogen-carbon (Fe-N-C) based cathode in fuel cell operation conditions was studied. The effect of Nafion to catalyst ratio as well as carbon additives on the activity was studied. It was found that ionomer plays a key role in proton and water transport within the MEA. To compensate intrinsic low electronic conductivity of Fe-N-C materials additional carbons such as Vulcan XC72R, Ketjen Black 600 EC, and carbon nanotubes (CNTs) were added to MEA inks. X-ray Phototelectron Spectroscopy

studied the effect of these carbon additives on chemical composition of catalysts. It was determined that inks with 35wt% of Nafion ionomer resulted in the optimal performance of the Fe-N-C cathode catalyst in the air.

1 Introduction

As Proton Exchange Membrane Fuel Cells (PEMFCs) become a viable option for clean energy production, cost is the major concern. Currently, platinum contributes to over 40% of the total cost of a PEMFC.[1] Because of this, there has been a huge push to develop non-platinum group metal (non-PGM) catalysts. These catalysts do not contain any precious metals including platinum or palladium. One rapidly developing class of non-PGM catalysts for oxygen reduction reaction (ORR) are nanomaterials based on transition metal-carbon-nitrogen networks (M-N-C). One of the synthetic approaches to make a M-N-C material is based on high temperature pyrolysis of transition metal salts in combination with nitrogen rich organic molecules.

In order for non-PGM catalysts to achieve their highest catalytic activity, they must have a well-developed pore structure and high density of active sites. For more than a decade, the University of New Mexico has been developing an original synthesis method for non-PGM catalysts and other classes of materials, called the Sacrificial Support Method (SSM)[2-6] SSM produces materials with open-frame hierarchical morphology at the micro- and meso-scale. SSM is based on infusion of silica particles with transition metal and organic precursors. After high temperature pyrolysis in inert or reactive atmosphere, the silica template is etched away leaving self-supported M-N-C catalyst with tailored mesoporosity. By using templates with different

sizes, surface area can be tuned, and pore size distribution can be tailored over a range of 10-500nm.

The most realistic method of estimating catalytic performance of non-PGM catalysts is testing within Membrane Electrode Assembly (MEA). This type of testing can be done according to the US Department of Energy (DOE) recommended protocol.[7] Within an MEA there is a complex interplay between catalyst and ionomer within an MEA affecting its overall performance.[8-10] Ionomer transports ions to active sites and serves as a media to remove water from active sites. The effect of ionomer to catalyst ratio on the performance has to be understood and optimized. For any particular electrocatalysts, there is an optimal amount of ionomer within the MEA that results in the best performance. While the kinetic performance improves with higher ionomer content, likely due to better ionic transport and conductivity, the mass-transport is hindered due to excess ionomer or water blocking the pores.[11] Previous work has been done to examine the effect of catalyst to ionomer ratio in platinum based catalysts. These studies show that systems with lower catalyst to ionomer ratios between 10-30wt% have the best performance.[12-15] More recently there have been a number of publications presenting MEA performance data using a non-PGM-based cathode catalyst. These studies looked weight percentages of Nafion ranging from 25wt% to 75wt%. In both studies, the best performing MEAs were those made with 50wt% Nafion while higher Nafion containing inks performed significantly worse.[16, 17]

There is a tendency for a decrease in the overall performance when higher amounts of Nafion are used.[18] One of the possible explanation of this loss in the performance is the excess Nafion separating the catalyst particles, breaking the electronic pathway and losing electronic conductivity. One way of compensating this process is to add conductive material, such as carbon, to the electrocatalyst before integration into the MEA. Carbon additives can act as a

bridge, interconnecting catalyst particles and reestablishing a continuous electronic pathway. Moreover, carbons may play a role in the overall hydrophobicity of the MEA, affecting water transport properties.

The goal of the current study is to determine the role ionomer plays in overall MEA performance. Nafion content was varied from 25 to 45wt% and two different Fe-N-C catalysts were explored as cathode catalyst materials. Carbon additives (Vulcan XC-72R, Ketjen Black 600, and in-house synthesized carbon nanotubes[2]) were also studied to determine their contribution into the overall MEA performance. X-ray Photoelectron Spectroscopy (XPS) was used to evaluate the chemical composition of catalysts after addition of carbon additives.

2 Experimental

2.1 Catalyst preparation

The catalysts studied in the present work were synthesized by modified Sacrificial Support Method. Iron nitrate (2.5g, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich) was mechanically mixed with 25g of nicarbazin (NCB, Sigma Aldrich) and 10g of LM150 fumed silica (Cabot, surface area $\sim 150\text{m}^2\text{ g}^{-1}$). Pre-mixed material was loaded into the 100ml agate ball-mill jar with 16 agate balls (diameter 1cm). Mixture was subjected to ball-milling at 450RPM for 1 hour. Homogenous powder was pyrolyzed at $T=950^\circ\text{C}$, $t=30\text{ min}$ in the flow of Ultra High Purity (UHP) nitrogen, 100ccm. After heat treatment, silica was removed by 25wt% of HF, followed by washing with DI water until neutral pH. Obtained powder was dried overnight at $T=85^\circ\text{C}$. In order to remove un-washed H_2SiF_6 , second treatment in a reactive atmosphere (10at% NH_3 , 100ccm) was performed at $T=975^\circ\text{C}$, $t=30\text{min}$.

The additional ball-milling with nitrogen-rich organic precursors; urea and melamine (see figure 1) (in the ratio of 1g of non-PGM catalyst to 2.5g of melamine or urea) followed by heat treatment in UHP nitrogen at T=950°C, t=30min was performed in order to increase density of active sites.

Figure 1. Structures of nitrogen-rich organic precursors. a) Urea b) Melamine

2.2 Ink fabrication

A standard cathode ink was prepared as follows: 180mg M-N-C non-PGM catalyst and 7.9mg 2:1 IPA/H₂O solution, while the amount of the Nafion ionomer was adjusted to be 45wt%. The mixture was homogenized by high energy homogenizer (IKA) at 18000 rpm for 90min using a 10mm diameter rod. The ink was sprayed on carbon paper (SGL, 25BC) using an air brush. Catalyst loading was $4.0\text{ mg cm}^{-2} \pm 0.5$. An additional Nafion layer (2:1 IPA, Nafion) was then sprayed with a 0.3 mg cm^{-2} loading in order to prevent gas diffusion electrode delamination.

The standard ink formulation was varied to make inks with 25wt% and 35wt% Nafion and inks with carbon additives. For inks with carbon additives, 144mg non-PGM catalyst and 36mg carbon (20wt% Vulcan XC72R, KetjenBlack 600EG and carbon nanotubes) were used.

2.3 MEA fabrication and testing

The MEA was assembled using a 125µm thick gasket on the anode and 250µm thick gasket on the cathode. The sandwich of anode (0.4 mg cm^{-2} Pt), membrane (Nafion 211), and the cathode was pressed in a heated Carver press at 500 psi at 130°C for 10 min. The MEA was placed in a 5

cm² cell with serpentine flow channels, and bolts were tightened to 4.4 Newton meters. A Fuel Cell Technologies test station was used to obtain H₂/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 60s delay before data acquisition at 12 and 30 psi backpressure.

2.4 Bulk Electronic Conductivity

In order to measure bulk electronic conductivity an in-house measurement system was set up. See figure 2. The powder was placed in a Teflon casing with gold electrodes on either end. The bulk electronic conductivity was measured under 167 psi of pressure. The presented pressing conditions were selected in order to assure that there was good electronic contact between the powder and the electrodes. On the other hand, taking into account open-framed structure of the catalyst one should be extremely careful in order not to over-press the catalyst, but instead get a sense of the bulk electronic conductivity of the powder as a measure of how it packs. The pressing was made on air at room temperature. This was done for each carbon tested and both catalysts with and without additional carbon.[19, 20]

Figure 2. Set-up of in-house bulk conductivity measurement system. a) Teflon casing with the two gold electrodes b) Teflon casing with gold electrodes in press connected to conductivity meter

2.5 Morphology

Morphology of synthesized materials were determined by SEM (Hitachi S-5200 Nano SEM with an accelerating voltage of 10 keV) and TEM (JEOL 2010 instrument with an accelerating voltage of 200 keV).

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 and N 1s at PE of 20 eV for all of the samples. Data analysis and quantification were performed using the CASAXPS software. A Shirley background was used for quantification and curve fitting of Fe 2p spectra, while a linear background was used C 1s, N 1s and O 1s spectra. Quantification utilized sensitivity factors provided by the manufacturer. A 70% Gaussian/30% Lorentzian line shape was used for the curve-fits.

2.7 Multivariate analysis

Multivariate analysis of the data was done using PLS-Toolbox 5.0 for Matlab. Principal Component Analysis (PCA), using an autoscaling as a preprocessing option (mean centering and scaling to unit variance), was the default method of data analysis. PCA extracts the key mathematical principal components (PC) from a large data matrix by converting it into two smaller matrices that are easier to examine and interpret. The first PC accounts for the largest part of the variance in the data, the second PC accounts for the second-largest part of the variance, and so forth. The results of PCA are usually displayed as score plots (reflecting the significance of each sample in a principal component), loading plots (reflecting the significance

of each variable in a principal component) and bi-plots (showing both samples and variables for two principal components). Bi-plots will be used herein.[21]

3 Results and Discussion

3.1 Morphology.

Morphology of synthesized catalysts was analyzed by Scanning Electron and Transmission Electron Microscopy methods (SEM and TEM). As it can be seen from Figure 3 material has 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 $\sim 1000 \text{ m}^2\text{g}^{-1}$ with pores of $\sim 50\text{-}70 \text{ nm}$ caused by the decomposition of organic molecules. Surface area was measured using the Brunauer–Emmett–Teller (BET) method. Such porous structure is beneficial for effective transport of oxygen to active sites as well as for water management. As mentioned above, the porosity and pores size distribution can be controlled by varying the silica to organic precursor ratio and/or by type of silica.[22]

Figure 3. Images of Fe-NCB catalyst prepared by Sacrificial Support Method (additional ball-milling with urea): a) SEM and b) TEM.

3.2 Bulk Electronic Conductivity.

Table 1 shows the bulk electronic conductivity results. The top group is the carbons by themselves. Carbon nanotubes are the most conductive. Addition of all three carbons to urea-based catalysts increased conductivity with Vulcan having the highest effect. Addition of carbon nanotubes to melamine based catalysts increased conductivity, while addition of Vulcan and Ketjen Black 600 decreased conductivity.

Table 1. Bulk Electronic Conductivity Measurements.

3.3 Surface composition

Ideal carbon additive should improve conductivity and should not change the composition of the metal-nitrogen-carbon electrocatalysts by introducing chemical groups that may compromise its hydrophobic properties and stability. Introduction of amorphous carbon and surface oxides may increase hydrophilicity of the catalysts, cause flooding and increase carbon corrosion compromising activity and stability of the catalysts. Introduction of excess of graphitic carbon may increase hydrophobicity of carbon and worsen water transport properties. Therefore, XPS was used to study the effect of carbon additives on the chemical composition of catalysts. Table 2 shows the elemental composition and chemical speciation of carbon, derived from high resolution C 1s spectra (Figure S5) obtained from catalysts powders without and with different carbon additives. Out of all the carbon additives, only addition of Vulcan XC72 changes overall elemental composition by introducing larger amount of carbon at the expense of nitrogen and iron. This loss of iron could explain the decrease in bulk electronic conductivity in the melamine-derived catalyst with the addition of Vulcan XC72R. Nitrogen speciation plays an important

role in the mechanism of ORR. Relative distribution of pyridinic, pyrrolic, graphitic and nitrogen coordinated to the metal have been discussed by many in attempt to determine possible active sites for oxygen reduction.[3, 22-24] Importantly, the overall nitrogen and iron speciation is not affected by the addition of carbon (not shown). The speciation of carbon, on the other hand, changes significantly after carbon additives introduction. None of the carbon additives introduces carbon oxides, while graphitic content is increased for all carbon additives. KB200 has a smallest effect on carbon chemistry introducing slightly more graphitic carbon into the catalyst. Vulcan XC-72 introduces the highest amount of graphitic carbon and lowers the amount of C-N centers significantly. CNTs have similar effect causing increase of graphitic carbon, decreasing the amount of surface oxides and, thus decreasing wettability of the catalyst.

Table 2. XPS elemental composition, at % and relative amounts of different types of carbon derived from high resolution C 1s spectra

3.4 Electrochemical Performance.

There are three important regimes within a polarization curve. The kinetic regime at 0.8 V indicates the reaction efficiency. The transition region at 0.6 V indicates the switch between kinetic limited to transport limited performance. Lastly, the transport regime at 0.4 V indicates the pure mass-transfer part of the polarization curve.

Figure 4 shows fuel cell polarization curves for all Nafion wt% for both urea (UR) and melamine (MM) non-PGM catalysts without any carbon additives at 12 psi backpressure. The best performance for both catalysts is as follows: in the kinetic region (0.8 V) 45wt% Nafion is best for both, in the transition region (0.6V) 35wt% is best for both, and in the transport region (0.4 V) 25wt% Nafion is best for urea based catalysts and 35wt% is best for melamine based

catalysts. This points that the graded MEA fabrication, starting from high Nafion content closer to the membrane ending up with the smallest content on the gas diffusion electrode will result in the best performance.

Figure 5 shows fuel cell polarization curves for all Nafion wt% for both urea (UR) and melamine (MM) non-PGM catalysts with Vulcan XC72R as carbon additive at 12 psi backpressure. In both cases adding carbon improves performance for MEAs with 45wt% Nafion, while hinders performance in the MEAs made with lower amounts of Nafion. This supports the hypothesis that when higher amounts of ionomer are used, the performance is poor due to transport hindrance and broken electronic pathways, adding carbon can enhance the performance.

It is believed that the better electrochemical performance seen in the melamine-derived catalysts is due to the increased number of nitrogens in melamine compared to urea.

Figure 4. H₂/Air polarization curves obtained for Fe-NCB catalyst synthesized with both urea and melamine nitrogen precursors for all amounts of Nafion at 12 psi backpressure.

Figure 5. H₂/Air polarization curves obtained for Fe-NCB catalyst synthesized with both urea and melamine nitrogen precursors for all amounts of Nafion at 12 psi backpressure with 25wt% Vulcan XC72R carbon additive.

3.5 Multivariate Analysis.

Table S1 is a summary of the measured current densities at 0.8V, 0.6V and 0.4V for each MEA tested at both 12 and 30 psi air backpressure. Figure 6 shows the resulting bi-plots when

principal component analysis was applied to this data. Bi-plots were used because they provide a more instructive visualization of the groups of samples that are similar to each other and variables that are the most or least important for a specific sample group. Variables and samples that are highly correlated will be in the same region on a bi-plot.[21]

Y-axis separates the plot into principal component 1 representing transport regime on the left and representing kinetic regime on the right. Principal component 2 separates the plot along the x-axis into the top half representing the better performing samples and bottom half worse performing samples at all potentials. The resulting four quadrants provide insight into correlations between the variables. Quadrant I indicates that higher Nafion content is important for kinetic regime, specifically the melamine samples with added Ketjen 600 and carbon nanotubes. Also both the urea and melamine samples without carbon show good performance in the kinetic regime when 35wt% Nafion was used. The correlation between the good performance in the transition regime (0.6V) and 35wt% Nafion can be since in Quadrants I and II. Quadrant II indicates that a higher Nafion content should be avoided for better transport regime. Here both the urea and melamine samples without carbon additives show good performance in the transport regime when 25wt% Nafion was used. Quadrant III points to the fact that all samples with added carbon and lowest wt% Nafion have worse performance than samples with added carbon and higher Nafion contents. Again this fits the hypothesis that only when higher amounts of Nafion are used, adding carbon is effective in increasing performance. Finally, quadrant IV indicates that, in general, all samples with 45wt% Nafion have the worst performance. The optimal ink configurations resulting in the balance between kinetic and transport regime are inks made based on both melamine and urea catalysts with 35% Nafion, carbon-free and with Ketjen black. As XPS results above have shown, KB200 had a smallest effect on carbon chemistry among the

three carbon additives used, while CNT and Vulcan XC72 introduced too much graphitic carbon changing the hydrophobic properties of the catalysts substantially and resulting in the worst performance.

Figure 6. Bi-plots provide a more instructive visualization of the groups of samples that are similar to each other and variables that are the most or least important for a specific sample group. Each quadrant represents the following: Quadrant I-higher Nafion content is important for kinetic regime. Quadrant II- higher Nafion content hinders transport regime. Quadrant III-all samples with added carbon and lowest wt% Nafion have the worst performance. Quadrant IV-all samples with 45wt% Nafion have the worst performance.

4 Conclusion

Ionomer and its integration with catalyst play a key role in MEA performance. However, the relationship between Nafion, non-PGM catalyst, carbon additives, and overall performance is complex with non-linear interconnections. We derive a few conclusions from experiments performed in this work: 1) higher amount of Nafion is important for the kinetic regime for all samples but it hinders transport properties; 2) it is clear from the results that for urea and melamine based catalysts adding carbon does not make sense for an optimum electrode. However in cases where high energy efficiency is required (high cell voltage) higher Nafion content becomes the best choice and, in consequence, carbon additive should be used. 3) The best performing samples were electrocatalysts with 35wt% Nafion and no carbon additives. It is important to remember, that the optimization of Nafion content and carbon additives performed herein are unique for samples with different morphologies.

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6 References

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Figure 1. Structures of nitrogen-rich organic precursors. a) Urea b) Melamine

Figure 2. Set-up of in-house bulk conductivity measurement system. a) Teflon casing with the two gold electrodes b) Teflon casing with gold electrodes in press connected to conductivity meter

Figure 3. Images of Fe-NCB catalyst prepared by Sacrificial Support Method (additional ball-milling with urea): a) SEM and b) TEM.

Catalyst	Conductivity at 167psi (S/cm)
Vulcan	16.6
KB600	6.7
CNT	17.5
UR-no carbon	7.6
UR-Vulcan	9.6
UR-KB600	8.2
UR-CNT	9.4
MM-no carbon	7.2
MM-Vulcan	6.8
MM-KB600	6.1
MM-CNT	7.6

Table 1. Bulk Electronic Conductivity Measurements.

Sample Identifier	C 1s %	O 1s %	N 1s %	Fe 2p %	C gr	C-C/C*	C-N	CxOy
MM	92.0	3.9	3.9	0.09	44.4	24.6	9.9	21.1
MM + Vulcan XC72	95.0	2.8	2.1	0.05	57.0	19.1	5.9	17.9
MM + KB200	92.5	4.3	3.2	0.06	47.4	22.8	7.5	22.3
MM + CNT	93.2	3.6	3.0	0.07	51.8	21.3	7.6	19.3
UR	92.7	3.9	3.3	0.08	42.0	27.5	9.7	20.7
UR + Vulcan XC72	94.2	3.5	2.3	0.05	50.7	21.1	7.8	20.4
UR + KB200	93.1	3.4	3.5	0.06	45.6	25.2	9.5	19.7
UR + CNT	93.3	3.5	3.1	0.07	46.9	25.9	9.5	17.7

Table 2. XPS elemental composition, at % and relative amounts of different types of carbon derived from high resolution C 1s spectra.

Figure 4. H₂/Air polarization curves obtained for Fe-NCB catalyst synthesized with both urea and melamine nitrogen precursors for all amounts of Nafion at 12 psi backpressure.

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