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Short communication

Characterization of PEMFCs gas diffusion layers properties

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Abstract

Experiments have been carried out on different gas diffusion layer (GDL) materials in order to better understand the influence of this component on fuel cell performance. The study, focused on the mechanical behaviour of the GDL, shows the effect of the stress caused both by the hot-pressing and the compression in a cell on different types of carbon fibres based supports: a cloth, a felt and a paper. It has been observed that decreasing the stress applied on the GDL, which is of high interest for the durability of the MEAs, has moreover a positive effect on their performance.
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Keywords: GDL; Compression; Performance

1. Introduction

Among the components of the membrane electrode assemblies (MEA) of proton exchange membrane fuel cells, much interest has been put on the membranes and the active layers. Many works deal with the reduction of platinum loadings up to less than 0.1 mg cm^{-2} in order to reduce costs, using carbon supported platinum catalyst particles [1–4] or vacuum deposition processes such as sputtering [5] or electrodeposition [6]. Works have been made to optimise the ionomer content within the active layer [7,8] and the manufacturing process of this layer [9]. Until the recent years, less attention has been paid to the gas diffusion layer (GDL) whereas it is essential to have an efficient link between the current bipolar plates and active layers [10]. The right use of the GDLs is not easy since their main functions, which are to supply the active layers with reactants, to collect the current and to remove heat and water from the MEA, do not correspond to the same structural and physicochemical requirements. For example, air and water permeability increases with porosity, contrary to mechanical properties, electrical and thermal conductivities. Hydrophobicity, thickness, arrangement of carbon fibbers are parameters that influence differently each property mentioned above. Hydrophobicity of GDL allows water management in a fuel cell. That is to say, it will give the electrode the ability to drain liquid water outside the active layer without preventing vapour to hydrate the membrane. PTFE is currently used as a hydrophobic agent. As a consequence, the influence of the type of GDL and the amount of PTFE on fuel cell performances has been studied very often [11–13]. However, it is well known that conductivity and porosity of GDL decrease as the applied stress increases but the stress applied on the MEA during fuel cell tests is generally not known. Direct measurement of the influence of compression on MEA performances have been performed using different kind of commercially available GDL by Lee et al. [14]. Nevertheless, this study does not allow to relate the fuel cell performances with the GDL properties, since the latter are not known. More recently, Ihonen et al. performed a more detailed study proving that the mass transfer losses increase with the clamping pressure of the fuel cell both for woven or non-woven gas diffusion backings [15].

In addition, the GDL plays an important role concerning the durability of the MEAs, which is a point of major concern for the end users. Mass transport losses increase after long-term operation, due to degradation in water management. The loss of the GDL hydrophobicity caused by PTFE degradation could be an explanation [12,16]. The GDL represents a mechanical reinforcement for the floppy membrane and the very thin active layer. However, it can also generate strong local stresses, depending on its structure, on the active layers and on the membrane when it is constrained by hot-pressing or by compression in the stack.

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This experimental study has been focused on the comparison of three classical types of support made of carbon fibres: cloth, paper and felt. Cloth is a woven material contrary to paper and felt. We have also studied supports wet-proofed with Teflon and supports coated with a microporous layer made of carbon and Teflon, generally added on one or two faces of the supports in order to enhance the gases diffusion and the water management.

Mechanical and conductivity measurements have been systematically conducted on all these materials. Strain–stress curves have also been recorded on commonly used flat gaskets to compare their compressive behaviour (thickness versus applied compressive stress from 0 to 10 MPa). The microstructure of the supports have been observed with a scanning electron microscope in order to help the understanding of their mechanical behaviour. The mechanical device has been used to measure the though-plane electrical resistance of the GDLs under compression. Apart from the behaviour under compression which is the major part of this work, we have also done preliminary measurements of the porosity of some GDL.

Since the objective was to study the influence of the GDL on the fuel cell performance, fuel cell tests have been conducted to relate their characteristics to the polarization curves.

2. Experimental

2.1. Description of the samples

The experiments have been conducted on samples described in Table 1. The carbon cloth, felt and paper supports are respectively supplied by Zoltek, Freudenberg and Toray. The ELAT® GDL are supplied by DeNora North America, E-tek Division. The choice of the samples was done with respect to the material commonly used in our laboratory. For example, the ELAT® DS GDL have been used for years as a reference for our studies on the active layers, the catalysts, or the membrane. Other GDLs with coatings have been made by spraying on the different supports, inks made of carbon powder and PTFE mixed in ethanol and water.

2.2. Mechanical and electrical measurements

The mechanical and electrical measurements have been done with an INSTRON 4465 mechanical bench used in compression with a 5 kN cell. A four points resistance measurements device is included in the two copper cylindrical plates maintaining the samples. It has been shown that with these thin materials it was necessary to work with stacks of 10 samples to minimize the errors on the thickness measured versus the compressive stress on the range 0–10 MPa. Two successive compressions have been applied on the samples: the first one compares with the pressing commonly used to make the membrane electrodes assemblies and the second one shows the crushing or compression caused by the bipolar plates. The resistance measurements have been done meanwhile, so the only results available for the moment represent the addition of the bulk resistance of the 10 samples, the contact resistances between the samples and the two contact resistances between the samples and the copper plates.

Table 1
Description of the GDL studied

Ref. GDL supports	Type of support	Coating(s)	Un-compressed thickness (mm)
Zoltek 0%	Cloth 0% PTFE	None	0.34
Zoltek 12%	Cloth 12% PTFE	None	0.37
ELAT® DS[a]	Cloth 0% PTFE	Carbon + PTFE	0.44
ELAT® SS[a]	Cloth 0% PTFE	Carbon + PTFE	0.415
Freudenberg 10%	Felt 10% PTFE	None	0.19
Toray 0%	Paper 0% PTFE	None	0.29
Toray 10%	Paper 10% PTFE	None	0.29
Toray 30%	Paper 10% PTFE	None	0.29

[a] DS stands for double side; SS stands for single side.

2.3. Structural characteristics

A scanning electron microscope (JEOL JSM840A) has been used to observe the morphology of the different carbon supports before an after the compression experiments. Preliminary experiments have been done on uncompressed samples with a micromeritics multivolume pycnometer 1305 to compare the porosity of the GDLs.

2.4. MEAs and fuel cell tests

The GDLs have been compared on the cathode side using standard products for all the other components of the MEAs. They were hot-pressed on a "two layers" made by casting an ink containing the catalyst (20%Pt/C XC72 from De Nora N.A.) and 5% (w/w) Nafion® solution onto a Nafion® 112 membrane. Standard ELAT® electrodes from De Nora N.A. were used as the anodes.

The MEAs have been tested in 25 cm^2 single cells made of impregnated graphite plates with machined flow channels on an Electrochem test bench. The tests have been carried out at a cell temperature of 80 °C and at 4 and 1.5 absolute bars using humidified hydrogen, oxygen and air. The hydrogen, oxygen and air stoichiometry was kept at 1.2, 1.5 and 2.0 with minimum flows fixed at 150 ml min^{-1}. Adjusting the tightening of the cell and the thickness of the flat gaskets allows to control the extent of compression applied on the GDLs, both on the anode and cathode sides.

3. Results and discussion

3.1. Mechanical results

The three types of carbon fibres based materials present different compressive behaviours (Fig. 1). The main items like the compressive strain at two levels of pressure and the residual strain, respectively, during and after the first cycle have been extracted from the experimental datas (Fig. 2).

The cloth has the highest compressibility with the highest compressive strains on the 0–10 MPa range of compression. The paper presents two different behaviours at low and high compressive strengh during the first compression with a

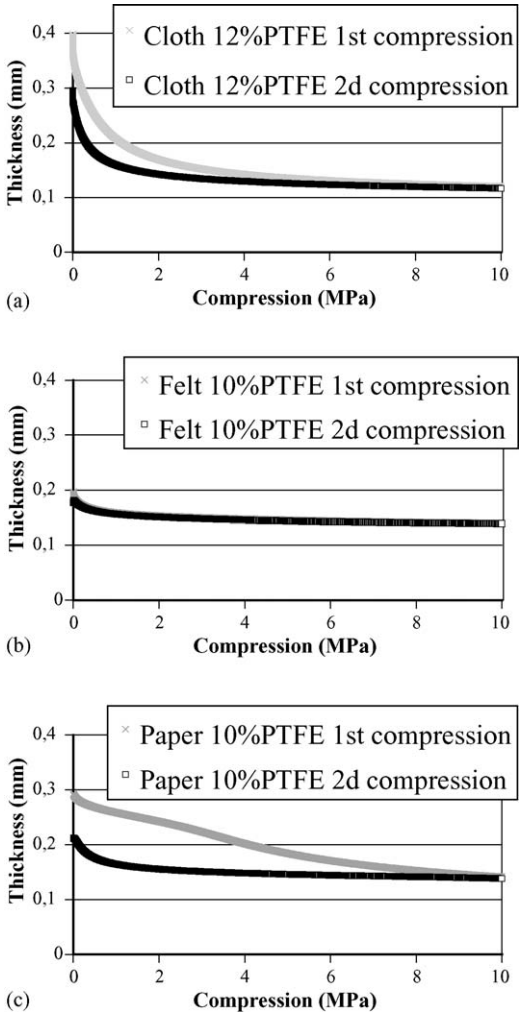

Fig. 1. Thickness vs. compressive stress for wet-proofed carbon (a) cloth, (b) felt and (c) paper. Behaviours during two successive compressions applied from 0 to 10 MPa.

small slope of compressive strain which increases strongly after 3 MPa. During the second compression, the behaviour of the paper becomes similar to the one of the felt, which behaves more like a hard stop. The cloth and the paper show the same level of residual strain after te first compression. On the contrary, the felt presents a very stable behaviour versus compression with the lowest compressive strain and almost no residual strain.

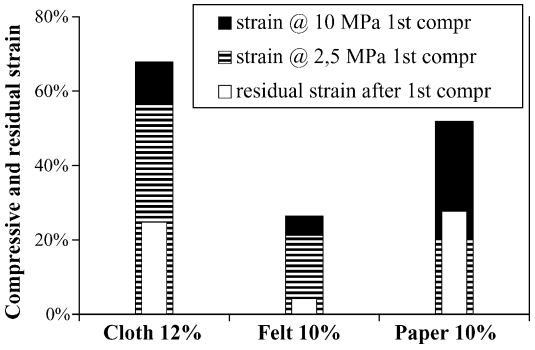

Fig. 2. Compressive strain and residual strain observed for the three materials during and after the first compression test.

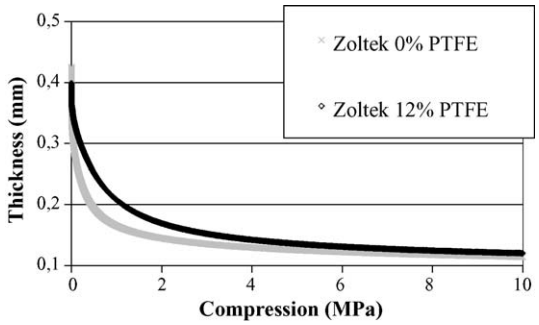

Fig. 3. Thickness vs. compressive stress for carbon cloth, without wet-proofing (0% PTFE) and with 12% (w/w) PTFE. Behaviour during the first compression.

The mechanical measurements have been done also on plain supports without PTFE in the volume and on finalized GDLs with micro porous coatings of carbon and PTFE added on the supports, in order to enhance the gases diffusion and the water management. The results are only presented here for carbon cloth. The major effect of wet-proofing the cloth (Fig. 3) and of these coatings (Fig. 4) is to decrease the slope of the compressive strain versus compressive stress curves, which means to extend the limit of compressibility toward higher stress compared with the plain supports. Whatever the kind of support, the effect is still the same.

3.2. Microstructure

The surface of the supports have been observed before and after the two compressions. The micrographs presenting the state of the materials after compression show that their different mechanical behaviours are related to differences in their microstructure (Fig. 5).

Concerning the carbon cloth, the highly compressive behaviour can easily be explained since it is a woven material. Within a thread the fibres can be packed together during compression. This would correspond to a reduction of the thickness of the threads. Moreover, the stitches of the cloth tighten up as the stress increases as if the threads of the two perpendicular wefts were pulled. The residual strain can be caused by the reduction of the size of the stitch. Finally, many

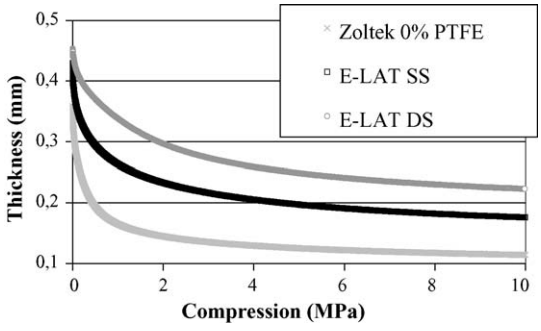

Fig. 4. Thickness vs. compressive stress for carbon cloth with 0% (w/w) PTFE and with microporous layer on one side (ELAT, SS) and both sides (ELAT, DS). Behaviour during the first compression.

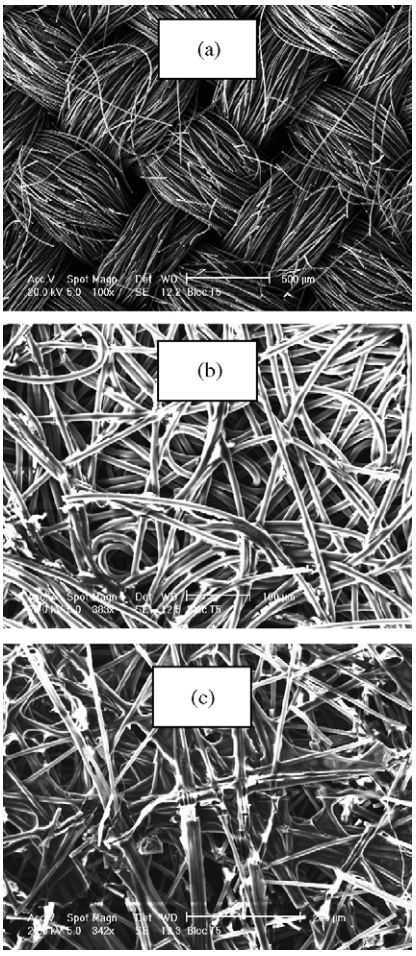

Fig. 5. Micrographs (scanning electron microscope (SEM)) of three different GDL supports (a: cloth, b: felt, c: paper) after two compressions at 10 MPa.

cracks are observed on the fibres of the carbon cloth after compression.

The picture of the paper surface explains clearly the mechanical behaviour of this material mechanically reinforced by a polymeric binder. After a level of stress which depends on the PTFE content, the linking polymer is no more able to insure the mechanical strength, the framework made of rigid fibres collapses, changing the rigid paper in a softer material. So, a residual strain remains after compression. On the contrary, the felt seems to be made of flexible and less brittle fibres which present the same aspects before and after compression. They are not ordered like in the cloth and they are entangled both in and through the plane. Moreover, there is no polymeric binder between the fibres. This particular structure can explain the non-compressive behaviour of the felt.

3.3. Conductivity measurements

In order to obtain more accurate results, conductivity measurements have been performed using 10 piled samples of each GDL. So, the measured electrical resistance is a combination of 10 bulk resistances, nine interfacial resistances (between each sample) and two contact resistances between the surfaces of the

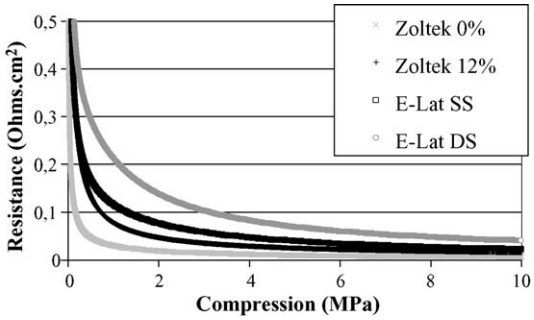

Fig. 6. Electric resistance vs. compressive stress for 10 piled samples of carbon cloth with 0 and 12% (w/w) PTFE and with microporous layer on one side (ELAT, SS) and both sides (ELAT, DS). Behaviour during the first compression.

sample and of the copper cylinders. The results are only presented here for carbon cloth 0% and 12% (w/w) of PTFE with and without microporous layers (Fig. 6). The measured electrical resistance decreases quickly with the stress applied on the GDL. It can mainly be ascribed to the contact resistances at the different interfaces. Indeed, the thickness of ELAT, DS gas diffusion layer is about 380 μm and about 340 μm under an applied stress of 0.5 and 1 MPa, respectively. If we consider that the intrinsic resistance of this support is constant within this range of stress and that the measured resistance only corresponds to bulk resistance, it would be about 1.1 times lower at 1 MPa compared to 0.5 MPa. However, the measured resistance is about 1.4 times lower. Whatever the kind of support, the effect is still the same. At 1 MPa, the measured resistance is about 200 mΩ cm^2 for 10 samples. As a consequence, the resistance of a single ELAT, DS is less than 20 mΩ cm^2 at 1 MPa within an MEA. This is the higher value measured on all the samples. For all the other samples, the resistance is lower than 10 mΩ cm^2 at 1 MPa. The global resistance increases with the number of microporous layers and with the amount of PTFE within the support. All these results are in accordance with the ones published by Ihonen et al. [15] and Mathias et al. [17] who report that measured resistances are less than 10 mΩ cm^2. Work is in progress to separate the relative contributions of the bulk and contact resistances on the total resistance.

When considering the aspect of the fibres of the cloth and the paper, it appears that the stress applied on the GDLs, in order to enhance their conductivity and the electrical contacts with the bipolar plates and the active layers, could dramatically affect the durability of the MEAs. Actually, the stress applied on the GDL is directly transmitted to the active layers and the membrane.

3.4. Polarization curves

Since the general aim of our research is related to the improvement of fuel cells performance and durability, it has been decided to conduct some performance tests (polarization curves) in various operating conditions in order to show what was the actual effect of the compressive stress on the performances.

ELAT® DS GDLs have been chosen to do these experiments because the carbon cloth was the material showing the maximum modifications on a wide range of compression as well for

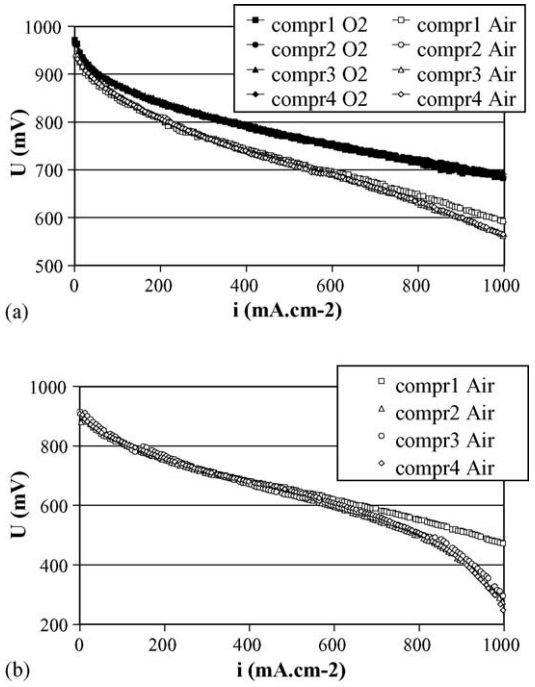

Fig. 7. Polarization curves for ELAT® DS GDL with different thickness of gaskets corresponding to different compression (compr1 = 31% (0.5 MPa); compr2 = 42% (1.5 MPa); compr3 = 46% (4 MPa); compr4 = 50% (10 MPa)).

the mechanical aspect (major strain) as for the electrical aspect (major decrease of the through plane resistance versus compression because of a major decrease in thickness).

The polarization curves have been performed with pure oxygen or air at different pressures:with pure oxygen at 4 absolute bars, air at 4 absolute bars and air at 1,5 absolute bars (Fig. 7). Four compressions have been compared by using four gaskets of different thickness and all behaving like hard stop, as it was observed by doing the same mechanical measurements as on the GDL. The four tests correspond to compressive strain ranging from 31 to 50% corresponding, respectively, to applied stresses ranging from 0.5 to 10 MPa. Under oxygen at 4 absolute bars, the performances are equivalent whatever the applied stress is. With air at 4 absolute bars and below 600 mA cm^{-2}, the performance are rather similar whatever the compression is. Above this current, the performance slightly decrease above 40% of compression. This phenomenon is more important with air at low pressure. This can be ascribed mainly to an increase of mass transfer loss. The slope of the linear part of the polarization curve does not increase with the stress applied on the GDL. The contribution of the GDL resistance on the whole resistance of the cell is negligible. If the resistance of the GDL decreases of 10 mΩ cm^2, the cell voltage would be increased of 10 mV at 1 A cm^{-2}. These results are in agreement with the work of Ihonen et al. [15] and Mathias et al. [17]. As the strain increases, gas permeability decreases and water management becomes more difficult. These results are obtained at 100%RH and it would be interesting to perform these experiments at lower relative humidity.

Always thinking about the durability of the MEAs, these results have been presented on a graph together with the stress

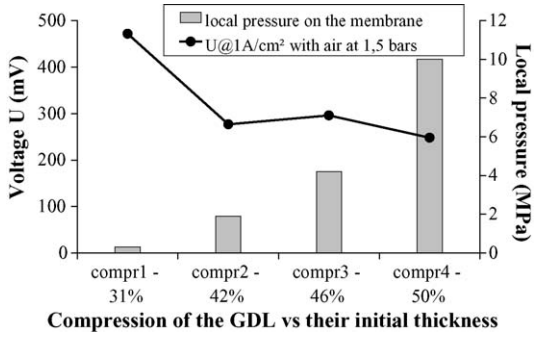

Fig. 8. Comparison of the voltage and of the local pressure applied to the membrane for different GDL compression.

which would be locally applied on the membrane for the different levels of compressive strain applied on the GDL (Fig. 8). This was done by using the compressive stress–thickness curves obtained during the second compression.

This figure shows clearly that the decrease of 20% in the compression of the GDL allows to decrease strongly the local pressure in the active zone while increasing significantly the performance at high current density. Knowing that the gasket used until now as a standard with this type of GDL was the one corresponding to compr3, this result shows the interest of this type of mechanical studies in order to better understand the fuel cells operation.

4. Conclusion

The main conclusion of this work is that enhancing the knowledge on the materials properties is of major interest to better understand and increase the performance. In the case of the GDLs, this work has shown that the compressive stress applied on the GDL has to be minimized so as to reduce the mass transfer loss at high current and low pressure. This should be an important point to look at, for example, for stack dimensioning.

A possible extension of this work will be a study on the actual link between the compressive stress applied to the active zone of the MEAs and their durability.

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