ELECTROCATALYTIC LAYER MICROSTRUCTURE-RESISTANCE RELATIONSHIP

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ABSTRACT

The effect of electrocatalytic layer microstructures of various conventional membrane electrode assemblies (MEAs) on their bulk resistance has been investigated. Materials characterization was carried out by optical microscopy and ac impedance spectroscopy. A base line for the microstructure – resistance relationship was established with three MEAs obtained from manufacturer A. These MEAs had the same compositions of cathodes and different compositions of anodes. The results of Type A cathode analyses show that the size of cracks in the electrocatalytic layers is the major cause for the linear resistance to increase from 274 to 643 Ω/cm. The linear resistance of Type A anodes increased from 204 to 527 Ω/cm. This increase was attributed to the different catalysts and Nafion® polymer loadings in Type A anodes. The resistance increase in anode A3 was correlated to the Nafion® loading increase and not to the microstructure change. This conclusion was confirmed by a study done using carbon coatings that contained various Nafion® loadings. The study showed that when the Nafion® content was less than 20%wt and more than 30%wt, the resistance of the carbon coatings increased. For the case of Nafion® content between 20 and 30%wt, the carbon coatings had the lowest resistances. The characterization results of two additional MEAs prepared by manufacturers B and C were compared to A. Type B MEA had an irregular electrocatalyst microstructure and high electrocatalyst resistance (560 Ω/cm). Type C MEA, which had the most uniform microstructure, had resistances of 94 and 106 Ω/cm for cathode and anode, respectively.

INTRODUCTION

Membrane electrode assemblies (MEAs) used in polymer electrolyte membrane (PEM) fuel cells consist of polymer electrolyte membranes and electrocatalytic layers. The major components of the electrocatalytic layers are a metal catalyst supported on carbon powder and the same proton conductive polymer electrolyte used for the membrane. The catalyst commonly used in PEM fuel cells for oxygen reduction and
hydrogen oxidation is Pt. The Pt-Ru alloy catalyst has been successfully used for hydrogen oxidation in the presence of carbon monoxide.

The MEA preparation involves several steps such as ink preparation from a catalyst and the polymer, ink deposition on a substrate, and drying and hot pressing of the deposited layer onto the polymer electrolyte membrane. The microstructure of the prepared electrocatalytic layers depends on the catalyst particle size, the catalyst/polymer weight ratio, the coating technique, the drying rate, the processing temperature as well as many other processing parameters.

The approach used in this paper for the quantitative microstructure characterization is analogous to the methodology used for metals and semiconductors. It is well known that perfect monocrystals and amorphous materials have the lowest resistances due to lack of imperfections and grain boundaries [2]. It is similarly expected that MEAs with small grains surrounded with wide cracks have higher resistance than the MEAs with uniform crack free microstructure.

In this paper the total ohmic resistance of a single electrocatalytic layer of an MEA is correlated to the microstructure of the layer. The first objective was to determine how the size of fluctuations in the electrocatalyst features, such as grains and cracks, affects the linear resistance in electrocatalytic layers with the same compositions. Since several of the MEAs studied differed in both the microstructure and the Nafion® polymer content, the second objective of this work was to study the linear resistance dependence on the Nafion® content in order to differentiate the effects of these two parameters on the resistance. For this purpose carbon coated membranes were prepared in-house. Materials characterization was carried out by optical microscopy and ac impedance spectroscopy.

EXPERIMENTAL

MEAs studied

MEAs obtained from three different manufacturers A, B, and C were used to study the influence of electrocatalyst layer microstructure on bulk resistance. Three MEAs received from manufacturer A were used to establish a base line for the electrocatalyst microstructure – bulk resistance relationship since the MEAs had known compositions. These MEAs had different compositions of the anode layers and the same compositions of the cathode layers. Since the MEAs were in the developmental stage, in addition to the known catalyst loading, the relative changes in polymer content and the changes in the catalyst loading were revealed by manufacturer A. Type A1 MEA had 2.5 times higher catalyst loading than Types A2 and A3, while Type A3 MEA had 2 times higher content of Nafion® than Types A1 and A2.

Two additional MEAs provided by manufacturers B and C were also used for microstructure-resistance study. Type B MEA had identical electrocatalyst on both anode and cathode sides, while Type C MEA had different electrocatalyst compositions on
anode and cathode. All the MEAs were tested as received without any additional treatment.

**Carbon coating preparation**

The carbon coating of the Nafion® 117 membrane was done using a carbon-Nafion® ink. The ink was prepared from Vulcan XR 7RC carbon powder and 5% Nafion® solution. The methods used for the ink and the coating preparations are described earlier by Wilson et al.[1]. All carbon coatings prepared contained the same loading of carbon powder (1.25 mg/cm²). However, the loading of Nafion® varied, and it was 10, 20, 30, 40, 45, and 50%wt. The carbon coating was made only on one side of the Nafion® 117 membrane. The areas coated were 16 cm². Two samples of each composition were prepared.

**Optical microscopy characterization**

The microstructures of the MEAs received from manufacturers A, B, and C and in-house prepared carbon coated membranes were observed by an Olympus BX 60 optical microscope at magnifications from 50 to 200. The size of MEAs examined was 150 cm². Two samples of each MEA type were tested. Each sample was randomly examined first and then five micrographs were taken from each layer. The micrographs were used for the quantitative characterization of the electrocatalyst microstructure that consisted of measuring and calculating the average grain diameter, the linear grain density and the maximum crack width.

The optical microscope was also used for measurements of the electrocatalyst and carbon coating layer thicknesses. The technique applied was based on the image focusing at different layer depths. For this purpose the cracks in the layers were used. The image was first focused on the surface of the layer and then it was focused on the membrane at the bottom of the layer. The difference in the positions of the fine focus adjustment knob between previous and later focusing was correlated to the layer thickness since one increment on the fine focus knob represents 1μm.

**Linear resistance measurements**

The bulk resistance of the layers was measured using a two electrode ac impedance method. The resistance was measured in the frequency range from 1 to 20 kHz using the Solartron 1280 B and z-plot software version 2.1. The measurements were performed under controlled temperature (23 ± 2)°C and relative humidity (47 ± 3)% conditions.

Two gold pins (area 7.8x10⁻³ cm²) attached to a plastic handle were used as electrodes. The pins were placed 1 cm apart. The resistance was measured laterally along the electrocatalyst surface. During each measurement, a constant pressure was applied to the
electrodes. The resistance was measured in the same areas where the micrographs were taken. The spots tested on the anode and the cathode sides of each sample did not overlap in order to avoid the effect of any physical changes in the layers caused by the electrode compression. The layer's bulk resistance was obtained at the intersection of the impedance response curve (Cole-Cole plot) with the impedance real axis. The resistance measured represents the total ohmic resistance that includes the electrical resistance of metal conductors used, and the electronic and ionic resistances of electrocatalyst.

The method reproducibility was checked by repeating the measurements at the same spot five times in both current directions (forward and reverse) between the pins. For the calculation of the results presented, the average of these measurements was taken. The standard deviation was <5%.

RESULTS AND DISCUSSION

Microstructure

The results of microstructure characterization for Type A MEAs are summarized in Table 1. The values presented are the averages of measurements taken per each electrocatalyst.

Table 1: Catalyst grain sizes, crack widths, and the linear grain densities for various MEAs.

| MEA Type | CATHODE | ANODE |
|----------|---------|-------|
|          | Grain diameter (μm) | Maximum crack size (μm) | Number of grains/cm | Grain diameter (μm) | Maximum crack size (μm) | Number of grains/cm |
| A1       | 115     | 24    | 87    | 247     | <4     | 40  |
| A2       | 185     | 48    | 54    | 67      | <4     | 150 |
| A3       | 164     | 112   | 61    | 67      | 8      | 150 |

Type A1 anode has a 2.5 higher catalyst loading than type A2 and A3 anodes and different microstructure than the other two anodes. It has grains with diameter 247 μm that are 3.7 times larger than the grains in A2 and A3 anodes. Due to larger grains, the linear density is lower than in A2 and A3 anodes (40 grains/cm vs 150 grains/cm). Cracks in anode A1 are < 4 μm wide and do not penetrate to the membrane surface. It appears that the A1 anode was deposited as a catalyst multi layer. Even though the crack size of anode A2 is also < 4μm, they propagate from the surface of the layer to the surface of the membrane. Cracks in A3 are wider than in anodes A1 and A2 (8 μm) and they reach from the top of the layer to the membrane surface. The thickness of anode A1 is 34 μm and it
is ~ 2 times thicker than anodes A2 and A3 which have an average thickness of ~16 μm. Therefore, it is apparent that the microstructure of type A anodes varied with the composition. Increased catalyst loading in anode A1 resulted in thicker layer with larger grains than in the other two anodes. However, the increased polymer loading increased the crack size in A3 anode.

Although the cathode catalyst layers in Type A MEAs have the same composition, their microstructures differ visually (Fig. 1 and 2) and quantitatively (Table 1). From Fig. 1 and 2, it is obvious that cathode A1 has smaller grains (115 μm) with large pores (~16 μm), than cathode A3. Cathode A1 micrograph shows that the grains are tightly packed and the cracks are narrow (< 8 μm). There are some short and localized enlargements of the crack width from ~ 8 to 24 μm (Fig. 1) that reveal the membrane surface. On the other hand, cathodes A2 and A3 have much larger grains 185 and 164 μm, respectively, with wider cracks (Table 1). In cathode A3 the cracks are 112 μm wide and in some areas completely surround the grains (Fig. 2).

The differences in the microstructures of Type A1 cathode and Types A2 and A3 cathodes, indicate that the preparation process of cathode A1 is different than of cathodes A2 and A3. Some of the possible reasons are that the ink of this electrocatalyst might be deposited in more than one layer or it may be made using different solvents. The appearance of cathodes A2 and A3 indicate that their preparation process is basically the same, with slight differences in their quantitative characteristics (grain size and crack width). Dissimilarity in the microstructures of cathodes A2 and A3 is most likely the consequence of the variations in the layer deposition parameters such as drying temperature or drying rate. All Type A cathodes have thickness ~ 16 μm.

![Figure 1: Type A1 MEA cathode catalyst has linear resistance 274 Ω/cm. Dark lines in the micrograph are the cracks in the electrocatalytic layer. Scale: 1 increment is 8 μm.](image)
Type B MEA has the same composition of anode and cathode layers and therefore their microstructures are identical. The layers have very non uniformly cracked structure with a maximum crack width of 140 μm. However, Type C MEA has cathode and anode with different compositions. The microstructures of both the cathode and the anode electrocatalysts are very uniform with cracks localized in small areas (diameter <160 μm).

The carbon coatings with 20 and 30%wt of Nafion® polymer have crack free microstructures. However, the samples that contain 10 and 40-50%wt of the polymer have uniform centers and cracks around the edges of the layer. The average thickness of the carbon coatings is 16 μm. Since the Nafion® loading did not change the microstructure or thickness of the carbon coatings significantly, the resistance change measured can be attributed solely to the Nafion® content.

Figure 2: Type A3 MEA cathode catalyst with linear resistance 643 Ω/cm. The white areas in this micrograph are the cracks widely open in the electrocatalyst that expose the Nafion® membrane. Scale: 1 increment is 16 μm.

Linear resistance

The linear resistance results obtained for all MEAs tested are presented in Table 2. For Type A MEAs, the results show that the cathode layers have higher resistance than the anode layers. This result is opposite to the one expected, if the grain size and the grain linear density are considered. Usually for other conductors (metals and semiconductors), the resistance increases if the size of grains decreases as the result of increased grain surface boundary. Another result that is also opposite to the metal and semiconductor behavior is the linear resistance of cathode A1. The resistance of cathode A1 is lower than cathodes A2 and A3 although it has the smallest grains and the largest grain linear
density. Among all microstructure properties measured, only crack width has the same change trend as the cathode resistance.

Table 2: Linear resistance of electrocatalysts measured for different MEAs.

| MEA TYPE | CATHODE LINEAR RESISTANCE (Ω/cm) | ANODE LINEAR RESISTANCE (Ω/cm) |
|----------|-----------------------------------|--------------------------------|
| A1       | 274                               | 204                            |
| A2       | 413                               | 388                            |
| A3       | 643                               | 527                            |
| B        | 560                               | 503                            |
| C        | 94                                | 106                            |

Cathode A1 apparently has the tightest cracks (Table 1) while cathode A3 has the widest. Therefore, the crack size is the major factor that affects the linear resistance in electrocatalysts with the same composition.

The linear resistance of anodes also increases from A1 to A3. It follows from the data in Table 1 that the crack size in this case is not a major parameter that can be correlated with the linear resistance variations. As previously described, the anode compositions and thicknesses are different. The higher catalyst loading of anode A1 creates a thicker layer with larger grains than in anodes A2 and A3. These two changes apparently caused the lowest resistance in anode A1. Furthermore, anode A3 has different Nation® content than the other two and the highest linear resistance. If differences in linear resistance between anodes A1 and A2 and anodes A2 and A3 are compared, it is concluded that linear resistance is affected more with the thickness change (from A1 to A2) than with the Nation® loading increase (from A2 to A3). The reason why the thickness affects the linear resistance is most likely due to the multilayer structure of anode A1 that stops the cracks from propagating through the entire electrocatalyst layer to the surface of a membrane. In this multilayer structure, the catalyst grains have continuous electronic and ionic contacts in 3D.

The effect of the Nation® content on the linear resistance of electrocatalyst was measured on carbon coated Nation® membranes. The dependence of linear resistance on Nation® content for the thin films studied is shown in Fig. 3. It is apparent that there is an optimum polymer concentration range for which the carbon coatings have the lowest linear resistance. For the carbon loading used (1.25 mg/cm²) this optimum dry polymer concentration range is 20-30%wt. This result is in agreement with data previously reported by Lee et al. [3] on the effect of Nation® loading on the total ohmic resistance.
of a PEM fuel cell. Therefore, Nafion® loading in electrocatalyst layers is an important factor that determines its linear resistance.

Type B MEA had the same electrocatalyst on the anode and the cathode sides. Their microstructure was non uniformly cracked. The high linear resistance can be attributed to the large cracks that exist in the layers. The difference in the linear resistances measured between these two layers can be a consequence of the membrane electrode assembly procedure.

![Figure 3: Linear resistance vs. Nafion® content of the carbon coated layers deposited on a Nafion® 117 membrane.](image)

Type C MEA has the least linear resistance than the other two types. Although the electrocatalyst layers have different compositions, their microstructures are very similar. They have scarcely distributed cracks localized on 160 µm areas. It appears that crack free microstructure is a dominant factor that determines the low resistance of this type of MEA since the compositions and the catalyst loadings of these two layers are different.

**CONCLUSIONS**

The electrocatalytic layer microstructures of various MEAs were correlated to their linear resistance. The microstructure features such as grain size, linear grain density and crack width were measured and used as quantitative parameters for the microstructure characterization. The trends of their changes (increase or decrease) were compared to the trend of the electrocatalyst linear resistance. For the electrocatalysts with the same compositions, the crack width size has a major effect on the resistance. Thus, an increase in crack width of 24 µm to 112 µm caused resistance to increase from 274 Ω/cm to 643

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Ω/cm. In addition to the crack size influence, the dry Nafion® loading in the electrocatalyst layer has a predominant effect on the resistance even though there are slight changes in the crack width. Therefore, the crack size and the Nafion® content are two major factors that affect the resistance of the electrocatalystic layers in MEAs for PEM fuel cells. Crack free electrocatalyst with the optimum Nafion® will have the least possible resistance for the composition used.

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Keywords: MEA characterization, MEA microstructure, electrocatalyst resistance.