Novel Superhydrophobic Gas Diffusion Media for PEM Fuel Cells: Evaluation of Performance and Durability

Saverio Latorrata*, Paola Gallo Stampino, Cinzia Cristiani, Giovanni Dotelli

Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy
saverio.latorrata@polimi.it

Micro-porous layer (MPL) is a crucial component for an efficient water management in Polymer Electrolyte Membrane Fuel Cells (PEMFCs). Nowadays, MPLs are obtained by depositing a dispersion, commonly known as ink, containing carbon black particles and PTFE onto a carbon cloth substrate. In this work PTFE was replaced by an innovative fluorinated polymer in order to improve hydrophobic properties of MPLs and consequently the water management of the whole system. Moreover, carbon nanotubes (CNTs) partially substituted carbon black in ink formulation. The new polymer allowed to decrease considerably the treatment temperature (260 °C) with respect to the one necessary with conventional samples based on PTFE (350 °C). Fuel cells assembled with the sample containing CNTs showed better performances than those obtained with traditional CNTs-free MPLs. Durability of the most performant sample was assessed. Ad-hoc Accelerated Stress Tests (ASTs) were developed; they showed that the main degradation for MPL is due to mechanical stresses, caused by reactants and water flow, which leads to detachment of materials and to a consequent dramatic mass transfer resistance increase.

1. Introduction

Currently fuel cells are considered as one of the most promising devices for green-energy production for both portable and stationary systems (Gallo Stampino et al., 2013, Ismail A. et al., 2012). Among the wide variety of available technologies, polymeric electrolyte membrane fuel cells (PEMFCs) have been largely studied by research groups worldwide, leading to a continuous optimization of each component of the device. In order to make these devices competitive with internal combustion engines, among others, the durability is a key point to be assessed. However, currently the lifetimes of fuel cell vehicles and stationary cogeneration systems are around 2000 h and 10000 h, respectively. Clearly, an intensive research is still needed to address the issues related to PEMFCs durability or degradation in order to achieve a sustainable commercialization.

Gas Diffusion Medium (GDM) is a fundamental component in the PEMFC assembly because it has to guarantee an efficient water management to the whole device. It is formed by a macro-porous carbon cloth substrate, the gas diffusion layer (GDL), and by a micro-porous layer (MPL) coated onto GDL and consisting of carbon particles mixed with a hydrophobic agent, such as PTFE. It has been widely demonstrated that their use led to a considerable improvement of global performances of the devices, allowing to enhance reactant and water transport, electronic and thermal conduction and providing mechanical support (Park et al., 2012). However, at the state of the art, there is no established procedure dealing with durability of these components (Zhang et al., 2009). Therefore, the development of a fast standardized method to evaluate the degradation phenomena of the components would be desirable. Studies about the GDM degradation already available in the literature (Ha et al., 2011) demonstrated a loss of hydrophobicity and some changes in porosity when they are processed with a sulfuric acid solution at medium-temperature. Both GDM modifications result in an increase of the retained water content thus impeding gas mass transport (Pasaogullari and Wang, 2004, Weber and Newman, 2005).

The effect on water management of the different MPL components has been extensively investigated during the last decade (Park et al., 2012) and carbon powder quality, wettability, carbon loading, thickness

and porosity were suggested to be responsible for the final MPL properties. Much less attention has been paid on the nature of the hydrophobic agent, keeping PTFE as the main choice for that purpose. Some works reported the use of different polymers such as fluorinated ethylene propylene (FEP) (Kandlikar et al., 2011, Lim and Wang, 2004), polyvinylidene fluoride (PVDF) (Cabasso, 1998) and perfluoropolyether (PFPE) (Stampino et al., 2012, Gallo Stampino et al., 2013). However, they were proposed only to treat GDLs to make them more hydrophobic than PTFE-based substrates. In a very recent study (Latorrata et al., 2014), authors have already demonstrated the effectiveness of the replacement of PTFE with FEP in getting better performance and lower mass transfer resistances.

In this work, details about the development of ex-situ accelerated stress tests (ASTs), both chemical and mechanical, to study the GDMs durability are given on optimized samples composition. Indeed, carbon nanotubes (CNTs), partially replacing carbon black in the MPL ink formulation, were added in order to achieve a better conductivity of the final sample and, as hydrophobic agent, FEP was employed being able to reduce diffusive limitations during the running of the fuel cell (Latorrata et al., 2014).

2. Experimental

A slurry was formulated by mixing a FEP-containing dispersion (DuPont) and isopropyl alcohol (Sigma-Aldrich) in deionized water; then carbon black (Vulcan XC72, Cabot) and multi-wall carbon nanotubes (Nanothinx NTX1) were slowly added. The mixture was vigorously stirred and homogenized by a high shear mixer (UltraTurrax T25) at 8000 rpm for 10 minutes. On the basis of previous works (Latorrata et al., 2014, Guilizzoni et al., 2013), the following ink composition was selected: $(CB+CNTs)/H_2O=0.13$ [w/w], $FEP/(CB+CNTs)=0.12$ [w/w] and $(CB+CNTs)/IPA=5.6$ [w/w], $CNTs/CB=0.1$ [w/w]. Another ink, with the same composition, except for the presence of CNTs, was prepared for making comparisons possible. The obtained inks were deposited onto FEP-hydrophobized GDL substrates via the blade coating technique (velocity of 15.4 mm/s, gap of 40 μm, shear rate of about 350 s^{-1}). Finally, the coated samples were calcined up to 260 °C to remove water, IPA and to sinter FEP (Latorrata et al., 2014).

The samples hydrophobicity was assessed by static contact angles measurements according to the sessile drop technique using an OCA 20 Dataphysics instrument (Latorrata et al., 2012). Scanning electron microscope (Cambridge Stereoscan 360) was used for the morphological analyses of both surface and cross-section of the GDMs.

Electrochemical tests were carried out at two temperatures (60 °C and 80 °C) and two relative humidities (80-100% and 80-60%, anode-cathode). A commercial Catalyst Coated Membrane (Baltic Fuel Cells), consisting of catalyst layers (active area of 23 cm^2) directly coated onto a 50 μm thick Nafion membrane, was employed. Polarization curves were recorded under galvanostatic conditions in the current density range from OCV to 1.32 A/cm^2, with steps of 0.09 A/cm^2. In the same range, EIS was carried out using a Frequency Response Analyzer (FRA, Solartron 1260). All spectra were obtained over a frequency range of 0.5 Hz–1 kHz. All the experimental data were fitted using the Zview® software (Scribner Associates) by using equivalent circuits in order to determine the different contributions to voltage losses (i.e. ohmic resistance, charge transfer resistance and mass transfer resistance). Evaluation of durability was also performed by keeping the fuel cell at constant current density (0.5 A·cm^{-2}) for about 1000 h, monitoring voltage trend as a function of time.

Both chemical and mechanical degradation can occur in GDMs during fuel cell operations. Chemical degradation can be generated by carbon corrosion and/or polymer decomposition, while mechanical degradation, mainly due to gases flow in presence of water, is related to detachment of material, in particular carbon layers of the MPL. Thus, two different separated ex-situ experiments were designed to analyze the effect of each degradation phenomenon. The chemical AST was performed by soaking GDMs in a 20% v/v sulfuric acid solution for a total time of 1000 h. This harsh condition would accelerate the chemical degradation of GDMs. Changes in physical-chemical and morphological properties of the samples were assessed at intermediate ageing times over the whole test period, and, in addition to that, the performance of fuel cells assembled with aged GDMs was tested too.

The mechanical AST was developed on the basis of a recent literature study (Chun et al., 2012). A dummy cell was created consisting of two 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 and degradation. 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 NL/min for hydrogen and air, respectively) for accelerating mechanical degradation. In the case of the mechanical AST, GDMs properties were evaluated only at the end of the ageing treatment, i.e. 1000 h. Operating conditions after ASTs were set at 60 °C and RH (A-C) 80-100%, where the best performances were obtained in standard conditions.

3. Results

Polarization and power density curves obtained for fuel cells assembled with both the CNTs-containing GDMs and the CNTs-free ones are shown in Figure 1. It is clear that the best performances, at any operating condition, are found for the CNTs-containing sample. At 60 °C and high cathodic RH (Figure 1a), such a GDM was able to guarantee the highest power density value, 0.7 W/cm^2. In addition to that, in the medium current density region, it exhibits the lowest slopes of the polarization curves, which implies the lowest ohmic resistances. These behaviours are clearly due to the considerably higher conductivity of CNTs with respect to conventional carbon black powder. However, no further increase above 10% wt of the CNTs content was considered acceptable from an economical point of view: CNTs are very expensive and the 10% concentration, here adopted, is an optimal compromise between costs and performances. MPLs based on CNTs also showed higher voltages in the high current densities region and consequently lower concentration polarizations, even though it was demonstrated (Latorrata et al., 2014) that also MPLs with the same amount of FEP and without CNTs in the ink formulation are able to reduce considerably mass transfer resistances in such a region. After conventional electrical tests for obtaining polarization curves, fuel cell assembled with the CNTs-based GDMs was run at constant current density (0.5 A/cm^2) for 1000 h in order to test their durability. Only one operating condition was employed, namely 60 °C and RH 80-100%, i.e. at which the best performance in terms of output power and polarization was achieved. The value of current density for the test was selected in order to replicate the working condition of commercial prototypes for energy generation.
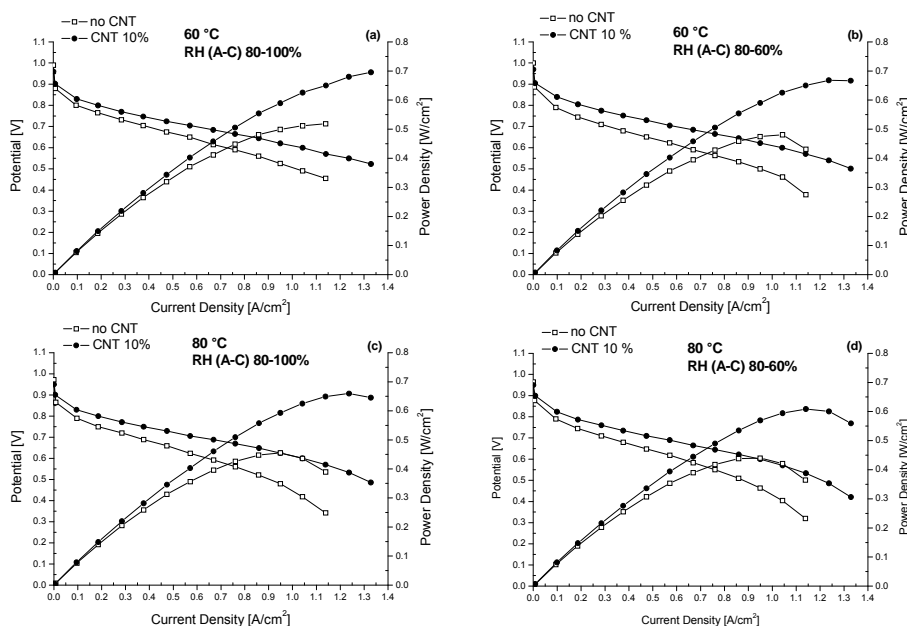

Figure 1: Polarization and power density curves obtained for fuel cells assembled with GMDs containing and non-containing CNTs. Operating condition: a) 60 °C, RH (A-C): 80-100%; b) 60 °C, RH (A-C): 80-60%; c) 80 °C, RH (A-C): 80-100%; d) 80 °C, RH (A-C): 80-60%.

A very good durability of these new materials combination is found. Indeed, Figure 2 shows, for the best performing sample (i.e. MPLs based on 10% wt of CNTs), the different polarization curves and electrochemical parameters from impedance spectroscopy evaluated after each week of running at constant current, until reaching the 1000 h to complete the experiment. No sensible variation on performance occurred during testing in the whole range of current densities, suggesting that also the electrochemical parameters kept constant over the time, as shown by the behaviour of the ohmic resistance, the charge transfer resistance and the mass transfer resistance. Ohmic resistance did not show any sensible variation during constant current durability tests, revealing that no evident contribution of GDM to changes in contact resistances or global conductivity occurred. The quasi-constancy of the charge transfer resistance along the tests at different times demonstrated that electrodes activity was not affected during these tests. Mass transfer resistance, as expected (Latorrata et al., 2014), increased upon increasing current density because of the diffusive limitations arising from the larger water generation. For

this parameter, after 840 h, a small variation between different tests begins to be visible, however it is not enough to cause an appreciable decrease of the global system performance.
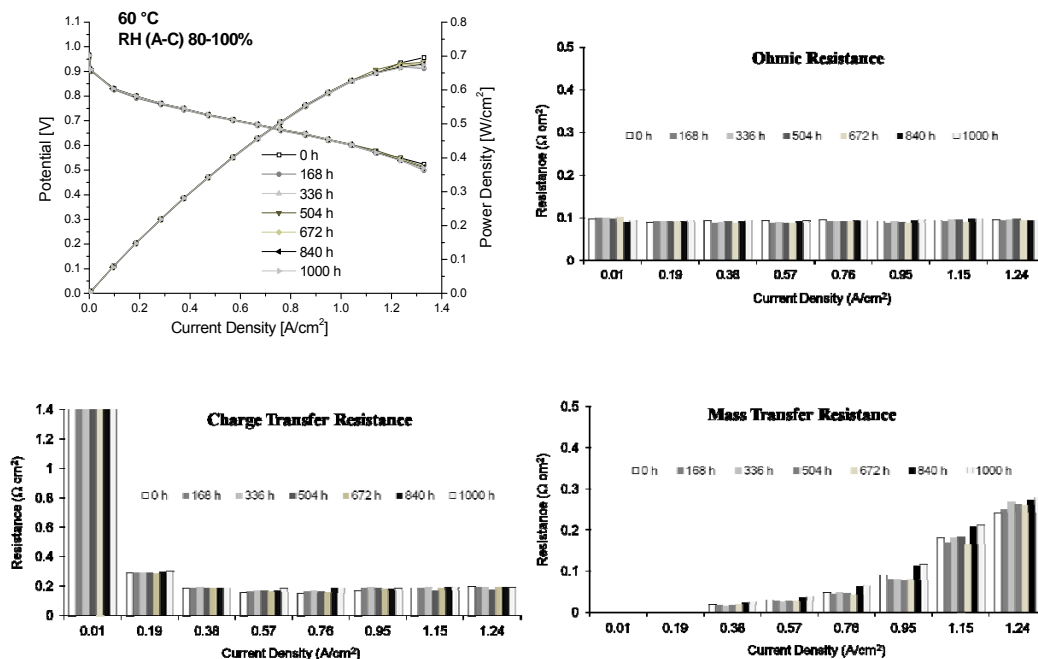

Figure 2: Polarization, power density curves and electrochemical parameters from EIS, obtained at different times of constant current durability tests.

In order to get information on materials response upon prolonged running under operating conditions as well as on the degradation mechanism, chemical and mechanical ASTs were applied; the tests were performed on the best performing samples, i.e. GDMs with 10% wt of CNTs. In Figure 3, the performances of the untreated GDM is compared with those of the mechanically and chemically degraded ones, upon 1000 h of experiments.
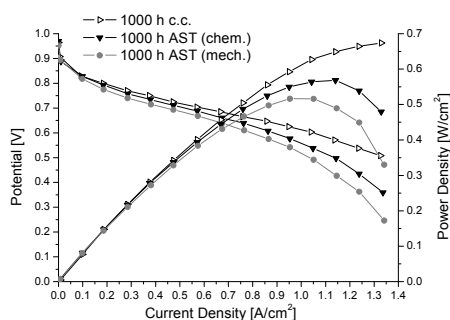

Figure 3: Polarization and power density curves of fuel cells assembled with untreated GDM, chemically degraded GDM and mechanically degraded GDM after 1000 h of experiments.

It is clear that the mechanical AST caused more serious damages in GDM than the chemical one, since polarization and power density curves of the mechanically aged sample showed the worst performances, particularly at high current density; therefore, it can be inferred that mechanical degradation plays a more significant role in determining the increase of mass transfer resistances and the consequent diffusion limitations.

In Figure 4, the ohmic resistance and the mass transfer resistance obtained for untreated GDMs (upon 1000 h of constant current test), for chemically stressed (1000 h) and for mechanically stressed (1000 h) GDMs are plotted as a function of the current density.

It is clear that mechanically stressed GDMs, with the highest ohmic resistance, are the worst performing samples. The trend of the mass transfer resistance confirmed that the mechanical degradation induces much more negative effects on the performance of the running fuel cell than the chemical one.
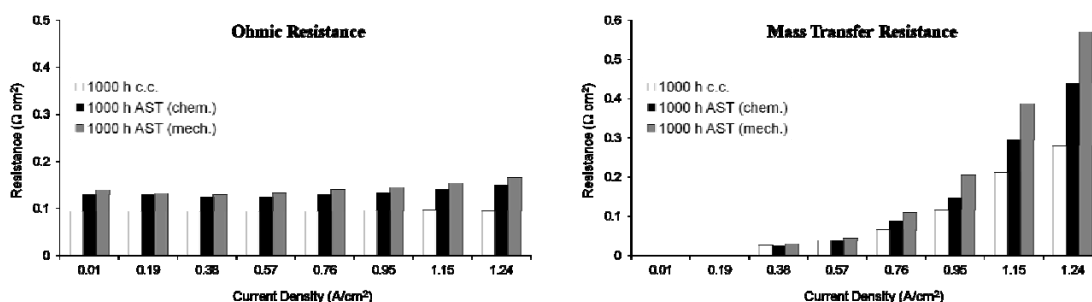

Figure 4: Behaviour of the ohmic resistance and of the mass transfer resistance as a function of the current density of fuel cells assembled with fresh (run at constant current for 1000 h), chemically degraded (1000 h) and mechanically degraded GDMs (1000 h).

All these evidences on electrical performances could be reasonably ascribed to a worsening of physical-chemical properties of the GDMs constituent materials. In order to find a possible correlation degradation-materials properties-performances, SEM images and static contact angles measurements were performed, aiming to determine the effects of both running time and ASTs on GDMs final quality.

Figure 5 shows that the degradation induced by mechanical AST caused more evident damages on the MPL surface: the continuous gas flow led to erosion and detachment of large part of the MPL, thus worsening the effectiveness in water removal and increasing the mass transfer resistance. Chemical AST did not deteriorate the MPL in the same way of mechanical one, even though, after 1000 h of ageing, some deep and large cracks become manifest. Anyway, the measured total weight loss of the chemically-stressed sample was 3% (w/w) to be compared with that of the mechanically-stressed sample equal to 20% (w/w).
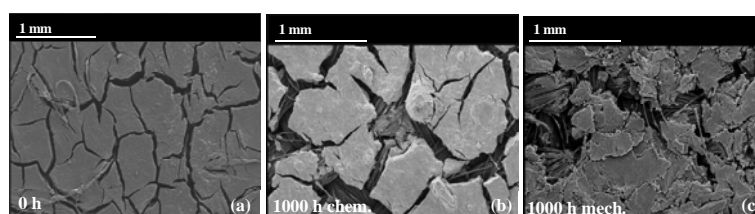

Figure 5: SEM images of fresh GDM (a), chemically degraded (b) and mechanically degraded GDM (c).

These images are also helpful to explain the negative changes of the running cell parameters observed with EIS for samples upon ASTs: material losses and detachment cause surface unevenness, leading to a worse contact between the MPL and the catalyst layer, therefore increasing the overall fuel cell ohmic resistance, particularly in the case of mechanically stressed GDM, the most damaged GDM.

However, no dramatic changes in mean static contact angles were observed (see Table 1) after ASTs with respect to the value measured for the fresh sample. This behaviour could possibly help to state that hydrophobicity is not the only key parameter to be optimized for water management. If this was the case, no marked effect on mass transfer resistances had to be detected, even in case of the mechanically stressed GDMs. Thus the efficiency in water management seems to be mainly due to the morphology of the surface and to the presence of the microporosity due to the carbon layer of the MPL.

Table 1: Static contact angle (average value and standard deviation) for fresh GDM, chemically degraded GDM and mechanically degraded GDM after 1000 h of experiments.

Fresh GDM	After Chem. AST	After Mech. AST
158° ± 2°	147° ± 5°	148° ± 5°

4. Conclusions

In this work, FEP as hydrophobic agent and highly conductive CNTs have been used to modify traditional formulation of inks to obtain MPLs. Samples based on CNTs showed improved electrical performances with respect to MPLs formulated with pure carbon black. Also a satisfying durability was achieved for this GDM upon running the cell for 1000 hours of tests at a constant current density value (i.e. 0.5 A/cm^2).

Ad-hoc chemical and mechanical ASTs on the most performant GDM resulted in a significant increase of both ohmic and mass transfer resistance and in sharp voltage losses mainly in mechanically stressed GDM.

By observing the MPLs surfaces after ASTs, it is clear that the mechanical degradation causes more damages with respect to chemical one.

The increase of mass transfer and ohmic resistances is more likely due to surface damages and loss of material, induced by ASTs, than changes in hydrophobicity, that is fairly preserved.

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