NANOMATERIALS
SCIENCE & ENGINEERING
Vol. 2, No. 3, pp. 135-143 (2020)

RESEARCH ARTICLE

https://doi.org/10.34624/nmse.v2i3.19554

Improvement of active layers homogeneity for the MEA's (Membrane Electrode Assembly) of PEMFC (Proton Exchange Membrane Fuel Cell): impact of the ink quality formulation

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Received 22 July 2020; accepted 16 September 2020; published online 22 September 2020

ABSTRACT

This study focuses on the improvement of active layers for PEMFC (Proton Exchange Membrane Fuel Cell) fuel cells. These active layers (anode and cathode) constitute the core of the cell where chemical reactions take place. The goal is to improve the performance and durability of these cells by working on these layers. Some research has shown the impact of homogeneity of active layer on fuel cell performance by working on printing processes. In our case, the aim was to obtain homogeneous active layer after coating deposition process by studying the formulation of the ink: the order of introduction of components and the dispersion processes. Several ink dispersion processes stood out, including a planetary mixer that gave satisfactory results in terms of particle size and deposit homogeneity. Moreover, the order of introduction of the components during the ink formulation seem to have an impact onto rheological parameter and also onto particles size.

1. INTRODUCTION

Nowadays, environmental issues are becoming more and more important in our society. Ecology and global warming are at the heart of these issues and play an important role in the automotive market. Today's society is seeking to reduce oil consumption in all areas but specifically in the automotive industry. Proton Exchange Membrane Fuel Cell (PEMFC) is an electrochemical cell allowing to environmentally friendly convert energy to replace the use of fossil fuels. This cell produces electricity through the oxidation of hydrogen (H_2) at the anode and the reduction of oxygen (O_2) at the cathode. The heart of the fuel cell, Membrane Electrode Assembly (MEA), is composed of an exchange membrane which is surrounded by two catalyst layers, an anode and a cathode. This part of the fuel is very important and has a real impact on cell performance and lifetime. Catalyst layers are composed of a catalytic powder of platinum-based nanoparticle deposited onto carbon support, ionomers, water and solvents. Several methods exist to print these layers: bar-coating, screen-printing, electrospray coating among others and Roll-to-Roll coating for a large scale. After being obtained, these actives layers are hot-pressed onto a membrane and assembled with Gas Diffusion Layer (GDL) in order to get the MEA. As the MEA gets thinner and thinner (membrane of 10 µm or less, decreasing of the active layer thickness due to the reduction of the catalyst loading) and with the objective not to have an impact onto the performance and durability, active layer must be as homogeneous as possible, without defects as agglomerates or cracks. Indeed, agglomerates in these layers could lead to damages on durability with deformation and rupture of the membrane. The formation of agglomerates could be favoured by different factors: the solvent used in the formulation as showed in the study of *D. Huang et Al*. [3] who have worked on the effect of solvent in catalyst ink on PEMFC performance, the catalytic powder which could also favour agglomerates [4] and contribute to heterogeneous active layers. The ideal is to find the right formulation so that the ionomer used is also well dissolved in the solution and the catalyst powder well dispersed. Indeed, the latter would have a different degree of polymerization and would result in a different structure that could lead to agglomeration as *T. Kim et Al.* [5] have highlighted in their work. The way of disperse could also facilitate the formation of agglomerates: *M. Wang et Al*. [6] have studied different time of dispersing the catalyst ink: it was dispersed with the ultrasonic bath at different time and speed. They have shown the importance to well dispersed ink and have been able to correlate catalyst agglomeration and fuel cell performance. C. Jeffery Jacobs [7] has also studied the influence of catalyst ink mixing procedures on PEMFC performance and especially has worked on three methods of dispersion: bead milling, high shear stirring and ultrasonic bath. He has observed an effect of the dispersion method on catalyst layer formulation, structures and agglomerates observed in the active layers. Only few studies have been carried out on ink process dispersion and the order of introduction of ink. That is why, research on how to avoid agglomerates into inks by working on formulation procedures could be interesting. This study will focus on the order of introduction of components for formulating the ink and three processes of ink dispersion: a high shearing mixing, a mechanical dispersion and planetary mixers. The aim is to optimize the ink formulation and to have homogeneous active layers. Moreover, one of our goal is both to obtain a viscosity above a certain threshold (at least 10 Pa.s), in order to be adapted to printing processes as screen-printing and bar coating, but at the same time to have a particle size below 1 µm.

Our results will show differences, in particular in the structure of the active layer but also in rheological aspects through characterisations.

2. EXPERIMENTAL PROCEDURE

The cathode-type catalytic ink was manufactured according to the following protocol. The first phase consists in dispersing TEC10V50E catalytic powder of platinum deposited onto carbon support Vulcan XC72 (Pt/C) (47.2wt%Pt, Tanaka®) in distilled water. The handling is carried out in a “glove box” due to nanoparticle risks in the catalytic powder. Once the powder has been dispersed in water; two PFSA polymers (ionomer 1 Nafion® *D2020*, ionomer 2), as well as the solvent (ethanol), can be added under suction. The ratio between ionomer and carbon is I/C=0,8.

Once the ink has been dispersed, it is placed under magnetic agitation at least one day before being used and characterised. The method used in this study to obtain the deposit is bar coating with a liquid thickness of 40 µm and a drying temperature at 40°C. The catalytic inks contain dry content of 23% linked to the use of bar-coated or

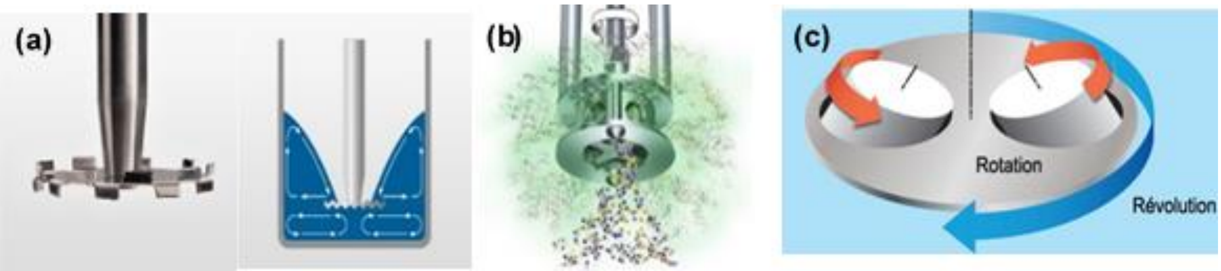

Figure 1. Operating principles of the different processes – (a) Disc Dispersal, (b) Module Rotor/Stator for high shearing mixing, (c) Planetary mixer system (Rot/Rev).

screen-printing processes. The catalyst loading in the active layer is 0,25 mgPt/cm².

2.1. PROCESS OF DISPERSION

Three dispersion methods have been tried, including mechanical dispersion (Dispermat®), high shear dispersions (Silverson®) and planetary mixers (Mazerustar from Kurabo® and Kakuhunter from Sodipro®) without mechanical modules into the flask of ink for the latter. At total, 4 different tools have been tried.

Mechanical dispersion from Dispermat® (*Disc Disp.)* is the process used as reference in the laboratory. It is a mechanical dispersion generated by a dispersal disc as shown in the figure 1.(a). The tests were carried out at 4000 rpm during 15 min. Silverson® (*Rotor/Stator*) constitutes a high shearing mixing. The modulus dispersion works on a rotor/stator system (moving part inside) with some open area on the side that can have different shapes (square, rectangular…) and does not move. The liquid goes inside the module from below and a high shear rate is created when the liquid come out the holes. The ink was mixed at 6000 rpm during 10 min (figure 1.(b)).

Planetary mixers work on the rotation of the container on itself in one direction and the revolution of the container around an axis in the opposite direction (figure 1.(c)). These two parameters are independent but a ratio (rotation on revolution) could be controlled. There is no dispersal disc inside containers. The biggest difference between the two planetary mixers is the wide range of levels of rotation/revolution for the Mazerustar (from 0,1 to 0,9) taken at 0,9 for the study (Rot/Rev 0,9) and the fixed ratio of 0,4 for the Kakuhunter (Rot/Rev 0,4).

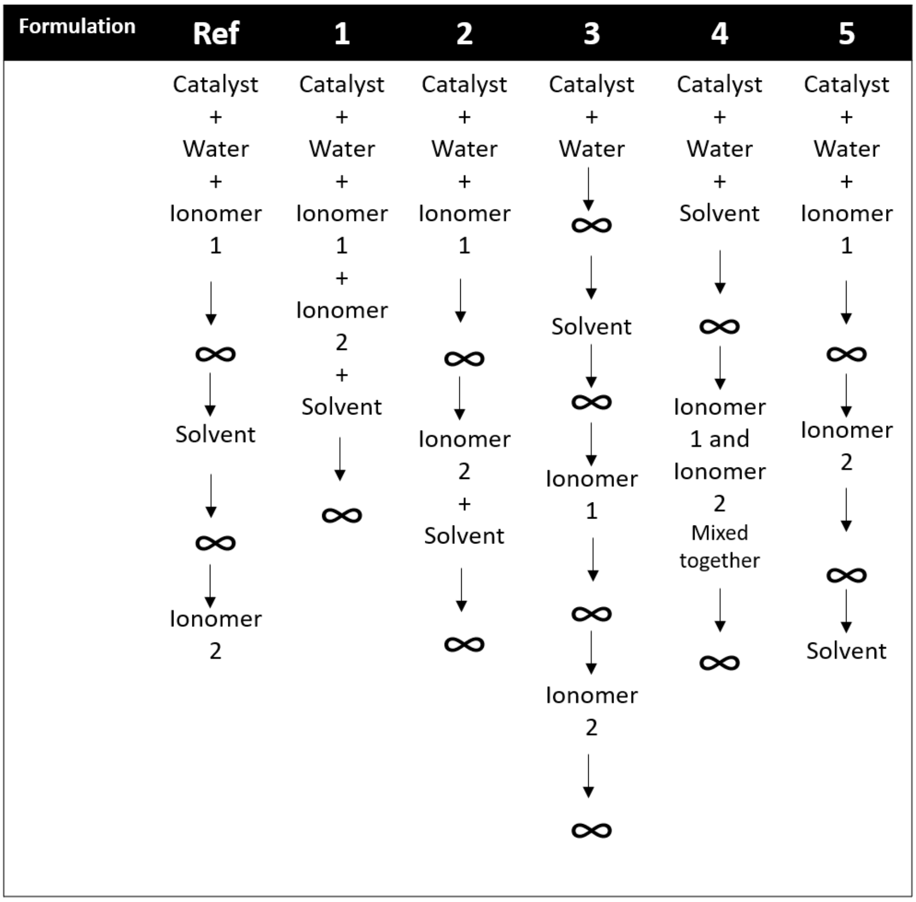

Figure 2. Five formulations carried out to study the order of introduction of components in ink formulation compared to the formulation of reference (Ref).

After being mixed by one of these dispersion processes, at least one day under magnetic agitation is necessary for the mixture stabilization.

2.2. ORDER OF INTRODUCTION

The influence of the order of introduction of the components in the ink was tested to see if any sequence favoured the appearance of agglomerates. The figure 2 shows the different formulations carried out, named from 1 to 5 compared to the formulation of reference (Ref) used before the study in the laboratory. The symbol ∞ corresponds to the moment of the mixing.

The formulation of reference (Ref) corresponds to a first mixing of powder, water and ionomer 1; in a second part, solvent is introduced and another mixing is carried out, ionomer 2 is added at the end. The formulation 1 corresponds to an introduction of all components into the container before dispersion. In formulation 2, ionomer 2 and the solvent are added together before dispersion. The formulation 3 corresponds to a dispersion between each addition of component. The formulation 4 proposes a pre-mixing between the ionomers before added to the mixture of catalytic powder and water. The formulation 5 reverses the order of introduction between ionomer 2 and solvent compared to the formulation of reference.

2.3. CHARACTERISATION

Several characterisations are carried out on the ink. First, a Kinexus rheometer was used to measure the following parameters: viscosity, flow threshold, viscous and elastic moduli. Rheological parameters measurements are essential to make the link between the formulation and the nature of the ink and whether or not it promotes the presence of agglomerates. For example, an ink that is fairly liquid less than 1 Pa.s will tend to sediment and therefore lead to ink heterogeneity. A more viscous ink will tend to be more stable over time.

The viscosity was determined for a shear rate sweep between 1000 s^{-1} and 0,01 s^{-1} and the viscosity value for comparison is noticed at a shear rate of 0,5 s^{-1}. The measure of amplitude oscillation enables to know the behaviour of the sample by measuring elastic (G') and viscous (G'') components. On the graphic, you have to look at the left side of the curves before the deformation becomes too large and destroys the ink. The closer the phase angle between the viscous and elastic moduli is near to 0°, the more the ink will behave like a solid and be stable. The amplitude oscillation measurement was performed for a strain between 0,1 Pa and 100 Pa. The frequency oscillation allows the stability of the ink to be investigated. The lower and the more constant the value of the

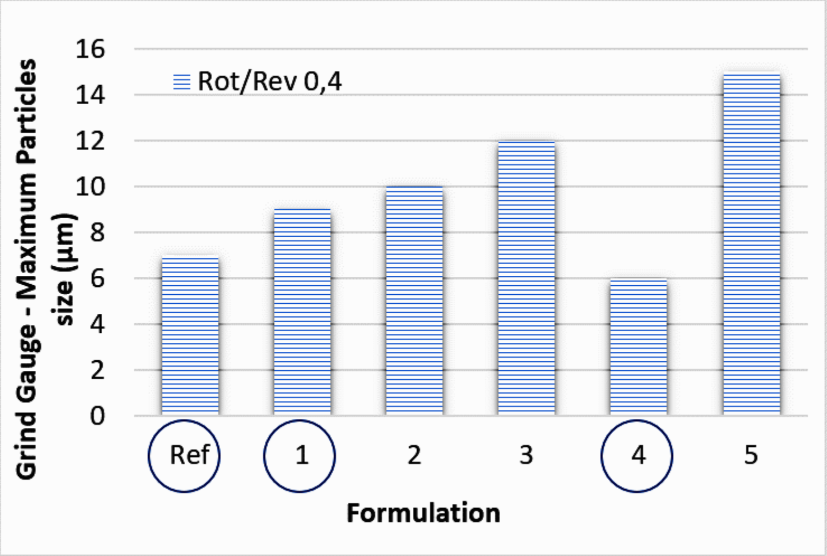

Figure 3. Graphic of the maximum particle size with grind gauge (µm) in function of the six formulations using planetary mixer Rot/Rev 0,4.

"phase angle" between the viscous and elastic components is, the more stable the sample will be and will behave as a solid. The frequency oscillation measurement was performed for frequencies between 0,1 Hz and 100 Hz at different strain values according to the value taken in the constant zone of the amplitude oscillation curves.

A grind gauge gives an idea of the maximum particle size in an ink and enable to eliminate inks with very large sizes. An electro-acoustic probe (EAP) was used to obtain an average particle size distribution in the ink. This ultrasonic scattering method consists in determining the particle size distribution of a non-diluted dispersion by measuring the attenuation of ultrasound at frequencies between 1 MHz and 100 MHz.

After being coated on a PTFE Teflon® substrate using the bar coating, the deposit was observed thanks to a scanning electron microscope (SEM). Agglomerates and homogeneity could be studied.

3. RESULTS & DISCUSSION

3.1. INK CHARACTERISATION

3.1.1. Selection of inks

The order of introduction of components has been modified for each formulation. Characterization was carried out using a grind gauge to eliminate the inks with the largest particle sizes. Figure 3 shows the maximum particles size for the 6 formulations dispersed with the planetary mixer - 0,4 (Rot/Rev 0,4). Formulations 2, 3 and 5 were exited from the rest of the study because of the highest particle sizes and the closed ways of formulation.

Formulations Ref, 1 and 4 were selected based on the results obtained with the grind gauge (minimum particles size) and some more complete characterizations have been done with these formulations.

3.1.2. Particles size and viscosity results

Inks were characterized through EAP to determine the mean particles size and the rheometer to measure the viscosity. Figure 4.(a) shows mean size particles in microns in function of the formulations Ref, 1 and 4 for the four dispersion processes. Figure 4.(b) shows the ink viscosity in function of the formulation Ref, 1 and 4. The reference (Disc Disp.) process is also integrated in these graphs to compare to the other processes with it.

First trend, smaller particle sizes were observed for the other dispersion processes (less than 10µm) compared to the reference process (Disc Disp.) for the formulation of reference (Ref) (around 16 µm), showing an improvement due to the dispersion process. Moreover, the way of dispersing seems to play on the size of the particles. Planetary mixer – 0,9 (Rot/Rev 0,9) allows a more homogeneous dispersion with particle sizes below 1 µm whatever the formulation (figure 4.(a)). Concerning the other dispersion processes, there is a correlation to be made between the formulation and the process because different particle sizes are obtained.

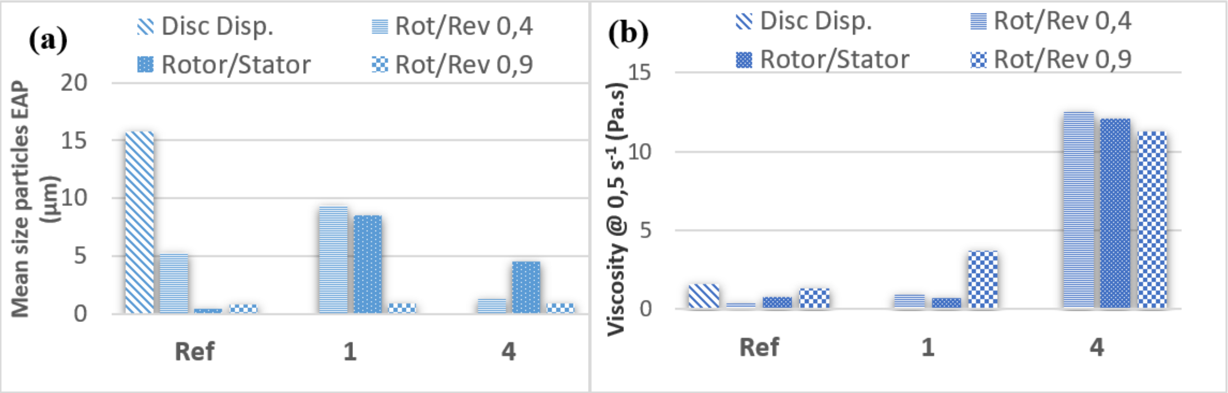

Figure 4. (a) Particle size (µm), (b) Viscosity @ 0,5 s^{-1}(Pa.s), measured for the formulations Ref, 1 and 4 and for the four dispersion processes.

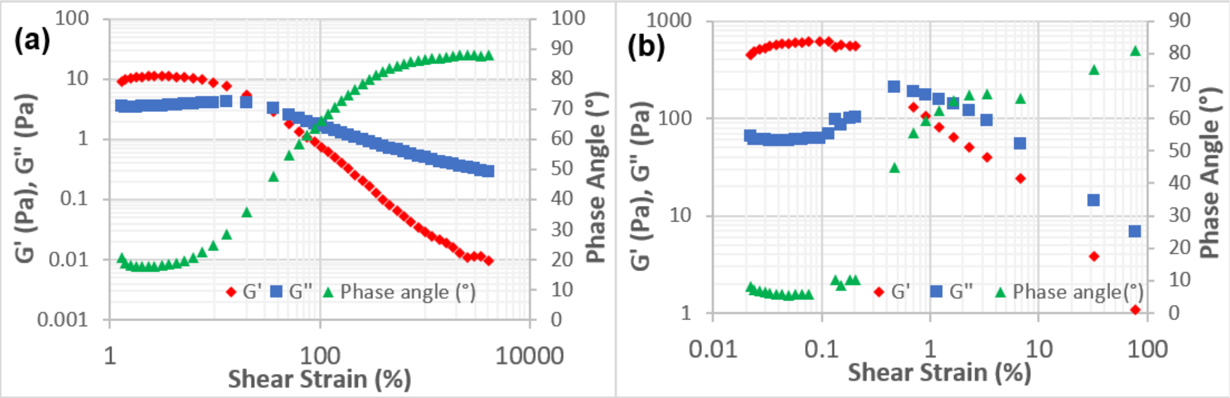

Figure 5. (a) Amplitude oscillation for formulation 1 ((low viscosity: 0,9 Pa.s), (b) Amplitude oscillation for formulation 4 (high viscosity: 12,5 Pa.s), both mixed with the planetary mixer – 0,4 (Rot/Rev 0,4).

Formulation 1 seems not to be adapted for the planetary mixer – 0,4 and rotor/stator processes with mean particles size around 9 µm. This latter was found to have good particle size for formulation Ref (around 900 nm). However, the rotor/stator process will not be held for a number of other reasons. In fact, it seems that it is a suitable method for a very liquid ink with a viscosity of less than 1 Pa.s. The shear performed will allow a better dispersion for a non-viscous ink. However, for our application, we need an ink with a viscosity between at least 10 to 50 Pa.s, adapted to our printing process. On the other hand, the planetary mixer Rot/Rev 0,4 did not have excellent result for the formulation Ref.

Other trends are noticed. Formulation 4 allows to obtain a more viscous ink (between 11 and 13 Pa.s) than the other formulations whatever the processes used (figure 4.(b)). Moreover, it can be seen that the particle sizes are smaller for this formulation 4 in general. One hypothesis would be that pre-mixing the two ionomers increases the viscosity of the ink and the mixing of powder, water and solvent allows a better dispersion of particles at the first step. The ionomers would bind more between the particles, allowing a better interaction and increasing the viscosity of the formulation. This is quite interesting: in fact, according to the printing process, it could be possible to have a more or less viscous ink according to the order of introduction of components.

Viscosity and particle size seem so to be related. The trend is that the particles size will be as smaller as the viscosity will be high. Indeed, more liquid inks (having a viscosity lower than 1 Pa.s) will tend to destabilize more quickly and therefore, the particles are likely to sediment or agglomerate. That is why, it is always recommended to leave under magnetic agitation to avoid sedimentation.

3.1.3. Rheological results

The figure 5 shows amplitude oscillations measured with the rheometer for the planetary mixer Rot/Rev 0,4. It compares the trends between two formulations having significantly different viscosity: formulations 1 with a low viscosity of 0,9 Pa.s and formulation 4 with a higher viscosity of 12,5 Pa.s in the aim to establish a link between viscosity and stability of the ink.

The curves obtained for the oscillation amplitude allow to highlight the viscoelastic behaviour of our inks. However, the fact that the elastic component G' is higher than the viscous component G" shows that the elasticity is preponderant compared to the viscous aspect. The ink is then viscoelastic – solid for the formulation 1 and 4. Nevertheless, we can notice that values of G' are quite different between the two formulations. Formulation 1 has a modulus G' of around 10 Pa, contrary to formulation 4 which has a modulus at around 600 Pa. The higher the value of the elastic component G', the more stable the formulation will be. Indeed, the elasticity maintains the structure of the samples. Moreover, if we compare the phase angles of the amplitude oscillation graphs, we obtain a phase angle of about 18° for formulation 1

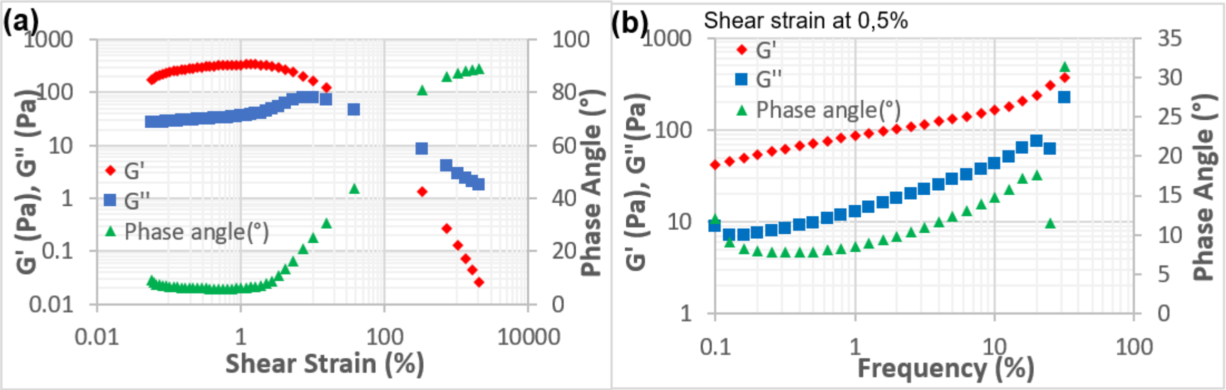

Figure 1: (a) Amplitude oscillation (b) Frequency oscillation for formulation 1 with the planetary mixer – 0,9 (Rot/Rev 0,9)

(figure 5.(a)), compared to a phase angle around 5° for formulation 4 (figure 5.(b)). The closer this curve is to 0°, the more the sample will behave like a solid. We have the solid behaviour/stability and viscosity relationship. Frequency oscillation has also been measured and confirm the non-stability of the less viscous ink.

The two remaining processes are the two planetary mixers with the different ratios. The planetary mixer with a high ratio of 0,9 (Rot/Rev 0,9) presents highly satisfying results whatever the formulation with particle sizes below 1 µm each time (figure 4.(a)). A higher ratio allows a more homogeneous and stable mixture to be obtained over time.

The rheological curves show a more obvious stability for the planetary mixer with a high ratio of 0,9 (figure 6). It shows an angle phase close to 5° on the constant zone in the amplitude oscillation graph. Moreover, the plate is longer as the deformation progresses, characterizing a more stable behavior than the rot/rev 0,4 on figure 5.(a). The frequency oscillation on the right also confirms this statement with a phase angle quite constant at the beginning. These results have also been shown for the formulation of reference (Ref) with a longer plate zone on oscillation amplitude characterizing stability.

In this study, considering the nature of the components used and the ratio between the components, the planetary mixer, more precisely with the ratio Rot/Rev 0,9, seems to be the best method of dispersing inks for catalytic layers for application of screen printing and bar coating processes. It was seen in figure 4.(a) that the particle sizes were particularly small (less than 900 nm) for the three formulations which also have different rheological properties. However, we noticed many differences in structure, especially when the deposition is observed at SEM.

3.2. SEM RESULTS

After being coated on substrate, surfaces of the active layers have been observed with SEM.

3.2.1. Process dispersion comparison

Active layers surfaces made with the reference formulation (Ref) with the four methods of dispersion were observed (figure 7) using a SEM. The mechanical dispersion seems to produce many agglomerates, as well as the planetary mixer with a ratio of 0,4 which present maximum particles size of 80 µm. The high shear rate dispersion (Rotor/Stator) presents a lot of cracks, which makes the layer non-homogeneous. The cracks length can reach 100 µm or more. However, cracks may allow gases to pass through more quickly and also allow water to be evacuated easier. But these cracks are places where chemical reactions cannot take place and, therefore, could produce less energy and be less performant. Moreover, these cracks can create significant deformations in the membrane during the transfer of the active layers

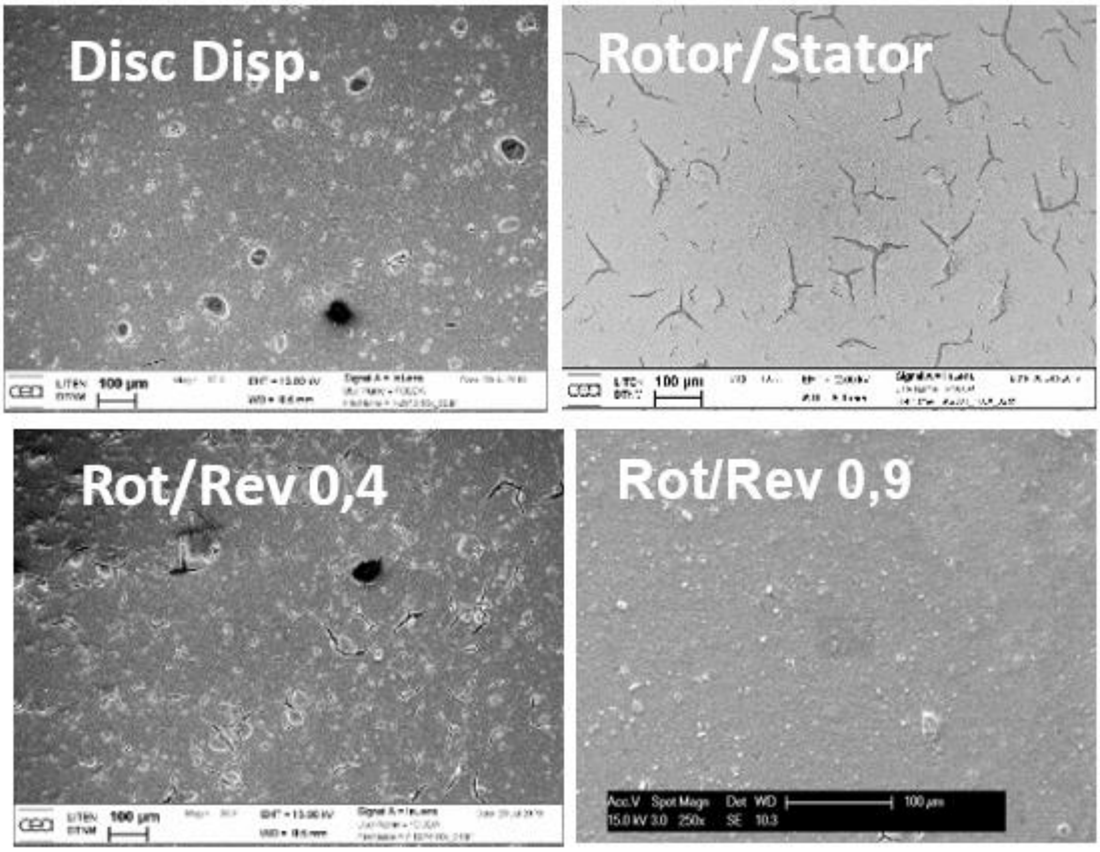

Figure 7. SEM images comparing the different processes for the reference formulation (Ref) (magnification: x250).

to the membrane and create weaknesses and holes. The deposit from which the ink has been dispersed with the planetary mixer – 0,9 presents few agglomerates and the maximum agglomerates size is 20 µm. It is mostly more homogenous. A higher ratio allows to have a better mixing of the ink and to not create agglomerates.

These images appear to correlate well with trends obtained from the EAP. However, the size of particles measured at the SEM do not match. The size of the agglomerates observed on SEM are higher than the one measured with the EAP. Other factors may come into play, such as drying conditions, which may also promote cracks and agglomerates.

The results appear to be good for the planetary mixer – 0,9. The results in section 3.1 showed that the particle sizes were relatively small regardless of formulations Ref, 1 and 4. However, rheology's parameters are different.

3.2.2. Formulation comparison using planetary mixer Rot/Rev 0,9

The figure 8 shows the active layer surface observed at SEM for the formulations 1 and 4 compared to the reference formulation (Ref) for a same dispersion process, the planetary mixer Rot/Rev 0,9. The aim is to show the impact of the order of component introduction into the ink for a same dispersion process. The pictures show that formulation 1 presents many heterogeneities (maximum size of agglomerate: 40 µm). Formulation Ref and 4 have also agglomerates but the surface is mostly more homogeneous with a maximum agglomerates size of 20 µm. In a general way for the observed samples, the maximum size measured on the SEM surfaces doesn't correlate, in term of value, with the maximum size particle measured with the EAP. This can be explained by the fact that the parameters of the coating process cannot be optimized and can lead to particles

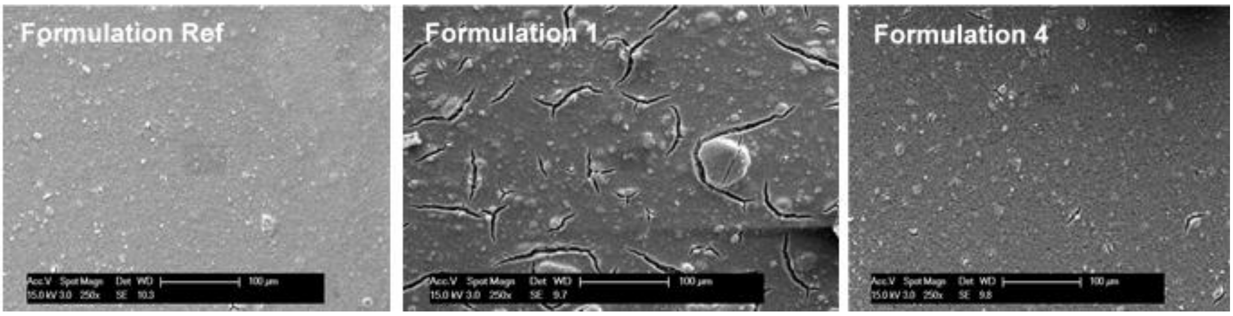

Figure 8. SEM images comparing formulations Ref, 1 and 4 for the planetary mixer 0,9 (magnification:x250).

agglomeration. The deposition method, the drying temperature and speed as well as the evaporation temperature of the solvent can influence on faults. If this latter is too high or too low, cracking or clumping may occur.

However, formulation of reference and formulation 4 could may both be suitable to the planetary mixer 0,9 to have a homogenous active layer. But if we look at rheology and especially the viscosity of inks, our application in screen printing or bar coating would more suit with a high viscosity. The formulation 4 will so be more adapted.

4. CONCLUSION & PERSPECTIVES

This study has dealt with the way of formulating the active layer's ink: the order of introduction of components but also the way to disperse. It was carried out on an ink including two ionomers. Better results were obtained for processes other than the reference process (Disc Disp.) for the reference formulation (Ref). Three other processes of dispersion were tested. They differ by their methods (high shear rate, planetary mixers….) but also by their mixing speed (ex: planetary mixers with ratio rotation/revolution 0,4 and 0,9). A higher ratio and speed have demonstrated that the ink could have a better homogeneity both in ink and on deposit. The planetary mixer with a ratio Rot/Rev 0,9 process was chosen as the most appropriate in our situation.

In addition, the particle size can be reduced thanks to the order in which the components are introduced. It has shown that formulation can play on rheological parameters, as the viscosity or the stability of the ink by interpreting the amplitude and frequency oscillations. The particle size seems to be linked to the viscosity: higher is the viscosity, smaller will be the particles. Moreover, the formulation 4, allowing a high viscosity due to a dispersion of the catalyst in the water and solvent and a pre-mixing between the ionomers, was also found to be suitable for our coating method.

To go further in this study, cross sections of catalytic layers are going to be made to observe and characterize the structure of the active layer. Single cell performance tests will also be carried out in order to see the impact of all these parameters and in particular the agglomerates.

REFERENCES

[1] Hui Xu, Chao Lei, Zachary Green, Tom McCallum, *Ionomer Dispersion Impact on Fuel Cell and Electrolyzer Performance and Durability (SBIR Phase II TTO)*, Department of Energy, Auburndale USA (2018).

[2] Eunae Lee, Do-Hyung Kim, Chanho Pak, *Effects of cathode catalyst layer fabrication parameters on the performance of high-temperature polymer electrolyte membrane fuel cells,* Graduate Program of Energy Technology, School of Integrated Technology, Institute of Integrated Technology, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea (2020).

[3] De-Chin Huang, Pei-Jung Yu, Feng-Jiin Liu, Shu-Ling Huang, Kan-Lin Hsueh, Yen-Cho Chen, Chun-Hsing Wu, Wen-Chen Chang, Fang-Hei Tsau, Effect of Dispersion Solvent in Catalyst Ink on Proton Exchange Membrane Fuel Cell Performance (2011).

[4] Mathieu Lepesant. Catalyseurs multimétalliques nano-organisés pour pile à combustible PEM. Matériaux. Université de Grenoble, 2014. Français. ffNNT : 2014GRENI052ff. fftel-01131225f

[5] Tae-Hyun Kim, Jae-You Yi, Chi-Young Jung, Euigyung Jeong, Sung-Chul Yi, *Solvent effect on the Nafion agglomerate morphology in the catalyst layer of the proton exchange membrane fuel cells*, (2016).

[6] Min Wang, Jae Hyung Park, Sadia Kabi, K.C. Neyerlin, Nancy N. Kariuki, Haifeng Lv, Vojislav R.

Stamenkovic, Deborah J. Myers, Michael Ulsh, Scott A. Mauger, *The Impact of Catalyst Ink Dispersing Methodology on Fuel Cell Performance Using In-situ X-ray Scattering,* Chemistry and Nanoscience Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, Colorado, 80401, United States.

[7] Clayton Jeffery Jacobs, *Influence of catalyst ink mixing procedures on catalyst layer properties and in-situ PEMFC performance,* Centre for Catalysis Research Department of Chemical Engineering University of Cape Town March, 2016.