Electrochemical Evaluation of Non-precious Metal Catalysts for Fuel Cell Applications

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Abstract

Copper and Iron-based catalysts for the oxygen reduction reaction (ORR) in proton electrolyte membrane (PEM) and anion electrolyte membrane (AEM) fuel cells have not outperformed platinum catalysts, but they could be a more cost effective alternative. The objective of this investigation is to determine the synthesis parameters to achieve optimal catalytic activity for pyrolyzed Cu and Fe carbon-supported catalysts for the ORR at the cathode in low temperature fuel cells. We synthesized catalysts by mixing the metal salt, nitrogen source, and carbon black support using a mortar and pestle, followed by pyrolysis under nitrogen gas. The metal salts used were: acetates, sulfates, and nitrates. Three different nitrogen rich sources were also studied and we found that only one nitrogen source contributed significantly to the electrochemical activity. After pyrolysis, an improvement in the catalytic activity was observed, however depending on the metal salt combination and metal content, as well as on the electrolyte used during the experiment, the ideal heat treatment temperature for each catalyst combination was different. The electrochemical activity was measured using the rotating ring disk electrode (RRDE) experiment in 0.1 M H_2SO_4 and 0.1M KOH electrolytes to mimic the acidic and alkaline environments of PEM and AEM fuel cells. The best catalyst overall was the optimized 5 w.t% metal content $FeSO_4$ carbon-supported catalyst heat-treated at 900°C. Fuel cell performance was measured for this catalyst at the cathode in both PEM and AEM fuel cells. A typical AEM fuel cell performance for NPGM catalysts was achieved for the $FeSO_4$ catalyst making it a good candidate for AEMFC applications.

Keywords: Fuel Cells, Oxygen-Reduction Reaction, Non-Precious Metal Catalysts

1. Introduction

The development of highly active and durable non-precious metal catalysts (NPMCs) for the oxygen reduction reaction (ORR), could reduce one of the major cost factors associated with the platinum group metal (PGM) catalysts currently used at the cathode electrode for proton electrolyte membrane fuel cells (PEMFC) and anion electrolyte membrane fuel cells (AEMFCs).[1-12]

We selected Cu and Fe for this investigation because, in nature, enzymes containing these metals have shown good activity for the ORR under mild pH conditions. For instance, catalyst development based on laccase, which has active sites with at least four Cu atoms where the ORR takes place, has resulted in the synthesis of catalytic copper triazole based complexes.[2] In recent studies, carbon-supported iron-based catalysts demonstrated significant ORR activity after pyrolysis, first in argon, then in ammonia, in part because of the porosity increase leading to more active sites when the Fe is coordinated with four pyridinic nitrogen atoms.[3]

Although NPMCs have significantly improved over the past decade, mass transport issues caused by thick electrode layers are a continuing challenge, and increasing the catalytic site density can help compensate for the lower activity.[4] In a recent study, an onset potential of 0.868 V was reported by Cantillo et. al, on the ORR activity for a pyrolyzed Fe CHF-1catalyst (CHF is covalent heme framework) at 700°C.[5] In addition, the mass-transport contributions from

different catalyst loading (ranging from 1-3mg/cm^2) were explored, reporting that a 2mg/cm^2 catalyst loading results in a maximum power density of 0.46 W/cm^2 for a PEM single cell experiment.

Among the different synthesis techniques, the preparation of catalysts from pyrolysis of separate metal, nitrogen and carbon precursors have provided active materials for the ORR reaction.[1, 3-8,11,12] This approach offers a great variety of possibilities in terms of precursors and synthesis conditions (temperature, and elemental composition). In 2010, Li et. al, studied the electrocatalytic properties in alkaline and acidic media of a Co-Fe-N chelate, prepared by a combination of pyrolysis, and acid leaching.[12] An onset potential of 0.92V was reported for the catalyst in alkaline media.

Although the most active NPMC to date contain iron, catalysts prepared with higher Fe loadings don't necessarily result in higher activity.[6, 10] In 2010, Liu et. al, reported the onset potential for the optimized 1.2Fe-CN$_x$-Ar-1000 catalyst to be 0.88 V vs. NHE, with a limiting diffusion current of approximately 3.9 mA/cm^2, and a PEMFC performance as high as 0.6 A/cm^2 at 0.5V.[10] One challenge for NPMC containing Fe is the poor stability in acidic electrolyte. [6,7,12] Some studies suggest that this could be a result of the Fe$^+$ leaching out of the catalyst and degrading the proton conducting membrane used in PEMFCs.[6, 10]

The purpose of our research is to investigate the synthesis parameters affecting the electrochemical activity of NPM carbon-supported Cu and Fe based catalyst for the ORR taking place at the cathode of PEM and AEM fuel cells. Such parameters include using various: metal to nitrogen ratios, nitrogen rich sources, heat treatment temperatures, and metal precursors.

2.Experimental Methods

2.1 Catalyst Preparation

Catalysts were synthesized by mixing Cu and Fe salts with a carbon black support and nitrogen precursors using a mortar and pestle. The preliminary parameters investigated were; CuNO$_3$ and FeNO$_3$ salts with a 5 wt.% metal content, and a combination of three different nitrogen precursors. Various metal concentrations (wt.%) were explored, from 5 wt.% to 20 wt.%. Mixing the catalyst for approximately 40 minutes helps reduce the particle size and facilitates homogeneous distribution of each component. The catalysts underwent pyrolysis (600°C-1000°C) under nitrogen gas for 1 hour in order to bind the metal/nitrogen/carbon and form catalytic centers.

2.2 Electrochemical Activity Measurements

The rotating ring disk electrode (RRDE) experiment was used to measure the electrochemical activity and electron transfer mechanism in both acidic and alkaline environments. The RRDE experiments were performed using a multi-channel VSP3 potentiostat from Bio-Logic Science Instruments, a Pine instruments Modulated Speed Rotator (MSR) and RRDE electrode with a 0.2472cm^2 glassy carbon (GC) disk and Pt ring (AFE&RPGCPT from Pine Instruments) with a collection efficiency of 37%. The rotation speed of the working electrode was held constant at 1600 rpm. The scan rate for both the static and rotating voltammograms was 10mV/s. Using a saturated electrolyte with nitrogen for background correction (static), and with oxygen for the voltammogram obtained while rotating the working electrode.

Each catalyst was tested in 0.1 M H$_2$SO$_4$ and 0.1M KOH to simulate the acidic and alkaline environments of PEM and AEM fuel cells. A three electrode cell consisting of a Pt working electrode, a gold (Au) wire counter electrode, and a Hg/HgSO$_2$ and Hg/HgO reference electrode for the experiments carried out in acidic and alkaline electrolyte respectively. The potential of the reference electrode vs. RHE was measured after purging the electrolyte with hydrogen for 30 minutes and measuring the open circuit potential using a Pt working electrode. All potentials are reported vs. RHE.

Catalyst inks were prepared using a 30/70 wt.%, ionomer to catalyst ratio, using 5 wt.% Nafion® solution (sigma-Aldrich) along with methanol as a solvent. Inks were magnetically stirred for two days as well as sonicated for 10 minutes prior to testing. Each experiment required a catalyst loading of 600 μg/cm^2 on the GC electrode; this was achieved by depositing 5μL aliquots of the ink at a time on the electrode.

2.3 Fuel Cell Testing

PEM and AEM fuel cell performance was measured for the best catalyst using a single fuel cell test station. The catalyst was only tested as the cathode electrode of the cell, and to prepare the electrode, separate ink was made and spray-painted on the 5cm^2 gas diffusion layer. The anode electrodes were prepared using Pt.

The fuel cell experiments were performed using a Fuel Cell Technologies test stand and single cell hardware. Polarization curves were obtained using a VSP3 potentiostat from BioLogic along with a 10 A booster. The PEMFC experiments were performed under 80°C, with a backpressure at both electrodes of 29.4 psig, and all gases were at 100% relative humidity (RH). The hydrogen gas flow at the anode was 100 sccm, and the oxygen gas flow at the cathode was 200 sccm. For the AEMFC experiments, the operating temperature was 60°C, with no backpressure, and with100% RH for all gasses. With an anode flow of 100 sccm H_2 and the cathode flow of 100 sccm O_2. Catalyst loading on the cathode electrode was 2mg/cm^2.

3. Results and Discussion

3.1 Preliminary RRDE Results

For the preliminary testing of the Cu and Fe based catalysts a nitrate salt was used (5 wt.% metal content), three different nitrogen sources, and a carbon black support were combined and prepared as described in the methods section. The catalysts underwent pyrolysis for the temperatures selected (600°C-1000°C) and were made into inks and tested with the RRDE technique.

After all the preliminary experiments, the best performance for each Cu and Fe based catalyst in acidic and alkaline environments can be seen in Figures 1 and 3. Fe based catalysts show a higher catalytic activity than Cu based catalysts. In Figure 1, the onset potential of the $CuNO_3$ and $FeNO_3$ catalysts heat-treated at 800°C are 0.885V and 0.983 V respectively, this value was obtained when the current density reaches 50μA/cm^2, whereas the Pt onset potential in acid is closer to 1.2V. The limiting current density for the Cu catalyst was slightly higher than the Fe catalyst, and both Cu and Fe catalysts surpass the Pt limiting current density.
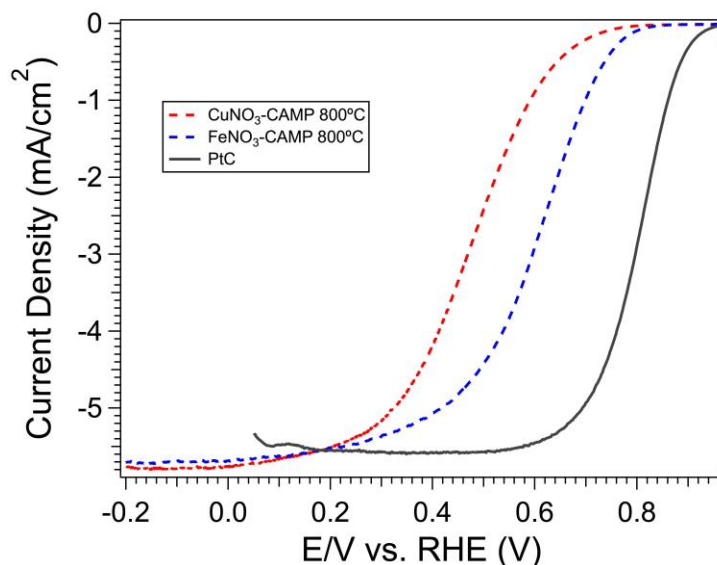

Figure 1. Preliminary RRDE results for $CuNO_3$ (red-dashed) and $FeNO_3$ (blue-dashed) catalysts heat-treated at 800°C, compared to Pt catalyst (gray). The faradaic current density as a function of the potential with reference to the reversible hydrogen electrode (RHE) in 0.1 M H_2SO_4 can be seen in the voltammogram. Scan rate: 10 mV/s, WE: GC disk, CE: Au coil; RE: $Hg/HgSO_2$, Rot. Speed: 1600rpm, Loading: 600 μg/cm^2

The RRDE technique was used to investigate the number of electrons transferred. The direct ORR pathway can be understood by the following reactions

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \ ... E^\circ = 0.410V \tag{1}$$
$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \ \ ... E^\circ = 1.229V \tag{2}$$
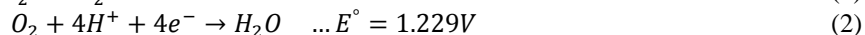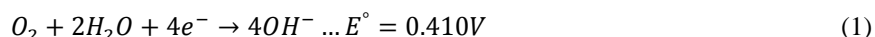
To evaluate the ORR activity of the catalyst as a function of applied potential, the electron transfer number can be calculated using the disk current (I_{disk}) and the ring current (I_{ring}) using the following relationship

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}} \tag{3}$$

Where N is the collection efficiency (37%) of the RRDE. Figure 2A shows a four-electron transfer mechanism was calculated for the Cu and Fe based catalysts, indicating the ORR took place. The Pt ring electrode was held constant at 1.2 V during the RRDE experiment. The number of electrons transferred for all of the Cu and Fe based catalysts tested in this study followed a similar trend. Various NPMC studies have reported values ranging from 3.75-3.99 mA/cm^2 for the number of electrons transferred, indicating a four-electron pathway is preferred.[1, 4,5,10,12]

As can be seen in Figure 2B, the preliminary RRDE results in 0.1 MKOH indicate that the FeNO$_3$ catalysts heat-treated at 900°C shows a slightly higher activity than CuNO$_3$ catalysts heat-treated at 800°C. A similar onset potential to Pt was achieved with the FeNO$_3$ catalyst heat treated at 900°C. However, the current density was not as good as the current density of Pt. The CuNO$_3$ catalyst has a comparable onset potential to both the FeNO$_3$ and Pt, but it also shows the lowest current density Previous NPMC studies, have reported limiting currents between 2-4.8 mA/cm.[2 5, 10,12] In the limiting current region, values between 4.6-5.6 mA/cm^2, were obtained for all the catalysts in this study, indicating comparable results with the literature.
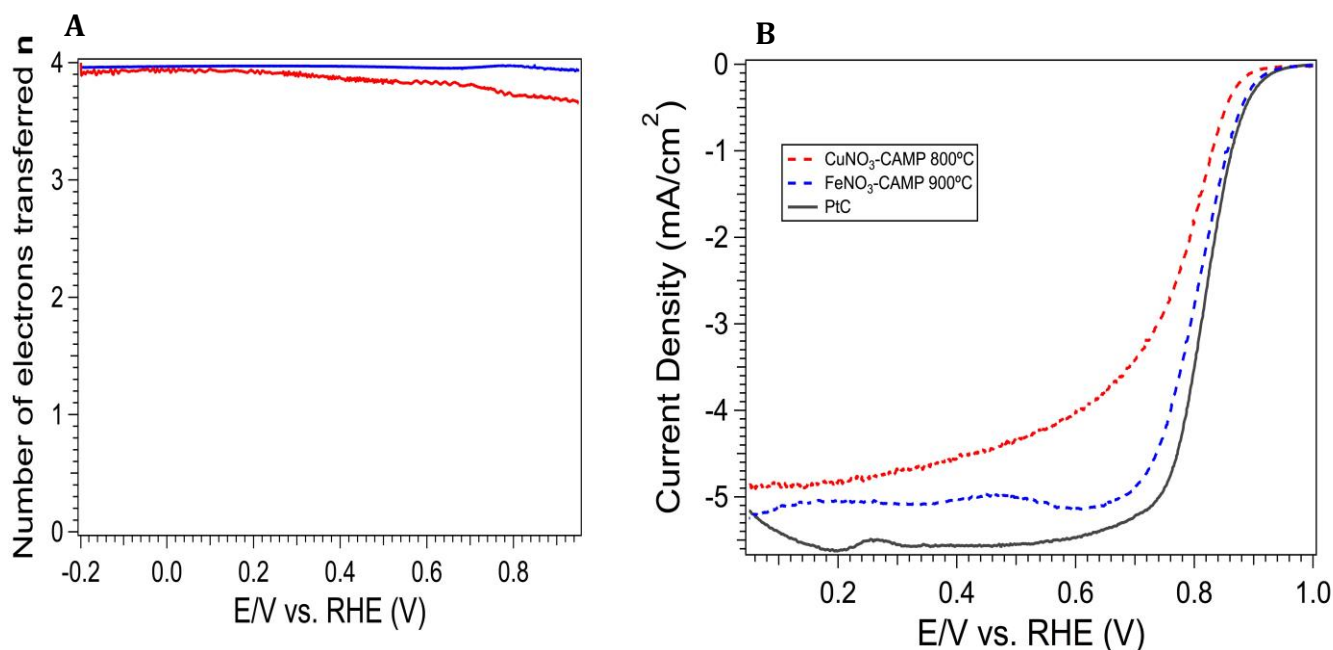

Figure 2. (A) A four-electron transfer mechanism was calculated for the FeNO$_3$ and CuNO$_3$ catalysts using the ring current. Indicating the ORR took place during the experiment. (B) Faradaic current density as a function of the potential with reference to the RHE in 0.1 M KOH can be seen for the CuNO$_3$ (red-dashed) catalyst heat-treated at 800°C and for the FeNO$_3$ (blue-dashed) catalysts heat-treated at 900°C compared to Pt.

Table 1. Synthesis parameter optimization for Cu and Fe based catalysts. Variation of metal salt, metal content, heat treatment temperature and nitrogen source used to make each catalyst impacted the electrochemical performance tested in the RRDE experiment. The optimized parameters are underlined for both Cu and Fe based catalysts.

Catalyst Synthesis Parameters	Cu-Based Catalyst	Fe-Based Catalyst
Metal Content (wt.%)	5, 10, <u>15</u>, 20	<u>5</u>, 7.5, 10,15
Metal Salt	<u>CuNO$_3$</u>, CuSO$_4$, CuOAc	<u>FeSO$_4$</u>, FeNO$_3$, FeOAc
Heat Treatment Temperature	800°C, <u>900°C</u>, 1000°C	800°C, <u>900°C</u>, 1000°C
Nitrogen Source	1, 2, 3, 4*(all combined)	1, 2, 3, 4*(all combined)

After the catalyst synthesis parameter optimization process, which entailed over 300 experiments, we determined that the ideal synthesis parameters for the Cu based catalyst consisted of using the nitrate salt, only nitrogen source 1, a 15 wt.% metal content, and heat treatment temperature of 800°C. Similarly, for the Fe based catalysts, using the iron sulfate salt, nitrogen source 1, a 5 wt.% metal content and a heat treatment temperature of 900°C. The highest activity for the Fe based catalyst was obtained with the lowest Fe content; this result is in agreement with previous work.[6, 10,12]

3.2 RRDE Results for Optimized Parameters

The RRDE results for the optimized synthesis parameters demonstrate the improved catalytic performance of Cu and Fe based catalyst in both acid and alkaline environment. Figure 4 shows the voltammogram for preliminary Cu and Fe catalysts compared to Pt, and to the optimized Cu (solid-red) and Fe (solid-blue) catalysts in 0.1 M H$_2$SO$_4$. The optimized 15 wt.% CuNO$_3$/800°C catalyst, and the optimized 5wt.% FeSO$_4$/900°C catalyst show a 2.6% and 2.5% increased catalytic activity when compared to the preliminary catalysts in an acidic environment.
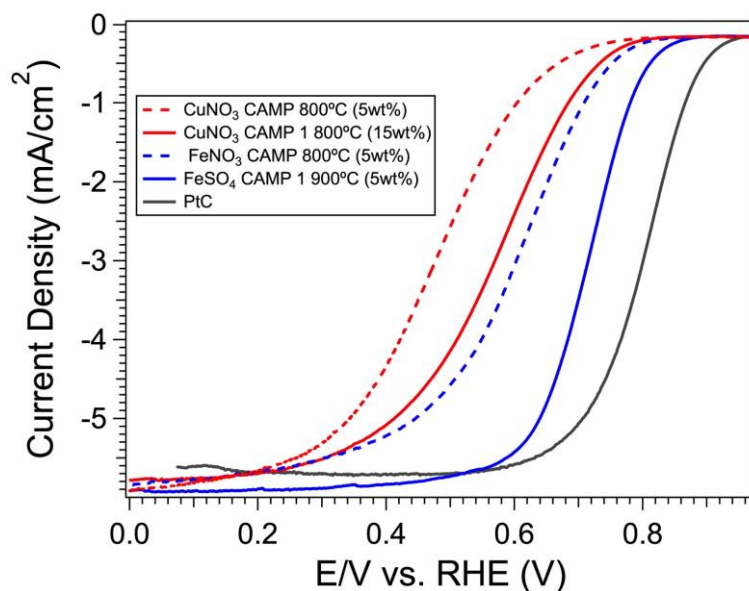

Figure 4. The faradaic current density as a function of the potential with reference to the RHE in 0.1 M H$_2$SO$_4$, for CuNO$_3$ (red-dashed) and FeNO$_3$ (blue-dashed) catalysts heat-treated at 800°C, compared to Pt catalyst (gray), and the optimized catalyst CuNO$_3$ (re-solid) and FeSO$_4$ (blue-solid). Scan rate: 10 mV/s, WE: GC disk, CE: Au coil; RE: Hg/HgSO$_2$, Rot. Speed: 1600rpm, Loading: 600 μg/cm^2

As can be seen in Figure 5, the optimized 5wt.% FeSO$_4$/900°C catalyst surpasses the performance of the Pt catalyst with an improved onset potential and limiting current in alkaline environment. It also outperforms the catalyst ORR onset potential reported by Li et. al, of 0.92V in alkaline media.[12] When compared to the preliminary RRDE results

(red and blue-dashed), it is clear that both Cu and Fe optimized catalysts (solid curves) showed an overall improvement in terms of both onset potential and increased current densities. The optimized 15 wt.% $CuNO_3$/800°C catalyst had an overall improved catalytic activity when compared to the 5 wt.% $CuNO_3$/800°C preliminary catalyst with an onset potential of 0.882V, which is a good onset potential for NPMC.

In the case of the Cu catalyst, by increasing the metal content from 5 wt.% to 15 wt.% a significant improvement in the catalytic activity was observed. However, for the Fe based catalysts increasing the metal content actually had a detrimental effect. The Fe-based catalyst improved its onset potential from 0.940V to 0.983V, simply by using the iron-sulfate salt instead of the iron-nitrate salt, and it obtained the highest current density out of all the catalysts in this study. The optimized 5wt.% $FeSO_4$/900°C catalyst is the best catalyst overall in both 0.1M H_2SO_4 and 0.1M KOH electrolyte.
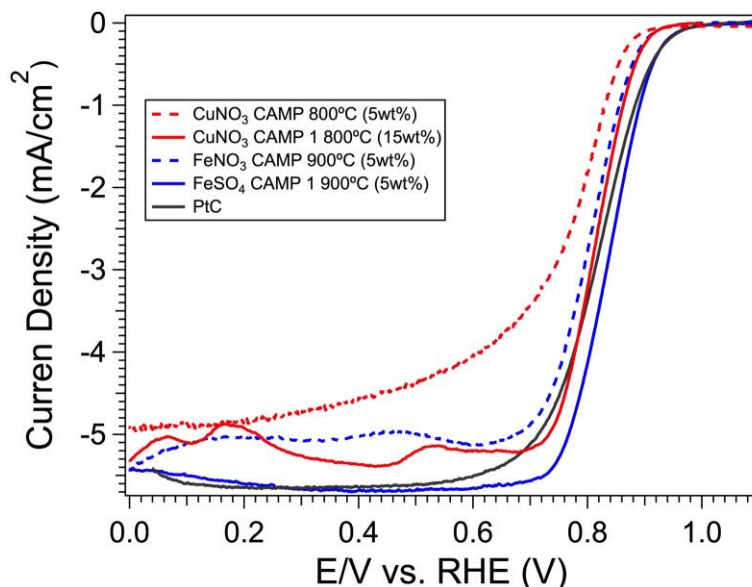

Figure 5. The faradaic current density as a function of the potential with reference to the RHE in 0.1 M KOH for $CuNO_3$ (red-dashed) and $FeNO_3$ (blue-dashed) catalysts heat-treated at 800°C, compared to Pt catalyst (gray), and the optimized catalyst $CuNO_3$ (re-solid) and $FeSO_4$ (blue-solid). Scan rate: 10 mV/s, WE: GC disk, CE: Au coil; RE: Hg/HgO, Rot. Speed: 1600rpm, Loading: 600 μg/cm^2.

3.3 Fuel Cell Testing

The optimized 5wt.% $FeSO_4$/900°C catalyst was tested as the cathode electrode in both PEM and AEM single cell test stations as outlined in section 2.3. Catalyst loading on the cathode electrode was 2mg/cm^2, based on previous work.[5, 10]

Figure 6 shows the polarization curve for the (A) PEM and (B) AEM fuel cell. As was expected from the RRDE results, the performance was not as good as Pt in acid, however a typical NPMC performance was achieved. The RRDE in 0.1 M KOH,in Fig 6 (A), the overall PEMFC kinetic overpotential region begins at around 0.8 V, while the cathode AEMFC kinetic overpotential starts at around 1.0 V in Fig 6 (B).
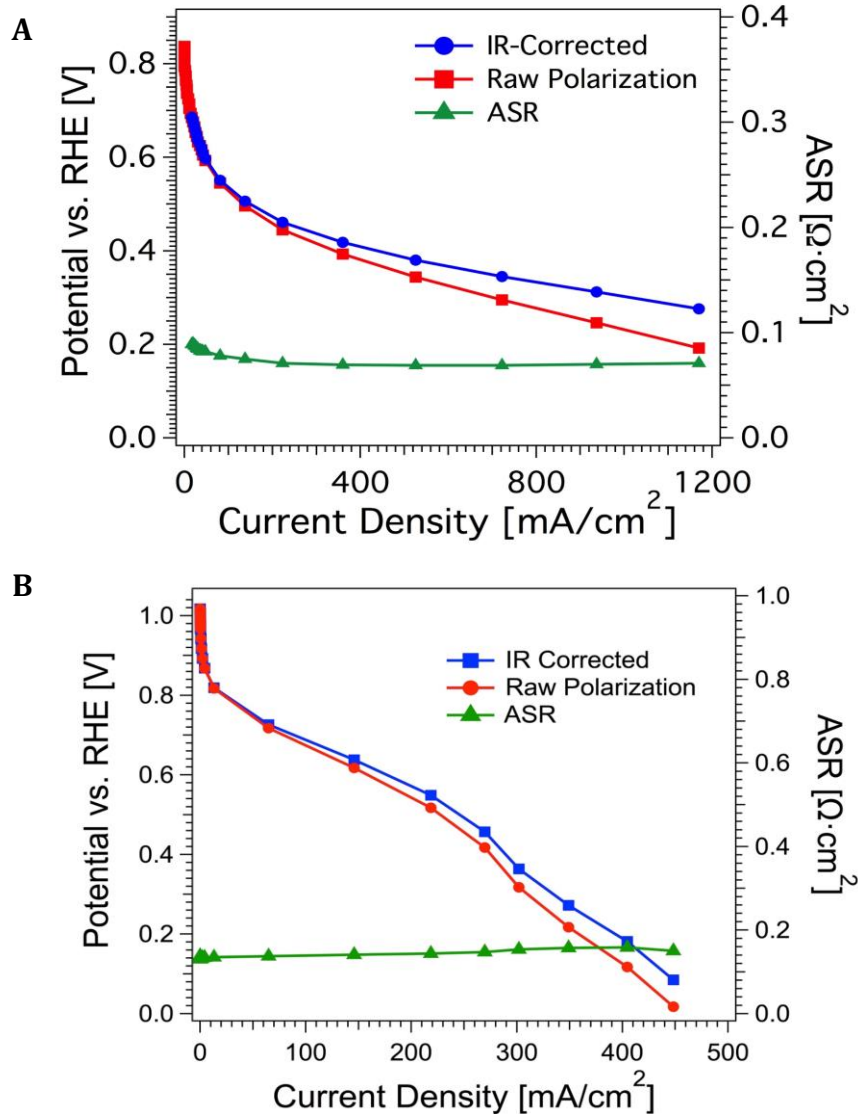
Figure 6. The internal resistance (IR) corrected polarization curve (blue) and the resistance curves (green) for the optimized 5wt.% FeSO$_4$/900°C catalyst as the cathode in a single cell (A) PEM and (B) AEM fuel cell can be seen.

4. Conclusion

Both Cu and Fe catalysts improved compared to the initial preliminary experiments. With a 2.5% increase for the optimized Fe based catalyst, and a 2.6% increase for Cu based catalyst. CuNO$_3$ 15wt% has the highest activity among Cu catalysts, while FeSO$_4$ 900°C (5w%) is the best catalyst overall. Various parameters affecting the activity of NPMC for the ORR taking place at the cathode were explored with Cu and Fe based catalysts. Such as: metal salt, metal content, nitrogen source, and heat treatment temperature. CuNO$_3$ (15wt%), N.S.1, HT at 800°C is the best Cu based catalyst in acid, while FeSO$_4$ (5w%), N.S.1, HT at 900°C is the best catalyst overall. FeSO$_4$ was tested in both AEM and PEM fuel cells, and as was expected rom the RRDE results the performance in acid was not as good. However a typical NPMC performance for AEM fuel cells was achieved, indicating that this may be a promising

catalyst for AEMFC applications. The catalytic activity of some of our catalysts is similar to Pt in alkaline environment.

In the future we will be working on removing excess metal with and acid treatment to increase catalytic centers, therefore improving the performance. In this study we approached Cu and Fe catalyst synthesis in a systematic method to develop and understand the preparation parameters that affect the electrochemical activity and performance of pyrolyzed Cu/Fe-N-C based catalysts.

5. Acknowledgements

6. References

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