

Effects of Ink Formulation on the Structure and Performance of PGM-Free Catalyst Layer in PEMFCs

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Abstract: We proposed a novel method of fabricating PGM-Free catalyst MEAs so that the intrinsic catalyst activity from RDE can be translated into MEA performance. The method is based on the catalyst coated membrane (CCM) method using optimized ionomer to carbon (I/C) ratio and solvent mixture of catalyst ink. Using this method, the PGM-free catalyst MEA achieved the current density 44.9 mA cm⁻² at 0.9 V_{iR-free} in H₂/O₂ and 150 mA cm⁻² at 0.8 V in H₂/air, which exceeds the performance targets of US Department of Energy (DOE) for PGM-Free catalyst MEA. The property (solvent composition, dispersion of catalyst and ionomer in an ink), structure (pore structure) and the MEA performance have been characterized using, mercury intrusion porosimetry (MIP) and MEA testing. A property-structure-performance relationship has been established.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) is a promising energy conversion technology, which provides the clean and efficient power sources for vehicles propulsion. One of the major factors affecting the performance of the PEMFCs is the slow oxygen reduction reaction, which needs to use the precious group metal (PGM) catalysts. However, PGM is very expensive and the PGM reserve is very limited in the earth which makes PGM unsustainable for large scale application. To solve this critical issue, the PGM-free catalyst is the solution. There are several types of PGM-Free catalysts emerged from numerous research groups.(1, 2) Among these catalysts, Fe-N-C based catalyst: iron atoms coordinated with nitrogen and anchored on porous carbon, shows very promising ORR performance using rotating disk electrode (RDE) while it has the potential to compete with PGM catalyst. Recently, the great effort has been devoted to the development of PGM-Free catalyst with great RDE performance to close the performance gap

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between PGM and PGM-Free catalysts. But to the best of our knowledge, differing from the PGM catalysts, the progress on the fabrication of membrane electrode assembly (MEA) for PGM-free catalyst has made little progress. The fabrication of PGM-free MEA is very important for PGM-free catalyst development: the optimal MEA fabrication method would sacrifice much less performance in MEA from its theoretical ORR activity (i.e., RDE performance). Previously, the majority of reported PGM-Free MEA performance was obtained from the MEA fabricated using the gas diffusion electrodes (GDE) method, on which the PGM-free catalyst ink was painted over the gas diffusion layer. However, the electrode made using this method is too thick to efficiently transport the O₂ gas molecules. Besides, there is a serious reproducibility issue with the GDE method. MEA performance, made by GDE method, highly depends on the person who fabricated it, because catalyst ink was manually coated on gas diffusion layer (GDL) using a blade. For a reliable fabrication method, the quality of the fabricated MEAs should be highly consistent, namely, with good reproducibility so that the performance difference between MEAs made with the same conditions using the same method is negligible. In this regard, a new fabrication method has the paramount significance in making high performance PGM-free MEAs with great reproducibility.

The catalyst coated membrane (CCM) technique is a commonly used in making PGM catalyst MEAs because the catalyst and ionomer particles of a catalyst ink can be directly sprayed over the membrane surface with good dispersion and forming an ideal interface between the catalyst layer and membrane. The porosimetry and morphology of the catalyst layers of the MEA can be easily controlled using the spraying method. The ionomer/catalyst interface formed in the catalyst ink can also be preserved in the solid catalyst layer using the spraying method. In addition, CCMs made by using a commercial spray machine have very high reproducibility, which makes the optimization of MEA fabrication possible. Based on this high reproducibility, using a machine spraying technique, the MEA fabrication method was optimized on catalyst ink composition and ionomer/catalyst ratio (I/C ratio). After fabrication method optimized, the PGM-free catalyst MEAs shown the very excited results, met or exceed the DOE 2025 PGM-Free catalyst targets.

Experimental

For the anode electrode, 20 wt. % Pt/XC-72 catalyst and ionomer ink were prepared by mixing the catalyst powder and ionomer dispersion (25 wt. %, Aquivion D-79-25BS). The ionomer to carbon ratio was controlled to be 0.45 as well as the mixture of 1-propanol and deionized-water (DI-water). The prepared ink was firstly sonicated for 30 minutes in a water bath with a temperature under 30°C. The prepared ink was then sprayed onto a Nafion 212 membrane (5 cm²) by Exacta Coat spray machine (Sono-Tek, NY), and the Pt loading at the anode was controlled as 0.2 mg_{Pt} cm⁻². For the cathode, the prepared ink was sprayed on the opposite side of the anode, and the loading was controlled around 4.0 mg_{catalyst} cm⁻². Two pieces of SGL-22BB served as the gas diffusion layer sandwiched an MEA. MEAs were measured using a fuel cell test station (Fuel Cell technology, Inc., Albuquerque, NM, USA). First, the cell was heated to 80 °C without flow, then 200 sccm of N₂ in the anode and cathode for 2 hours to hydrate the membrane and ionomer. Air/oxygen flowing at 500 mL sccm and H₂ (purity 99.999%) flowing at 300 sccm was supplied to the cathode and anode, respectively. The pressures during the fuel cell tests are 150 kPa_{abs} on both sides for reactant gases. The Dew point of anodic flow and cathodic flow is 80, and 80 °C cell temperature was maintained during the recording of VIR polarization curves. Flow rates of air 500 sccm and H₂ 300 sccm were controlled as 300 sccm and 500 sccm (H₂/O₂(air)) for anode and cathode, respectively. The MEAs were tested using scan current method: 0 to 1.0 A, 0.1 A per step; after 1.0 A. 1.0 A per step; 30 sec holding time for each step.

Results and discussion

Fabrication method comparison

First, the performance of MEAs made from GDE method and CCM method were compared. The MEA made by spraying method shows similar performance with that of GDE (Fig.1) . Under H₂/O₂ condition, above 0.65V, the polarization curve of CCM MEA overlaps with that of GDE MEA, and the current density at 0.9 V _{iR-Free} is 31 mA · cm⁻² for GDE and 35 mA · cm⁻² or CCM MEA, respectively, which is slightly higher than that of GDE MEA. However, for air performance, CCM MEA and GDE MEA perform almost the same above 0.60 V, but at high current density

region, beyond $750 \text{ mA} \cdot \text{cm}^{-2}$, CCM MEA performs much better than GDE MEA. From these results, it is clear that spraying method can fabricate a better quality MEAs. The performance of this kind of MEA is better than most reported PGM-Free MEAs tested under similar condition.

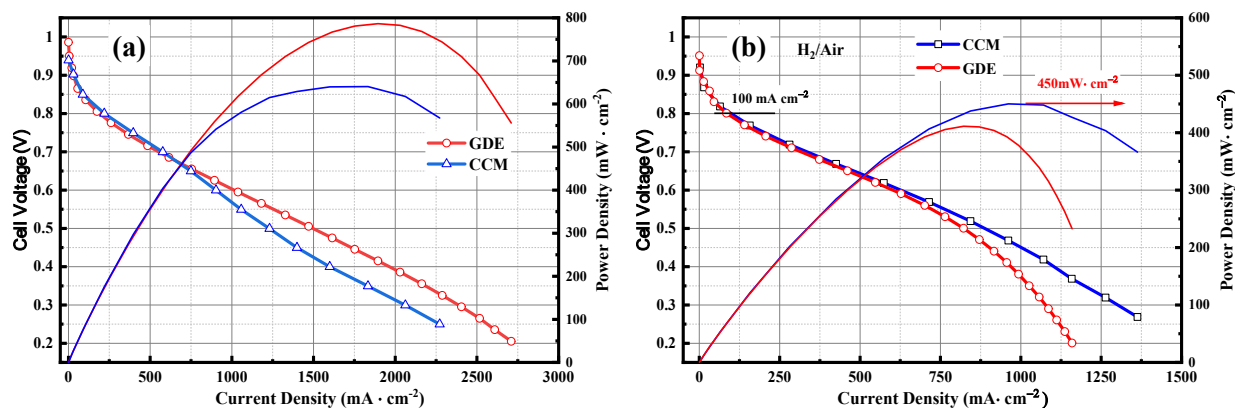


Figure 1. Polarization curves of MEAs made with Fe-N-C- catalysts **hot pressed** MEA versus **not hot pressed** MEA, $\text{H}_2\text{-O}_2$, reactant flow rate: 300/500 sccm H_2/O_2 , (a) $\text{H}_2\text{-Air}$, reactant flow rate: 500/1000 sccm H_2/Air . (b) MEA geometric active area: 5.0 cm^2 ; catalyst loading: $0.1 \text{ mg Pt}/\text{cm}^2$; $4 \text{ mg}/\text{cm}^2$ (Anode: cathode=20% Pt/C (E-TEK): Fe-N-C- catalysts); membrane: NF212(H^+); temperature: $80/80/80 \text{ }^\circ\text{C}$ (Anode/Cell/Cathode); RH: 100%, backpressure: $1.5 \text{ atm}_{\text{abs}}$; ionomer/carbon ratio: 0.8.

Ink formulation

Three IPA/ H_2O ratio were chosen, 1:1, 4:1 and 1:4 for the ink formulation for high water and low water and equal water content of three sets of conditions. MEAs made with three ratios were designated as 1:1-MEA, 4:1-MEA and 1:4-MEA. For pure oxygen performance (i.e., $\text{H}_2\text{-O}_2$), 1:1-MEA and 1:4-MEA have the exact same performance until 0.55 V and slightly better performance for 1:1-MEA below 0.55 V while 4:1-MEA has much less performance than those two. For air performance, the order of performance is 1:1-MEA > 4:1-MEA > 1:4-MEA (Figure 2b). The mercury porosimetry data of these three MEAs explain well about the performance of these MEAs (Figure 2c). For all MEAs, the mesopore specific pore volume (mL/g) (table I) is in the order of 1:1-MEA (0.391) > 4:1-MEA (0.199) > 1:4-MEA (0.147), which perfectly demonstrate that the meso-pore is dominant for MEA performance in the high current density region. The micro-pore specific pore volume does not match the MEA performance trend, suggesting that the micro-pore has much less effect on the MEA performance. This also indicates that the mass transport of air

mainly occurs within the meso-pore, not in micro-pores. Specifically, the optimization of ink formulation leads to a significant performance enhancement, for air, 1:1-MEA reaches $65.9 \text{ mA} \cdot \text{cm}^{-2}$ at 0.8 V with the peak power density of $400 \text{ mW} \cdot \text{cm}^{-2}$. For the current density at $0.9 \text{ V}_{\text{IR-Free}}$, all three MEAs reach $32 \text{ mA} \cdot \text{cm}^{-2}$ (close to DOE 2025 target, $44 \text{ mA} \cdot \text{cm}^{-2}$). In addition to the polarization curves, high frequency impedance was measured for these three MEAs (Figure 2d). Interestingly, 1:1-MEA has the smallest semi-circles, indicating the lowest cathodic resistance (table II) which matches the pore structure as well as MEA performance. The mercury porosimetry and AC impedance data all suggest that the ink formulation indeed affects the structure of the catalyst layer, consequently, the performance. Specifically, in table III, the best performance was from the MEA that made by water-IPA (1-1) solvent. Here, we have high frequency resistance data and polarization data as well as mesopore percentage data all consistent to each other, demonstrated that our optimization work is solid and effective.

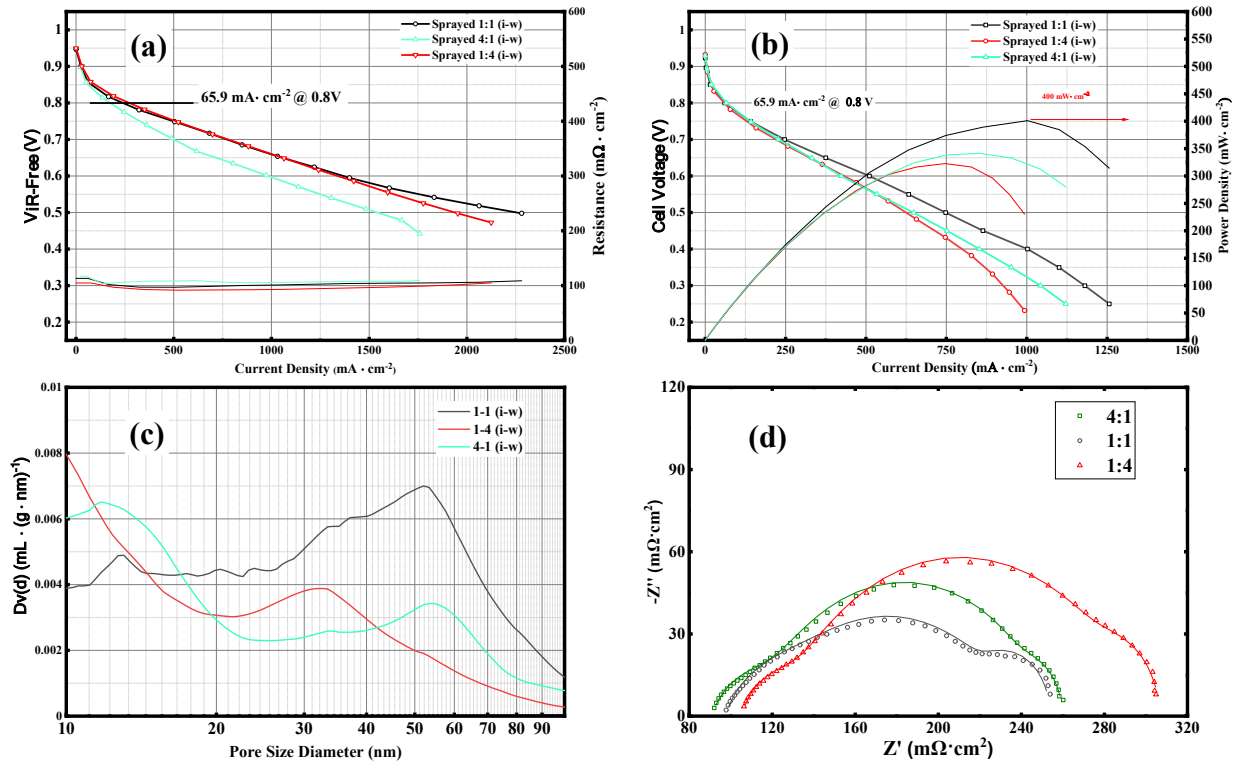


Figure 2. Polarization curves of MEAs made with Fe-N-C- catalysts using different IPA/H₂O, H₂/O₂, with IPA/ water ratio =1:1, 4:1, and 1:4, reactant flow rate:300/500 sccm H₂/O₂, (a) H₂/Air, reactant flow rate:500/100 sccm H₂/Air; (b) Mercury porosimetry results; (c) high frequency impedance (HFR) measurement results; (d) impedance measured at constant current, 1.0 A/cm², from 10000HZ to 10 HZ, after MEA polarization measurement. MEA geometric active area: 5.0 cm²; catalyst loading: 0.1 mg Pt/cm²: 4 mg/cm² (Anode: cathode=20% Pt/C (E-TEK): Fe-N-C-catalysts); membrane: NF212 (H⁺); temperature: 80/80/80 °C (Anode/Cell/Cathode); RH:100%, backpressure: 1.5 atm_{abs}; ionomer/carbon ratio: 0.8.

TABLE I. Summary of the MIP test results for catalyst layer.

	i-Pa-water (1-1)	i-Pa-water (1-4)	i-Pa-water (4-1)
Pore volume 0-20nm (mL/g)	0.104	0.128	0.107
Pore volume 20-200nm (mL/g)	0.391	0.147	0.199
Mesopore percentage (%)	79.1	53.3	65.0

TABLE II. Summary of the HFR test results for catalyst layer.

water/i-Pa	R_Ω	R_{anode}	R_{cathode}	R_{mt}
4:1	91.0	30.4	127.3	11.7
1:1	97.3	37.6	90.9	28.6
1:4	105.5	24.5	159.7	18.1

After ink formulation, we focused on the I/C ratio of the catalyst layer of MEA. Excessively high I/C ratio could cause a series mass transfer issue while too low I/C ratio could undermine the utilization of catalyst because the ionomer coverage over catalyst surface could be insufficient, particular, when I/C ratio drop to a certain level. In this case, the most optimized I/C ratio should be applied on MEA to utilize active sites as much as possible while keeping enough proton conductivity and maintaining a good mass transfer rate. To find the best I/C ratio, 4 MEAs made by Fe-C-N PGM-Free catalyst in different I/C ratio, 0.8, 0.7, 0.6 and 0.5 using 1:1 (IPA: water) as solvents for the catalyst ink were tested. The MEAs behave similar in low current density (LCD) region while quite difference appears when current density is beyond 1000 mA·cm⁻², in the high current density region (HCD). In this region, the MEA performance increased with decreased I/C

ratio (Fig.3a) and reached maximum at I/C=0.6, further drop of I/C ratio to 0.5 did not result in any improvement. The lower I/C ratio may benefit the mass transport on both O₂ diffusion through the ionomer film and pore structure (i.e., more pore volume) while it may lead to lower catalyst utilization, lower mass activity due to less coverage of ionomer over the catalyst particle (table III). Further decrease of I/C ratio did not improve HCD MEA performance too much (Fig. 3a) which may be limited by the proton conduction (further improve O₂ diffusion through ionomer film but may suffer the reduction on proton conduction due to less ionomer film). The Tafel analysis (Figure 3b and table III) shows that too much ionomer causes lower Tafel slope, the lowest Tafel slope is 41.6 mV/dec for the highest I/C ratio, 0.8, which may be caused by too thick ionomer film, increasing the O₂ diffusion barrier at LCD region, causing the mass transport at LCD region. The lower Tafel slopes of PGM-Free catalyst MEA, 40s mV/dec, indicates that their serious mass transport issue for PGM-Free catalyst MEAs while PGM catalyst MEA usually have Tafel slope around 68 or 72 mV/dec.

TABLE III. Summary of Figure.2.

I/C ratio	Current density @ 0.9 V _{iR-Free} in O ₂ (mA·cm ⁻²)	Current density @ 0.8 V in air(mA·cm ⁻²)	Peak power Density in air (mW·cm ⁻²)	Tafel slope (V/dec)
0.5	35	120	548	-0.05035
0.6	44.9	116	525	-0.04623
0.7	37	103	490	-0.04874
0.8	44.6	84	480	-0.04166

For the air performance, the MEA performance increased with the decreased I/C ratio, in both LCD and HCD regions, consequently, peak power density (Figure 4 and Table III). This is easy to understand because the mass transport of oxygen in nitrogen blanket is the major issue for PGM-Free catalyst MEAs, the lower I/C ratio led to the catalyst layer with thinner ionomer film, which facilitates the O₂ diffusion through the ionomer film, leading to better performance. It is worthwhile to point out that 120 mA/cm² at 0.80 V has been reached which is close to the DOE target of 150 mA/cm². It seems that there is still room to increase the current density at 0.80 V and we may try to further optimize the I/C ratio. Additionally, peak power density of 0.6 and 0.5 I-C ratio MEA exceed 500 mW · cm⁻².

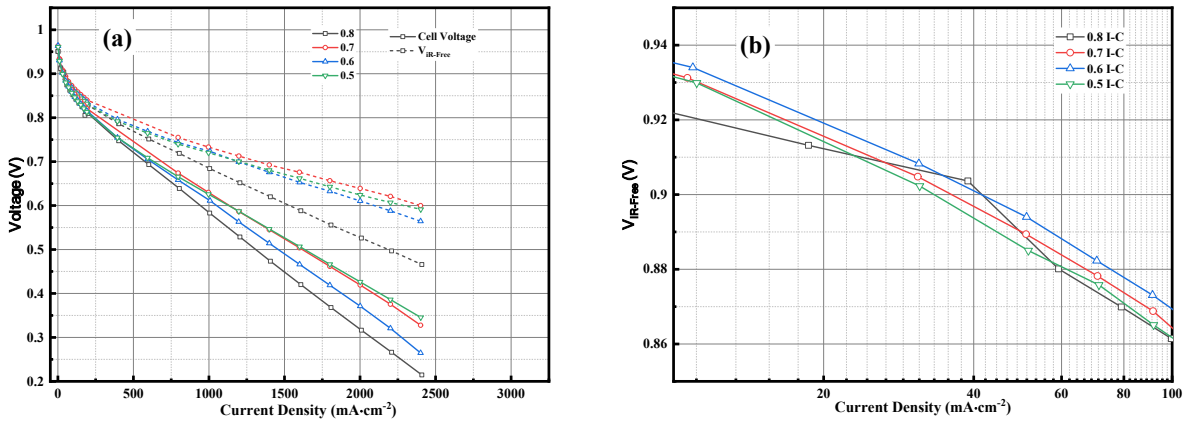


Figure 3. Polarization curves of MEAs made with different I/C ratio using Fe-N-C- catalysts, H₂-O₂, reactant flow rate: 300/500 sccm H₂/O₂; (a) Tafel Plot of (b) from 0.90 V-0.94 V VIR curve in (a). MEA geometric active area: 5.0 cm²; catalyst loading: Cathode: PGM-Free 4 mg/cm², and anode: 0.1 mg Pt/cm² (Anode : cathode = 20% Pt/C (E-TEK): Fe-N-C-catalysts); membrane: NF212(H⁺); temperature: 80/80/80 °C (Anode/Cell/Cathode); RH:100%, backpressure: 1.5 atm_{abs}; ionomer/carbon ratio: 0.8, 0.7, 0.6, 0.5.

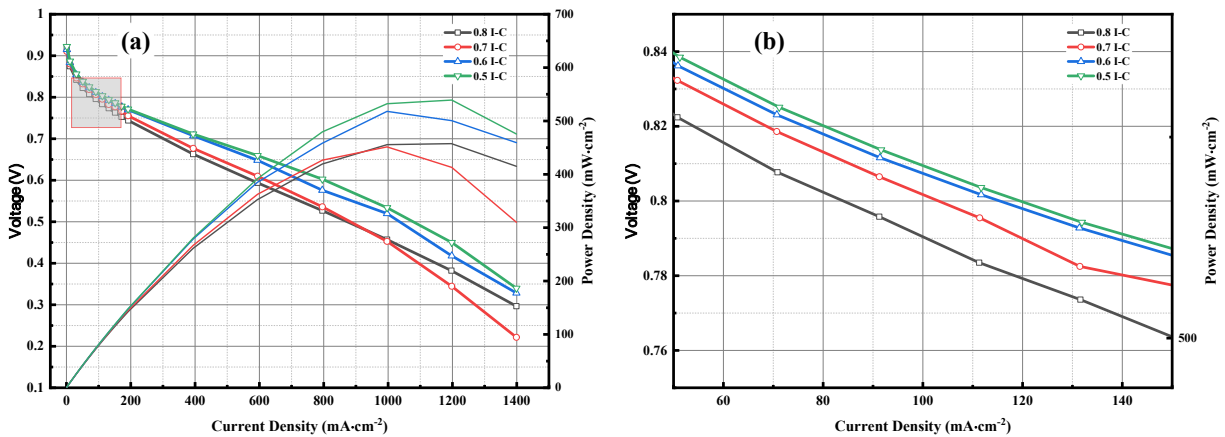


Figure 4. Polarization curves of MEAs made with Fe-N-C- catalysts using different I/C ratio, reactant flow rate: 300/500 sccm H₂/Air, (a); zoom in of polarization curves in (a) for 0.8V(b). MEA geometric active area: 5.0 cm²; catalyst loading: 0.1 mg Pt/cm²:4 mg/cm² (Anode: cathode=20% Pt/C (E-TEK): Fe-N-C- catalysts); membrane: NF212(H⁺); temperature:

80/80/80 °C (Anode/Cell/Cathode); RH:100%, backpressure: 1.5 atm_{abs}; Ionomer/carbon ratio: 0.8, 0.7, 0.6, 0.5.

Conclusion

The optimized MEA fabrication method based on spraying is successfully developed. The ink formulation reveals the property-structure-performance relationship and the optimization of I/C ratio leads to the much improved MEA performance. The mass activity of MEAs reaches 44.9 mA/cm² at 0.9 V_{IR-Free} (H₂/O₂) exceeds the 2025 DOE target.

References

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