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Comparing Different Cross-Section Cutting Methods for SEM Analysis of Membrane-Electrodes Assemblies

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A study is presented to compare different methodologies for the cross-sectional visualization of membrane-electrode assemblies (MEAs) with SEM. Four techniques for cutting MEAs have been tested and analyzed: the sharp-edge cutting, CO_2 laser, embedded-mechanical polishing, and ion-milling. Characteristics of each procedure are compared. Sharp-edge cutting, being fast and low cost, may preserve layers porous morphology rather unaltered, but obtaining a good cross-section in a wide area is stochastic and with low probability. CO_2-laser beam cutting alters severely carbon and Nafion layers as a consequence of the burning of carbon based materials. Embedded-mechanical polishing is a well stablished and reproducible method that shows accurately the thickness of the layers, however it is too aggressive with highly porous structures that may appear smoothed or removed. Ion-milling is also good for accurate thicknesses measurements, and more conservative with the porous morphologies than the previous one, but they are also smoothed.

Introduction

The multiple layer structure of membrane-electrode assemblies (MEAs) makes of cross-sectional analysis a basic tool for their study. Cross-sectional visualization shows thickness and morphology of the layers as well as changes occurring during assembly and operation in a fuel cell. However, the notably different mechanical properties of the layers complicate obtaining good cross-section planes where thicknesses and morphologies appear intact at the microscopic scale. Preparation of cross-sectional planes for SEM visualization requires appropriate cutting procedures that do not alter the morphology of the layers, avoiding uneven surfaces, mixing of layers, crumbling, smoothing of porous faces, and/or delamination. It is possible that no single method may accomplish with all such requirements, so different cross sectioning procedures may have to be used for a complete characterization.

Different methods have been used for cross-section preparation of MEAs and components, from most simple ones, like cutting with a sharp edge or fracturing in liquid nitrogen (1), to methods using more specific equipment, like laser cutting, embedded-mechanical polishing, focused ion-beam (2), and microtome (for TEM) (3). To our

knowledge, no comparative study among these methods applied to MEA studies is available.

The present study aims to analyze different methods for cross sectional preparation and observation of MEAs. One principal objective is finding a methodology for preserving the porous morphologies, like those of the catalyst layer or the gas diffusion layer of an MEA, in the cross-section. Due to their soft constitution by agglomeration of particles loosely adhered, porous layers are characterized by low mechanical stability, so easy modification of their morphology occurs by procedures normally used in cross-section preparation. Highly macroporous layers, like catalyst layers prepared by the electrospray deposition technique, can be easily modified during cross-section preparation. However, the analysis of such morphology is of high interest because it is determinant for their behavior as cathodic catalyst layer in a PEMFC with improve mass transport and durability (4,5).

With this aim, four preparation methods for cross-section analysis of MEAs have been tested in order to make a comparative study showing advantages and disadvantages for each one. The methods are cutting with a sharp-edge, CO_2 laser-cutting, embedded-mechanical polishing, and ion-milling.

Experimental

Membrane electrode assemblies were prepared with Nafion NR212 membrane (Ion Power Inc.), and two types of commercial gas diffusion electrodes, BASF (ELAT GDE LT250EWALTSI, BASF, 0.25 $mgPt \cdot cm^{-2}$), and Fuel Cell ETC (0.3 mg/cm^2 40% Platinum on Vulcan - Cloth GDE). Also electrodes with catalyst layers deposited by the electrospray technique (4,5) were observed in cross-section. For SEM a Hitachi FE-SEM SU-6600 microscope was used.

For sharp edge cutting, a standard laboratory snap-off blade knife was used. For CO_2 laser cutting a laser cutting machine was used (Gravograph, LS100, 35 W, 50-500DPI resolution).

The embedded-mechanical polishing is a common method to prepare metallographic samples for cross sectional observation. The use for MEA observation is less common, and requires adjusting some parts of the procedure. The samples are embedded using EPOMET® G, a hot compression thermosetting resin, to reduce shrinkage during curing and edge retention. The samples have been compressed under 80 bar at 150 °C. After curing the resin, the sample is cut in cross-section and the surface prepared by grinding and polishing. The grinding was performed with successive sweeps with SiC papers (P320, P600, P1200) and water, and finished by polishing with diamond paste (6 microns). The conditions were fixed at a pressure of 6 lb and a disk of 300 rpm for 3 minutes for all the stages of the preparation. Before introducing the sample in the microscope, carbon coating is applied due to the insulating character of the resin.

The ion-milling preparation was performed with a Hitachi High-Tech IM4000 system. This technique has been developed to produce smooth and clean sample surfaces for high-resolution imaging using electron microscopy. The system uses a wide Argon beam to irradiate specimens and the sputtering effect to polish the surface without

stressing it (6). The cross-section area is limited to a few mm, in the range of 2 and 4mm, although other models announce up to 10mm (7). Cross-sections of MEAs were prepared by cutting a small piece of the assembly with a sharp knife followed by sandwiching both sides with adhesive copper tape before mounting onto the sample holder. Ion-milling uses an argon ion beam to cut the planar cross section through the specimen along the edge of a titanium mask located between the specimen and the ion gun, mounted on a removable specimen holder that can be directly introduced on the microscope after the cut. Time and voltage conditions were optimized for MEA assemblies, especially to avoid damage to the Nafion membrane. The optimized conditions for the preparation of MEAs cross-sections were an accelerating voltage of 5 kV during 6 h, using 2.3 reciprocation·min^{-1} and a swing angle of ±40 °C. For cross-sectional cuts of catalyst coated membranes, the same conditions were used reducing the time to 3 h.

Results and discussion

Cutting with a sharp edge is a quick and easy method that may provide good cross-sectional observation with preserving morphology. However, it requires experienced and careful handling, and the probability for a successful preparation is not high. Finding an appropriate area in a sample for clear cross sectional visualization may be stochastic due to frequent intermixing of layers and delamination.

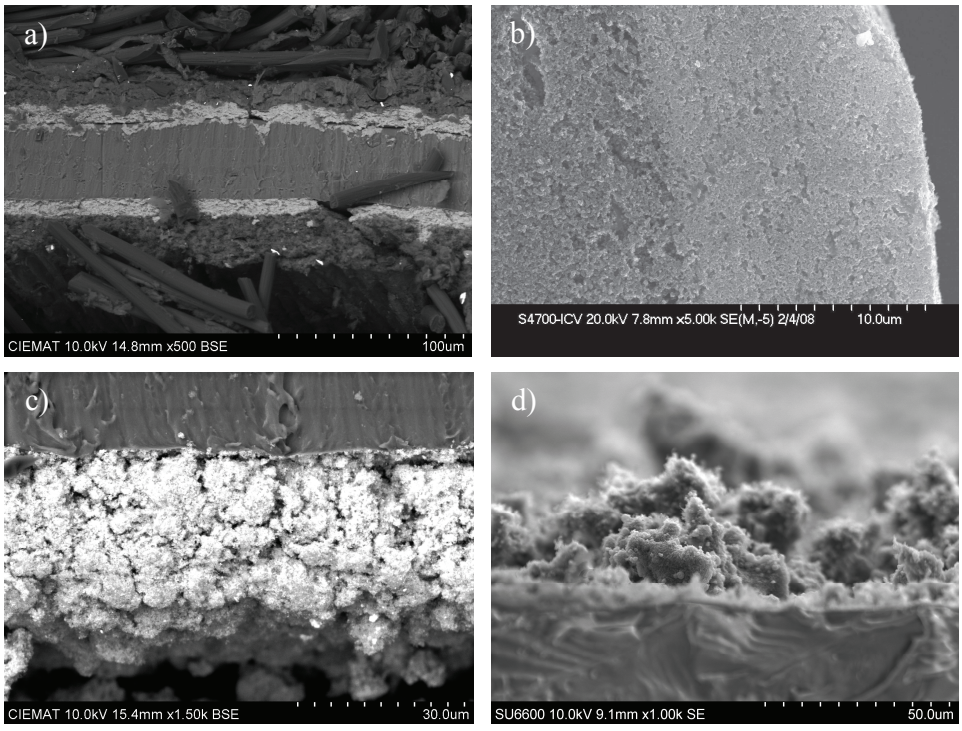

Figure 1. Cross section of an MEA prepared with a sharp edge. a) MEA with two commercial electrodes (ETEK, 0.25mgPt·cm^{-2}) and Nafion 212NR membrane. b) Catalyst layer of the commercial electrode (90^{o} rotated). c) Catalyst layer prepared by electrospray on Nafion membrane (in the upper part) with same catalyst concentration as in (b). d) Detail of the agglomerates of an electrosprayed catalyst layer before assembling the MEA.

Fig.1a shows a MEA with commercial electrodes in a region where the layers appear well defined. Some intermixing is observed in the cutting direction (from top to down) that interferes thickness measurements. Good preservation of porous morphologies by the sharp-edge cut is apparent in Figs.1b-d, where details of different catalyst layers are shown. Fig. 1b shows the catalyst layer of the commercial electrode, revealing a porous morphology with macropores in the 1μm range. Figs.1c and d show catalyst layers prepared by electrospray deposition that are characterized by larger macropores sizes, above 10μm, rendering thicker catalyst layers (Fig. 1c). The morphology before assembling the MEA is shown in Fig.1d in a cross section of a catalyst coated membrane before cell assembly. The image reveals dendritic growths on the agglomerates responsible for the superhydrophobic character of the electrosprayed layers (4,5). The possibility to observe such structure almost unmodified can be explained as a consequence of the edge dragging the material in the cross section plane, and leaving almost intact the structures behind that plane. So far, such morphologies have been revealed only in cross sectional samples prepared with a sharp edge and before MEA assembly.

Laser-cutting using a CO_2 laser usually proceeds by heating, melting and vaporizing of the material caused by laser beam incidence. For carbon based materials, like those of the electrodes of an MEA, burning also takes place in contact with air. The main parameters for a cutting process are the beam power, its translational speed, and the number of pulses per unit area (dpi). For cutting an MEA, different effects are observed for each layer, as can be seen in Fig.2. The cross section plane shows significant alteration at a micrometric scale for the different components that makes impossible thickness or morphology characterization.

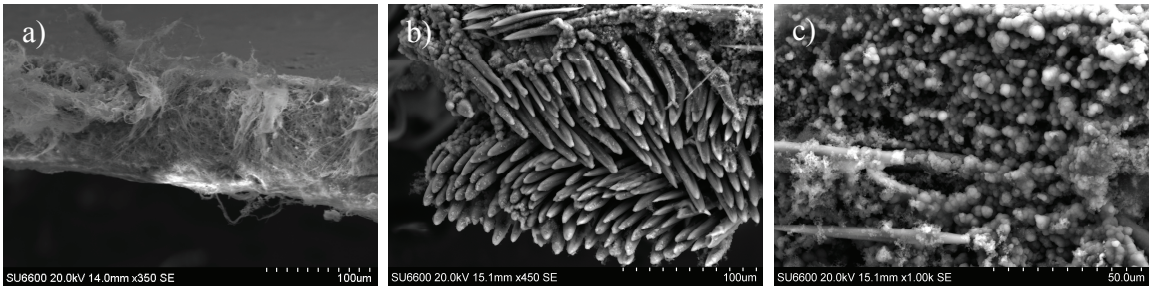

Figure 2. Cross section images of MEA components cut with CO_2 laser. a) Nafion membrane; b) Gas diffusion layer; c) Carbon cloth substrate.

Mechanical polishing of a resin embedded MEA provides better preservation of layers thickness, as shown in Fig.3. The different layers appear sharply defined allowing for the accurate analysis of thicknesses. On the other hand, the morphology of the porous layers, i.e. the catalyst layer and microporous layer, appears artificially smoothed, either by resin intrusion into the pores or by the polishing step, leading morphological information significantly altered (Fig. 3).

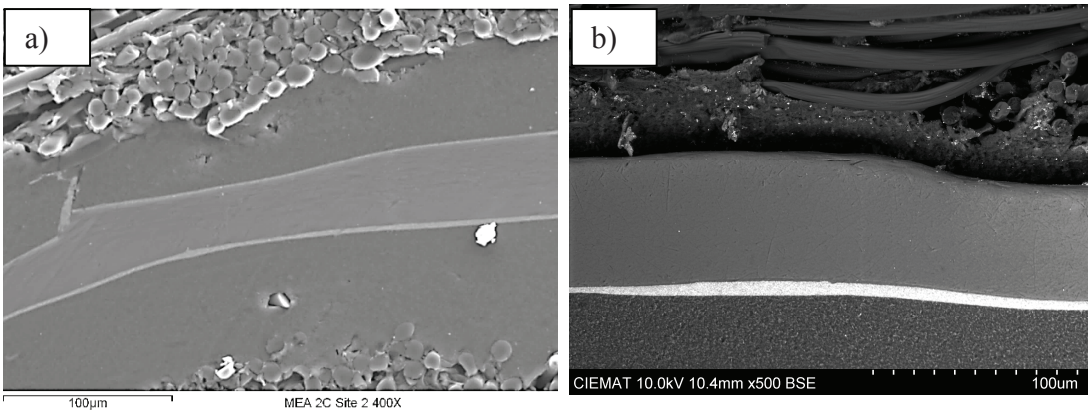

Figure 3. Cross section images of MEA prepared by embedding-mechanical polishing. a) MEA with a commercial ETEK 0.25mg Pt·cm^{-2} (lower electrode), and a commercial Fuel Cell ETC 0.25 mgPt·cm^{-2} (upper electrode). The membrane is Nafion 212NR. b) Similar MEA but with the upper electrode prepared by electrospray, which does not appear in the image since it was lost during cross section preparation. The images were taken with backscattered electrons to better show the catalyst layers of the electrodes (bright bands).

Observation of very porous and fragile layers, i.e. catalyst layers prepared by electrospray (cf. Fig. 1) was not possible with this preparation method, as shown in Fig.3b, where the electrospray catalyst layer is lost (see the void space in the upper electrode of the figure) during grinding and polishing processes. The high reliability and reproducibility of this preparation method allows observation of an MEA over wide areas, up to cm, as shown in Fig.4. This kind of image reveals changes in thickness of the layers caused by uneven pressure inside the cell, like by the woven fabric or the flow-field channels.

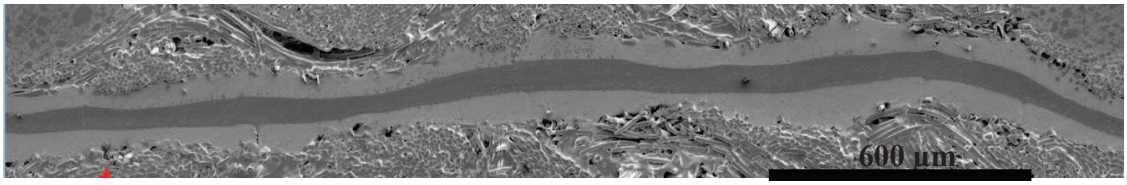

Figure 4. Wide-area cross-section image of an MEA prepared by embedding-mechanical polishing. The image was taken by parts and assembled.

Good preservation of all layers, including the softest electrosprayed layers, is attained with the ion-milling technique (Fig. 5). Cross section polishing with argon gas appears to better preserve the porous layers, although with somewhat smoothed morphology.

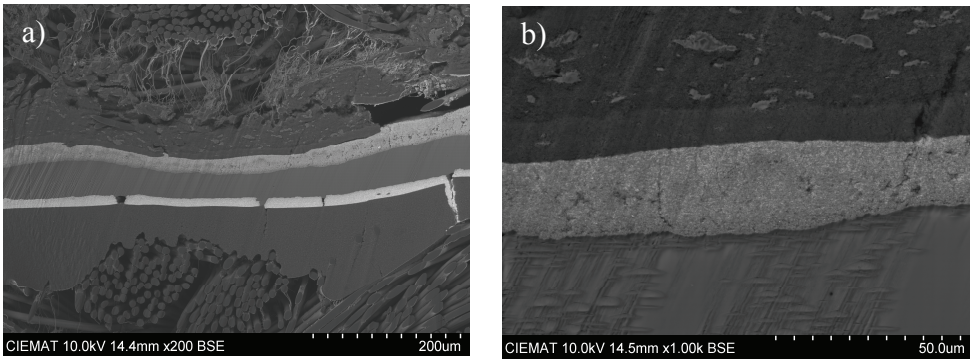

Figure 5. Cross section images of MEA by ion-milling. a) MEA with lower electrode is commercial ETEK 0.25mg Pt·cm^{-2}, while the upper electrode is an electrosprayed electrode. The membrane is Nafion 212NR. b) Detail of the electrosprayed catalyst layer morphology.

Although the soft electrosprayed catalyst layer is observed after the ion-milling process, however its porosity appears significantly altered, which shows very similar morphology as that of a commercial electrode (Fig. 6).

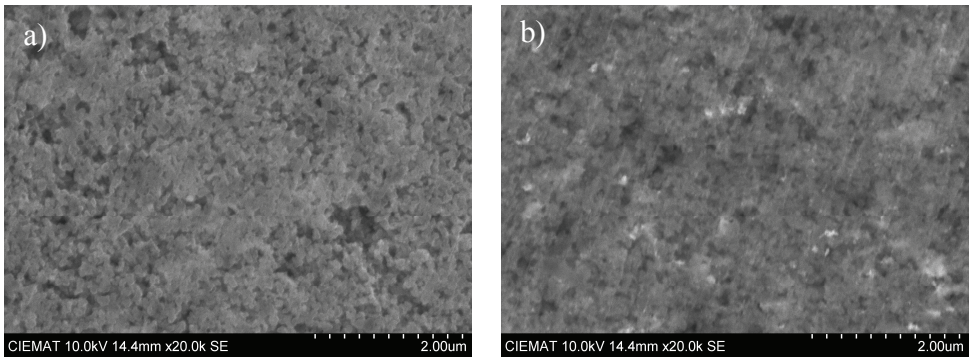

Figure 6. Cross section images of MEA prepared by ion-milling. a) Electrosprayed catalyst layer. b) Commercial catalyst layer ETEK 0.25mg Pt·cm^{-2}.

The ion-milling technique shows properly the thickness of all layers, but changes the porous morphology. Another limitation of this technique is the length of the profile that cannot be extended beyond a few millimeters.

A summary of the results and conclusions with the different cross-section methods tested is given in Table I.

TABLE I. Analysis of the different methods used for cross-sectional cutting

Cutting Method	Reproducibility	Thickness preservation	Morphology preservation	Preparation time	Comments
Sharp edge	low	medium-low	high	minutes	cheap tools, preserves porosity
CO_2 laser	high	low	low	minutes	laser machine, alters morphologies
Embeddin g-polishing	high	high	low	2-3 hours	laborious, aggressive with soft material
Ion-milling	high	high	medium-low	4-5 hours	expensive equipment, short observation length (mm)

Conclusions

The methods tested for cross-sections preparation of MEAs to be observed under SEM show complementary characteristics, so their use depends on the objectives of the study. For the analysis of porous structures, the sharp-edge cutting appears most adequate since it may leave unaltered the morphologies. However the method is rather stochastic and relies largely on the experience and skills. More reproducible results may be obtained with the embedding-polishing method and or the ion-milling. These methods yield profiles of the porous layers rather smoothed, but the edges of the layers are well defined so they are most appropriate for thickness analysis. The ion-milling method is more conservative with the porosity but it can only be applied to small, millimeter wide, areas of the MEA. It is not discarded that the future optimization of all these methodologies, principally sharp-edge cutting, embedding-polishing, and ion-milling, may improve the shortcomings observed in this work.

Acknowledgments

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