ABSTRACT
Manufacture of fuel cell electrodes by the thin-film method was originally proposed by Wilson et al. [1, 2] for proton-exchange membrane fuel cells (PEMFCs). This technology was subsequently utilized for the manufacture of direct methanol fuel cell (DMFC) electrodes by Ren et al. [3]. Key processing steps in the thin-film process are catalyst ink formulation and its application. The catalyst ink is typically composed of supported or unsupported catalysts, binder (ionomer), solvents and additives. Rheological properties of the ink, amount of binder, and choice of solvents are tuned to match the particular ink application process used to fabricate the electrode, as each coating process has its own unique requirements. Besides affecting the coating process, the choice and ratios of these components can significantly affect the electrochemical performance of the electrode.

In this study, catalyst inks are designed and investigated for the spraying process, for utilization in the continuous fabrication of DMFC electrodes. For this purpose, the effect of the binder (ionomer) content on the performance of the electrodes is studied in detail. Decal-transfer electrodes are fabricated on a custom-built automated spraying apparatus with individually specified anode and cathode binder contents, and assembled to form a catalyst coated membrane (CCM) type membrane electrode assembly (MEA). These electrodes are rigorously tested to specifically identify their electrochemical performance, catalyst utilization and electrode morphology.

INTRODUCTION
The membrane-electrode assembly (MEA) is a key component of a DMFC. Its components, design and fabrication contribute to the overall cost of a fuel cell and its performance. The essential components of an MEA are two porous electrodes, which provide catalyst sites where electrochemical reactions occur, and a proton conducting ionomer membrane, which provides for an ionic pathway between the anode and the cathode. Additionally each electrode is flanked by diffusion media, which assist in the mass transport process for effective supply of reactants to the porous electrodes and the removal of reaction products, as shown in Figure 1.

BACKGROUND
The electrodes are typically porous structures of nanometer-sized catalyst particles dispersed in a suitable binder medium. Catalysts can be supported on carbon media to promote dispersion and thereby lower catalyst loading. It is important to allow adequate pathways for diffusion of the reactant media to the catalyst site, removal of reaction products, as well as good electrical and protonic conductivity. The electrons generated during the reaction have to be transported to the external circuit, whereas the protons have to cross the electrolyte to complete the reaction at the counter electrode [4]. Electrical conductivity in an electrode is either provided by the carbon support, in case of supported catalyst, or the catalyst particles themselves in case of unsupported ones. Proton conducting
pathways are created by the addition of ionomer to the electrodes. The interfaces between the electrode, the membrane, the diffusion layer and the three-phase boundary between the reactant, the catalyst and the ionomer dictate the performance of the fuel cell.

Motivation

In the thin film electrode fabrication process, nanometer sized catalyst particles (unsupported or supported) are mixed with a suitable amount of ionomer in solution form, along with other solvents to form an ‘ink,’ which can be deposited onto the substrate of choice, and subsequently dried to form the electrode. The ink composition and the method of ink application have a significant impact on the structure of the electrode, and in turn its performance. Several ink application processes have been considered: Tape casting [12, 13], Screen Printing [14, 15], Spraying [16, 17], etc. The ionomer (typically Nafion) added to the catalyst ink acts as a binder, as per the thin film electrode fabrication method and also provides proton conducting paths.

A few studies have explored the effect of ionomer content on DMFC electrode performance. Ren[18] prepared and tested thin film MEAs made by the decal transfer method using unsupported catalyst, and 15 %wt. Nafion in the anode and 7 %wt. in the cathode. Thomas [19] studied the effect of ionomer content in the catalyst layers of a DMFC, and found that in the anode, made by unsupported Pt:Ru (1:1) catalyst, the ionomer content can be reduced or even eliminated, whereas on the cathode, unsupported Pt, an ionomer content of 10.5 %wt. is suggested to provide an adequate three-phase boundary. Reshetenko et al. [16] uses a Nafion-to-catalyst ratio of 0.12 for the anode (unsupported Pt:Ru (1:1)) and 0.26 for the cathode (unsupported Pt) of a DMFC fuel cell. For comparison, the Nafion content in electrodes formed by supported catalysts is typically much higher. In a recent study, Sister et al.[20] found that in the anodic catalytic layer of a DMFC fabricated using 40 %wt. Pt:Ru supported catalyst, the optimal content of the ionomer is around 25%.

Considering the wide range of ionomer (Nafion) content suggested in literature for use in preparation of DMFC electrodes using unsupported catalysts, a parametric investigation study has been undertaken, the results of which are presented in the following paragraphs.

EXPERIMENT

DMFC MEA fabrication by the decal transfer method consists of a four steps: membrane preparation, electrode fabrication, electrode transfer, and finally the attachment of diffusion media on the 3 layer MEA produced, to form a 5 layer MEA.

Nafion-115 membranes were prepared by the following procedure. First, the membrane was cleaned to remove any unwanted substances. The cleaning process involved boiling the membrane in 3 %wt. H₂O₂ hydrogen for 1h and then boiling it in deionized water for 1h. The membranes were boiled in 1M H₂SO₄ for 1h and then boiled in deionized water for 1 h, as per the procedure defined by Ren [21]. Catalyst ink for the DMFC anode were prepared using unsupported Pt:Ru (1:1) HiSPEC™ 6000, platinum procured from Alfa Aesar, whereas Pt black (high surface area) also procured from Alfa Aesar was used as the cathode catalyst material. An equal ratio (1:1) mixture of deionized water and isopropyl alcohol (IPA) was used as a solvent in the ink. A 5% solution of Nafion was used as the
binder. The Nafion amount was systematically changed, results of which will be discussed in the coming sections.

The next step in the electrode fabrication involved the application of catalyst ink onto a suitable substrate. Kapton films have typically been used as the decal transfer substrates, as they can withstand the temperature and mechanical environment of spraying and the subsequent step of hot pressing, which is necessary for the transfer of the electrode from the substrate to the ionomer membrane. Kapton tokens were mounted onto a vacuum table that was maintained at a constant temperature of 60 °C [3]. A mask was affixed onto the vacuum plate, which had an area of the desired electrode size cut out of it. This allowed for clean edges of the electrode, and ensured that the catalyst ink is only deposited in the desired area. Spraying was performed by using a two-fluid external mixing Nordson EFD-781S nozzle, which was mounted in a purpose built 2-axis computer-controlled machine, as shown in Figure 2. This apparatus provided for a mounting platform for the nozzle and corresponding armature to allow for fine-tuning of the nozzle's aim and to adjust the working distance of the nozzle from the material. As shown in the figure, the spraying nozzle was positioned above a heated vacuum mounting plate. The nozzle was driven by a Nordson EFD ValveMate 8040 controller, which permitted for the triggering of the nozzle, when instructed by a host computer. The host computer controlled the motion of the nozzle head mounted on the X-Y table and synchronized it with the nozzle triggering at the desired locations. In this fashion the desired geometry of the electrode was sprayed uniformly onto the substrate.

For the decal-transfer process, a low-temperature, high-pressure route was taken; the transfer temperature was set at 130 °C while the pressure used was 5000 psi for 180 s duration. The last step of the electrode fabrication procedure is to attach the diffusion media to each electrode. Two appropriately sized pieces of diffusion media (ELAT LT-1400, ETEK) were affixed onto the 3-layer MEA formed with the assistance of temperature and pressure. A temperature of 120 °C and a pressure of 1200 psi was used for this step for a 60 s duration as described in [12].

A Fuel Cell Technologies test station was used, along with single cell 5 cm² hardware provided by the same company. A new MEA was first subjected to a 24 hr. break-in period. The break-in procedure involved the following steps:

- Cell installation in single cell hardware (bolt torque set at 40 in-lb.)
- Perform leak test
- Backpressure set at 20 psi
- Cell temperature set at 90 °C
- Dry oxygen supplied to cathode at 250 SCCM
- 1M Methanol solution supplied to anode at 2 ml/min
- Cell maintained at 0.2 V for 24 Hrs.

After the break-in period, the MEA was tested in conditions summarized in Table 1.

\[ \text{Figure 2: 2-axis spraying machine.} \]

**Table 1: Testing conditions for 5cm² single cell DMFC MEA.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>Cell Temperature</td>
<td>65 °C/90 °C</td>
</tr>
<tr>
<td>Anode humidity bottle temp</td>
<td>24 °C (no humidification rqd)</td>
</tr>
<tr>
<td>Cathode humidity bottle temp</td>
<td>24 °C (no humidification rqd)</td>
</tr>
<tr>
<td>Anode line heater temperature</td>
<td>24 °C / not used</td>
</tr>
<tr>
<td>Cathode line heater temperature</td>
<td>65 °C</td>
</tr>
<tr>
<td><strong>Flow rates</strong></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>2 ml/min</td>
</tr>
<tr>
<td>Oxygen / Air</td>
<td>250 sccm</td>
</tr>
<tr>
<td><strong>Back pressure</strong></td>
<td></td>
</tr>
<tr>
<td>Anode back pressure</td>
<td>n/a</td>
</tr>
<tr>
<td>Cathode back pressure</td>
<td>20 psi</td>
</tr>
<tr>
<td><strong>Bolt Torque</strong></td>
<td>40 in-lb.</td>
</tr>
<tr>
<td><strong>Seal thickness</strong></td>
<td>20 mil</td>
</tr>
<tr>
<td><strong>Seal material</strong></td>
<td>Teflon coated fiber glass</td>
</tr>
<tr>
<td><strong>VI Curve</strong></td>
<td>Constant Current</td>
</tr>
<tr>
<td><strong>Current step size</strong></td>
<td>0.25 A</td>
</tr>
<tr>
<td><strong>Delay b/w readings (scan rate)</strong></td>
<td>180 s</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**
For the first series of tests in this study, five MEAs were prepared with different Nafion content. Both the anode and the cathode used had the same Nafion content. All electrodes used Pt:Ru black (1:1) as anode catalyst with a loading of 2.5 mg/cm², whereas Pt-black with a loading of 2.5 mg/cm² was used as the cathode catalyst.

Figure 3 shows the results of this study when Nafion content was symmetrically changed, that is, both anode and cathode had the same Nafion content. The best overall performance was achieved with a Nafion content of 10 %wt. It can be argued that lower Nafion content leads to thinner electrode layers [19], which allows for better mass transport. In comparison to unsupported catalysts, carbon-supported catalysts used in PEM fuel cells thrive with higher Nafion contents, with values as high as 33 %wt. being reported [2]. Supported catalysts have much larger particle sizes, by virtue of the carbon supports used, ~40 nm as compared to unsupported platinum blacks whose average sizes are around 2-3 nm. Too high a Nafion content would prevent good particle-to-particle contact, thereby drastically reducing electronic access to the interior region of the catalyst layer. Similarly, too thick a Nafion film surrounding a catalyst particle can prevent gas-phase access to the catalyst sites. Too low a Nafion content could potentially lead to catalyst sites that are not adequately connected by the ionomer, which is necessary for protonic conductance to the membrane.

![Figure 4: Power at different Nafion content.](image)

Figure 4, presents an alternate view of the same data, showing the power produced by these MEAs at 0.2V and at 0.4V. As Nafion content is increased from 5 %wt. to 10 %wt., there is an increase in performance, and then there is a steady decline as the content increases to 30 %wt. of Nafion content in the electrodes. The power curve at 0.4V shows little difference between the MEAs, because at that voltage, almost all the MEAs are performing very similarly. It is only at higher current densities that the difference between the MEAs is clearly evident. This result reinforces the notion that the higher Nafion content is detrimental to mass transport.

In the MEAs tested, the anode and cathode both had the same Nafion content, so it is difficult to identify the contribution of one over the other. The anode and cathode have different Nafion content requirements because of a number of reasons. On the anode, a liquid fuel is fed to the electrode, whereas on the cathode, a gas, air/oxygen, is supplied. This functional distinction would lead to different mass transport scenarios. Additionally the very nature of the catalyst, and the catalyst inks formed is different. Pt:Ru black catalyst tends to form agglomerates during the ink making process, and is generally much more difficult to process that Pt-black ink.

Figure 5 shows the surface morphology and pore structure of a Pt:Ru black electrode at 50,000x magnification. Evidence of this agglomeration is even apparent at the microstructure level; discrete clumps of catalyst and ionomer are clearly visible in the anode. This observation suggests the need for the identification of additives and solvents that prevent such agglomeration, which could potentially lead to much higher catalyst utilization in the anode, than is witnessed at present.

![Effect of Nafion Content On Cell Performance](image)
Figure 5: Pt:Ru black anode at 50,000 X

Figure 6 shows the microstructure of a Pt black electrode as observed in an SEM at 50,000x magnification. As compared to a Pt:Ru black electrode microstructure, this electrode has an entirely different microstructure. A much finer pore structure is visible with no evident clumping or agglomeration.

Figure 6: Pt black cathode at 50,000 X

In light of the observations made with the polarization curves of MEAs for which the anode and cathode Nafion loading was changed symmetrically, MEAs with asymmetric Nafion loadings were prepared in order to identify the contribution of one electrode over the other, with respect to varying Nafion content.

For the first batch of asymmetric Nafion loading tests, MEAs were prepared with the cathode Nafion content kept constant at 10 %wt., while varying the anode Nafion content from 5 %wt. to 20 %wt. in four equal increments. All electrodes fabricated used Pt:Ru black (1:1) as anode catalyst with a loading of 2.5 mg/cm², whereas Pt-black with a loading of 2.5 mg/cm² was used as the cathode catalyst. Figure 7 shows the VI curves for four different Nafion contents in the anode, while Figure 8 represents the same data presented in a different manner. At lower current densities the performance of the four MEAs is very similar, but at higher current densities, the MEA with 15 %wt. Nafion performs slightly better than the rest. From Figure 8, it is clear that increasing Nafion content has minimal impact at both higher current densities represented by the curve 0.2V, and also at lower current densities represented by the curve at 0.4V.

Figure 7: Effect of anode Nafion content on MEA performance.

Upon observation of Figure 4, (MEAs with symmetrical Nafion loading), an increase of Nafion content from 10 %wt. to 20 %wt. results in a loss of ~35 mw/cm² of power, whereas from Figure 8, increasing the anode Nafion content from 10 %wt. to 20 %wt. does not produce any significant power change. This result implies that changing the anode Nafion content in the range demonstrated above has minimal impact on the overall MEA performance.

These observations indicate that a significant contribution from the cathode could be expected. In order to verify this contribution, MEAs with asymmetric Nafion loadings were prepared, where the anode Nafion content is kept constant at 10 %wt., while varying the cathode Nafion content from 5 %wt. to 20 %wt. in four equal increments. All electrodes fabricated used Pt:Ru black (1:1) as anode catalyst with a loading of 2.5 mg/cm², whereas Pt-black
with a loading of 2.5 mg/cm² was used as the cathode catalyst.

Figure 8: Power at different anode Nafion content.

Figure 9 shows the polarization curves produced by these MEAs. At higher current densities, significant difference is observed between the performance of the different MEAs. Increasing Nafion content clearly is detrimental to mass transport in a DMFC cathode and negatively affects the overall cell performance.

Figure 9 shows that the best performance comes from a cathode with a 10% Nafion content. Over most of the performance range of interest, it appears that cathodes with 5% Nafion content and 15% Nafion content give similar performance values. We attribute the lowered performance to different root causes, however. The performance of the 10% Nafion cathode extends roughly linearly over the entire range of current densities, indicating that the lower performance is most likely due to a lowered effective conductivity of the cathode catalyst layer, whereas the exacerbation of performance problems at higher current densities for the 15% Nafion cathode suggests a gas-phase mass transport resistance through the catalyst layer as the partial pressure of oxygen in the cathode is driven to lower values. This trend appears to be corroborated by the performance at 20% Nafion content, which suggests a catalyst layer that has very low connectivity for oxygen transport, where only a small fraction of the total catalyst loading has effective contact with the oxygen GDL, thereby lowering performance across the entire range of current densities.

Figure 9: Effect of cathode Nafion content on MEA performance.

Figure 10 echoes the same observations, as shown by the power plots at 0.2V and 0.4V. It is hypothesized that increasing Nafion content clogs the fine pore structure observed in the cathode SEM micrographs, and limits mass transport. Also since the Pt black particle sizes are smaller and less prone to agglomeration as compared to Pt:Ru particles, excess Nafion could hinder particle to particle contact and reduce electrical connectivity within the electrode.

Figure 10: Power at different cathode Nafion content.

CONCLUSION

The effects of changing the Nafion content in the anode and cathode of thin film electrodes prepared by spraying...
The results show that increasing Nafion content significantly impairs the performance of the MEA, at ionomer loadings that would be beneficial to the performance of a hydrogen PEMFC. This effect can be attributed to impediments in mass transfer imposed by the ionomer, and to reduction in particle-to-particle contact, affecting the electrical conductivity within the electrode. Upon further examination, it was revealed that the anode does not play a significant part; rather it is the DMFC cathode, which suffers the most from increasing Nafion content. Based on these results, it is possible to adjust Nafion content in DMFC electrodes for optimal performance.

ACKNOWLEDGMENTS

Financial support by the Office of Naval Research MURI grants No. N00014-07-1-0758 is gratefully acknowledged. The authors would also like to acknowledge the support provided from the Cullen Endowed Professorship in Engineering, The University of Texas at Austin. Any opinions, findings, or conclusions found in this paper are those of the authors and do not necessarily reflect the views of the sponsors.

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