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DURABILITY EVALUATION OF INNOVATIVE FEP-BASED GAS DIFFUSION MEDIA FOR PEM FUEL CELLS

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Abstract **– Gas diffusion medium (GDM) is a fundamental component for a PEM fuel cell because its main function is to avoid flooding of the whole device. In this work, different amounts of fluorinated ethylene propylene (FEP) and carboxymethylcellulose (CMC) were used in GDMs preparation. Ex-situ chemical and mechanical accelerated stress tests (ASTs) were developed in order to assess durability of prepared materials. The highest amount of FEP in GDMs allowed to get the best performance. Moreover, the presence of CMC allowed to reduce overall ohmic resistance. A satisfying durability can be claimed since GDMs hydrophobicity, ohmic and diffusion resistances, kept quasi-constant after the different ASTs.**

Index Terms **– PEM fuel cells, gas diffusion media, durability, accelerated stress test.**

I. INTRODUCTION

Water management in polymer electrolyte membrane fuel cells (PEMFCs) is a crucial aspect which must be properly addressed in order to have high and constant efficiency during device operation [1]. This task is accomplished by gas diffusion medium (GDM). It is formed by a carbon cloth macro-porous substrate (gas diffusion layer, GDL) and a micro-porous layer (MPL) made from an ink and coated onto GDL [2].

Currently, MPLs are mainly prepared from inks containing carbon black particles and PTFE, the latter used as a hydrophobic agent [2]. Recently, authors proved that replacing PTFE with fluorinated ethylene propylene (FEP) is effective in improving mass transport properties and water management of the whole system. In this work different amounts of FEP were used, both for GDL and for MPL hydrophobization. Carboxymethylcellulose (CMC) was also employed both in inks preparation and in final MPL consolidation in order to have a better adhesion and durability. Durability is still a critical issue to be faced in fuel cells field in order to have a widespread commercialization of these devices. Thus, ex-situ chemical and mechanical accelerated stress tests (ASTs) were developed. Morphological and electrochemical tests were carried out on GDMs upon different times of ASTs, up to 1000 h.

II. EXPERIMENTAL WORK

Inks containing FEP, already proven to be superior to PTFE-based ones [3], were prepared. Thus, on the basis of the preparation route described in [3], a slurry was formulated mixing a FEP-containing dispersion (55 % wt), in deionized water; then, carbon black (Vulcan XC72R) was slowly added. The mixture was vigorously stirred by a high shear mixer at 8000 rpm for 10 minutes. CMC was added as a rheology controller on the basis of a previous work [4]. First of all, performance of CMC-free samples were evaluated. The so-obtained inks were deposited onto FEP pre-treated GDL substrates via the blade coating technique to form micro-porous layers [3]. Finally, the samples were calcined up to 260 °C to remove water, alcohol and to sinter FEP [3]. The chemical AST was performed by soaking GDMs in a 20 % v/v sulfuric acid solution at pH equal to 0, far below the typical pH value (2-3) of the running cell environment, for a total time of 1000 h. The mechanical AST was carried out on the basis of a recent literature study [5], but a simpler system was developed with a dummy cell consisting of GDMs both at the anodic and cathodic side, separated by a Nafion 212 plain membrane, i.e. without any catalyst, in order to avoid any possible electrochemical stress. Only air was fed on either side at a flow rate of 2 NL/min, considerably higher than those employed during standard running (0.2 and 1.0 NL/min for hydrogen and air, respectively) for accelerating mechanical degradation. This air stream was fully humidified (RH: 100 %). Even for mechanical AST, total time was 1000 h.

Electrochemical tests were performed in a single lab-scale (25 cm^2) cell at 60 °C with different relative humidities.

Electrochemical Impedance Spectroscopy (EIS) was carried out and the experimental data were analyzed and fitted using an equivalent circuit model (ZView® software).

III. Results and Discussion

GDMs containing the maximum amount of FEP, i.e. 12 % wt, allowed to obtain the best electrochemical performance. Indeed, as it can be observed from Table I, fuel cell assembled with such samples achieved the highest output power density and the lowest diffusion resistance. Such a finding may be due to the higher hydrophobicity, resulting from static contact angle measurements. A better water-repellency should be the reason of a more efficient removal of the excess water, produced by the cathodic reduction reaction.

TABLE I
Main properties of FEP based GDMs and results of electrical tests

Sample	P [W·cm^{-2}]	R_d [Ω·cm^2]	C.A. [°]	η (0 h)	η (1000 h) chem. AST	η (1000 h) mech. AST
FEP 12 %	0.42	0.143	155.4	0.382	0.372	0.369
FEP 9 %	0.40	0.19	150.1	0.365	0.332	0.319
FEP 6 %	0.39	0.25	149.2	0.359	0.316	0.294

Moreover, GDM FEP 12 % showed a better durability with respect to that one of the other samples, since global efficiency, calculated at 0.5 A·cm^{-2}, keeps quasi-constant after 1000 h of both chemical and mechanical AST.

Then, a sample with the same composition was prepared, soaked in a 0.75 % wt CMC solution and then thermal treated at 260 °C for 30 min. Fig. 1 shows polarization and power density curves obtained at 60 °C and RH 80-80 (A-C) for fuel cells assembled with GDMs containing and non-containing CMC. Moreover, both ohmic (Rs) and diffusion resistances (Rd) are reported as a function of current density.

From Fig. 1, it is clear that the presence of a CMC upper layer improves performance, particularly in the ohmic zone of the V-I curve, i.e. a lower slope with CMC-containing samples is evident. This behavior is due to the hydrophilic nature of CMC which acts as a water reservoir leading to a better hydration of the polymeric membrane; accordingly, a higher protonic conductivity and a lower ohmic resistance are obtained. Indeed Rs trend of CMC-coated GDMs as a function of current density confirms this: it is always lower than non-containing CMC samples. As expected, Rd increases upon increasing current, due to a greater water production. However, such an increase is absolutely limited and satisfying, since lower values than conventional PTFE-based [3] GDMs were obtained for both types of GDMs.

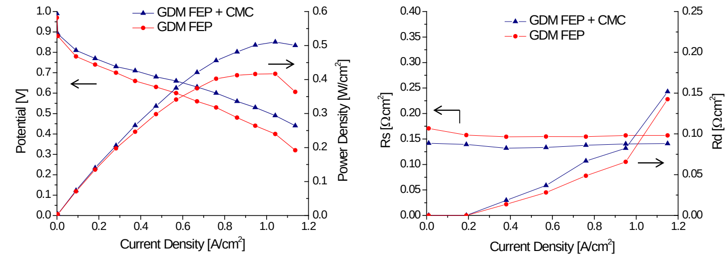

Fig. 1. Polarization and power density curves (left) and ohmic and diffusion resistances (right) as a function of current density of FEP based (12 % wt) GDMs with and without CMC.

Chemical and mechanical ASTs are in progress for CMC-based samples. Early results demonstrate that efficiency keeps constant as well as that one of no CMC samples. Anyway, final results about this part of the work will be showed during the conference.

IV. Conclusion

In this work FEP, which had been already demonstrated to be a better hydrophobic agent than traditionally employed PTFE, was used in different concentration in the preparation of GDMs for PEMFCs. The best performance in terms of maximum power density, fuel cell efficiency and durability, upon running the cell for 1000 h of ASTs, was achieved with the GDM with the highest FEP content (12 % wt). Then, CMC-based GDMs with the same content of FEP were also tested. CMC was effective in reducing overall ohmic resistance, thus improving the global performance of the device. Early durability tests on such samples pointed out constant electrochemical parameters and efficiency.

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