Sample preparation for the cross sectional observation of membrane electrode assemblies (MEA) of proton exchange membrane fuel cells.

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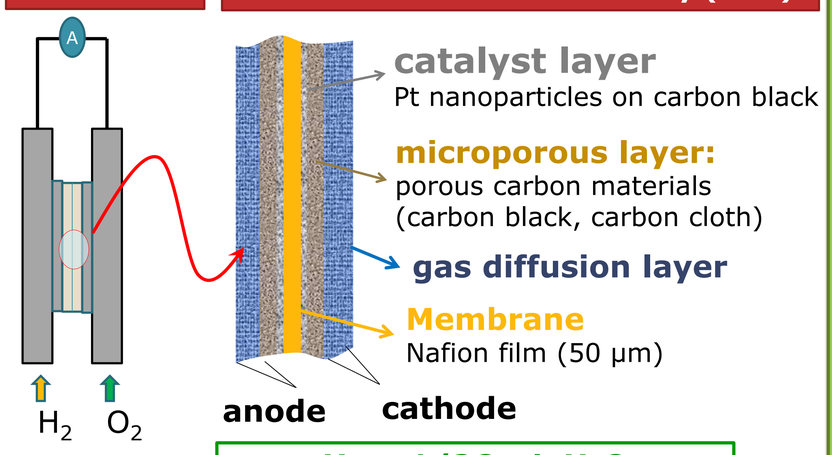
INTRODUCTION

Hydrogen fuel cells will play a principal roll in a future based on hydrogen energy carrier and predominance of decarbonized clean energy sources. Fuel cells will be the most efficient device for hydrogen conversion into electricity. Among fuel cells types, those based on proton exchange membrane (PEMFC) are closer to the industrial application due to their high power density, efficiency, and durability. In a PEMFC, the membrane-electrode assembly (MEA) is the central part, where the electrochemical reacctions occur:

- Anode $H_2(g) \rightarrow 2H^+ + 2e^-$
- Cathode $1/2O_2(g) + 2H^+ + 2e^- \rightarrow H_2O$ (l)
- Liquid water must be efficiently extracted from the cell

FUEL CELL | **Membrane Electrode Assembly (MEA)**



$H_2 + 1/2O_2 \rightarrow H_2O$

Good performance of an MEA depends on the adequate structure of each layer, that should keep transport and catalytic properties through-out the cell lifetime.

OBJECTIVE

The principal objective of this work is developing a method for preparation of MEA samples of PEMFCs to be studied by scanning electron microscopy (SEM) in cross sectional mode. This mode allows analyzing morphology and composition changes among layers. Different preparation methods have been employed for MEAs in order to determine optimal conditions for this particular observation mode.

MEA MATERIALS

Two different commercial electrodes has been studied (GDE1 and GDE2).

MEMBRANE

Type	Thickness	Manufacturer
Nafion NR 212	50.8µm	Ion Power (Dupont)

MATERIAL PROPERTIES OF MEMBRANE – ELECTRODE ASSEMBLIES (MEAs)

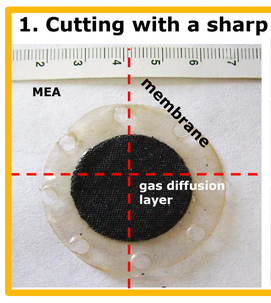
	Catalyst Layer (CL)			Microporous layer (MPL)	Gas diffusion layer (GDL)	Manufacturer	Reference
	catalyst	ionomer	[Pt]				
GDE1	Pt/C 20 wt% Pt C: Vulcan XC72R	Nafion 30%	0.25 mg·cm^{-2}	Vulcan XC72R + Teflon (1)	LT1200W Woven 454µm	BASF	ELAT GDE LT250EWALTSI
GDE2	Pt/C 40 wt% Pt C: vulcan XC72R	Nafion 30%	0.30 mg·cm^{-2}	Vulcan XC72R + Teflon (1)	GDL-CT Woven 410µm	FuelCellsETC	LLGDE

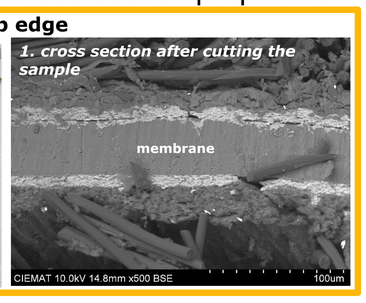
(1) Properties not specified by the supplier

CROSS-SECTIONS PREPARATION METHODS

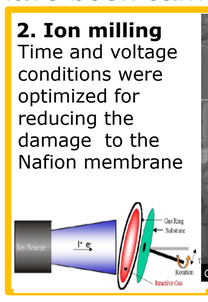
Three methods of cross-section preparation have been carried out.

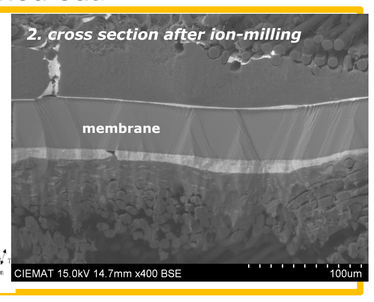
1. Cutting with a sharp edge



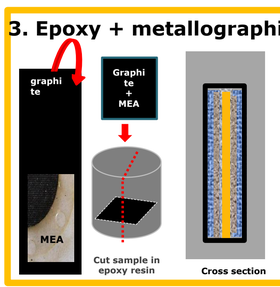


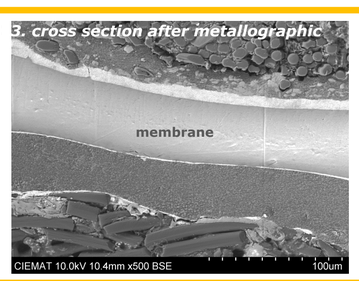
2. Ion milling
Time and voltage conditions were optimized for reducing the damage to the Nafion membrane



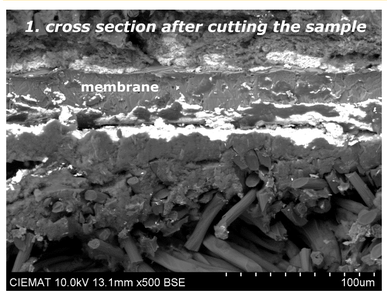


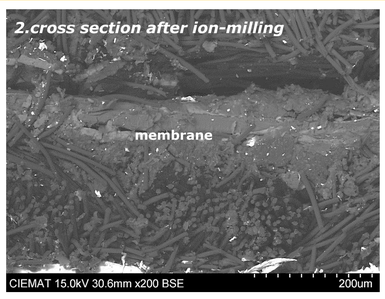
3. Epoxy + metallographic

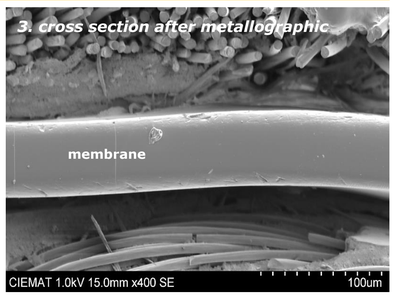




Specimens are "mounted" using a hot compression thermosetting resin. The epoxy resin reduce shrinkage during curing results in a better mount with edge retention. The samples have been compress to 80 bar and has been heat to a temperature of 150 or 180°C. After mounting, the specimen was cut in cross section and the surface of a metallographic specimen was prepared by grinding and polishing.



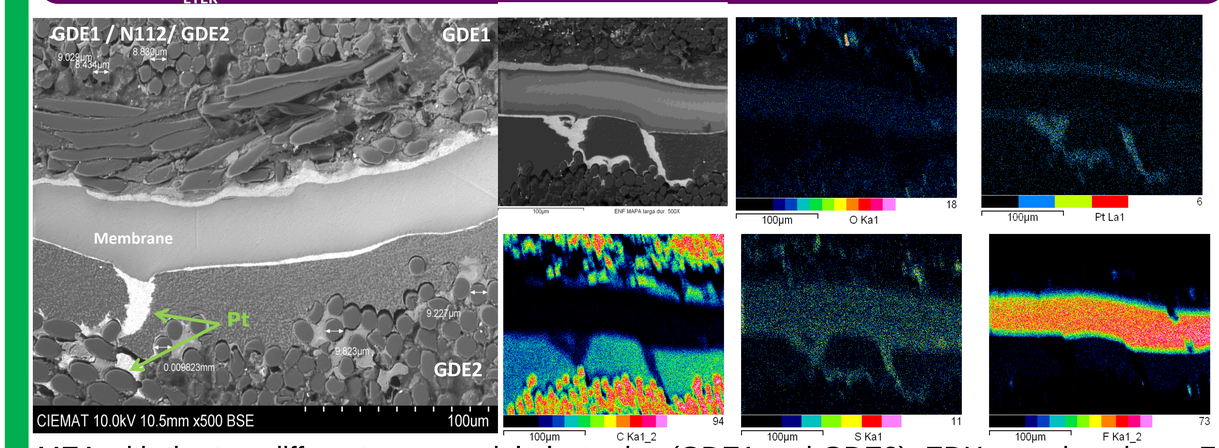




Problems with some preparation methods: 1) Cutting gives rise to layers overlay and poorly defined layer profile. **2)** Ion milling requires optimal time and voltage to avoid damaging the membrane. **3)** Epoxy resin "cold mounts" shows surface discontinuities and no surface flatness.

RESULTS WITH OPTIMIZED METHOD

CROSS-SECTION CHARACTERIZATION OF MEA BEFORE CELL OPERATION

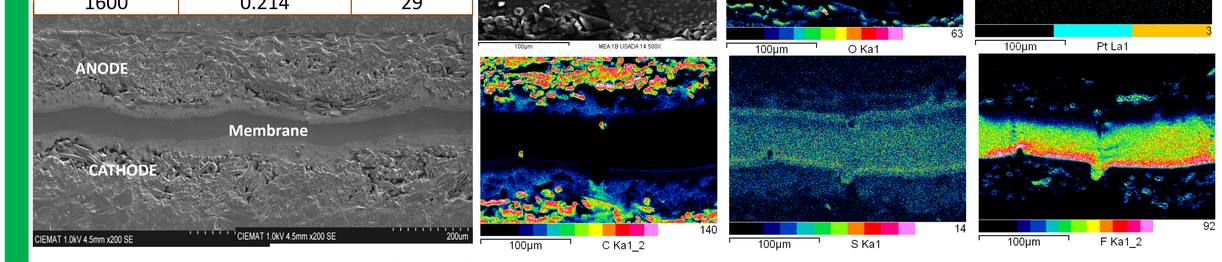


MEA with the two different commercial electrodes (GDE1 and GDE2). EDX mapping shows F and S homogeneously distributed in the membrane. Pt layer presents discontinuities and accumulations in GDE2 due to MPL cracks on the surface. (Method 3 Metallographic preparation).

CROSS-SECTION CHARACTERIZATION OF MEA AFTER CELL OPERATION

GDE1 /N112/ GDE1

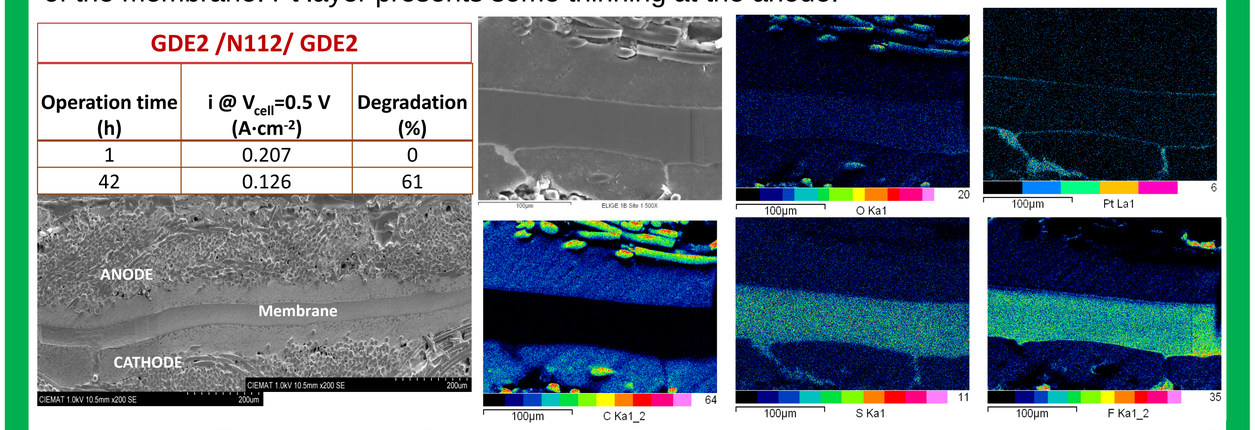
Operation time (h)	i @ V_{cell}=0.5 V (A·cm^{-2})	Degradation (%)
16	0.300	0
1600	0.214	29



Symmetric MEA with two GDE1. Operation causes F and S concentration at the cathodic side of the membrane. Pt layer presents some thinning at the anode.

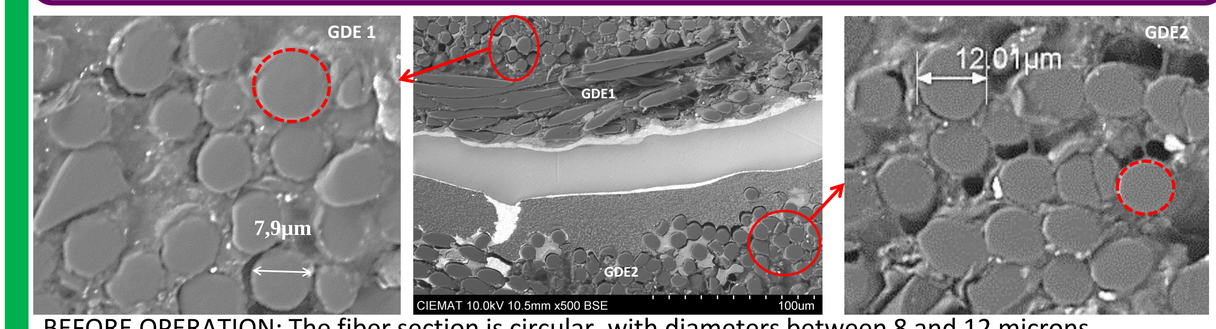
GDE2 /N112/ GDE2

Operation time (h)	i @ V_{cell}=0.5 V (A·cm^{-2})	Degradation (%)
1	0.207	0
42	0.126	61

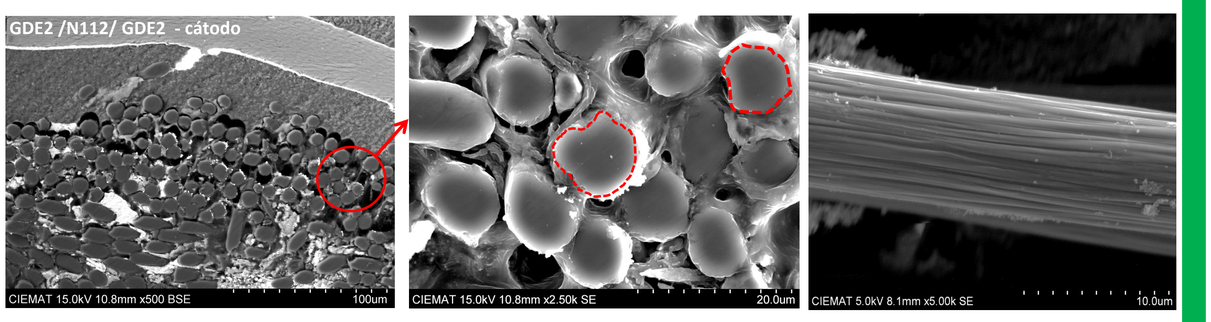


Symmetric MEA with two GDE2. After operation membrane shows different distribution of F and S. Loss of F is observed in the membrane and oxygen enrichment.

DIFFERENCES IN THE SIZE AND MORPHOLOGY OF FIBRES BEFORE AND AFTER OPERATION



BEFORE OPERATION: The fiber section is circular, with diameters between 8 and 12 microns.



AFTER OPERATION: The morphology of fibers changes. The section is more irregular and smaller due to corrosion processes. The appearance of grooves along the length of the fibers shows highly directional degradation.

SUMMARY

- Three methods of cross sectional MEA preparation have been analyzed. The metallographic preparation allows to appreciate a surface with high flatness in the cross section, which facilitates optimal contrast among layers and accurate analysis by means of EDX.
- Thickness and elements distribution in MEAs, before and after cell operation, can be evaluated.
- The metallographic preparation shows discontinuities and accumulations in Pt layers caused by cracks and defective synthesis, especially for GDE2.
- Size and morphology of fibers of GDLs show also degradation after cell operation.
- Ion milling method seems promising and is currently being optimized.

- A review of accelerated stress tests of MEA durability in PEM fuel cells. International Journal of Hydrogen Energy 34(1) (2009) 388-404. S.Zhang, X. Yuan, H. Wang, W. Mérida, H. Zhu, J. Shen, S. Wu, J. Zhang. https://doi.org/10.1016/j.ijhydene.2008.10.012 Journal of Power Sources 196 (2011) 4242–4250
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