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Effect of Different Hydrophobic Agents onto the Surface of Gas Diffusion Layers for PEM-FC

Paola Gallo Stampino[a,*], Riccardo Balzarotti[a], Cinzia Cristiani[a], Giovanni Dotelli[a], Manfredo Guilizzoni[b], Saverio Latorrata[a]

[a] Politecnico di Milano - Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta"
p.zza L. da Vinci 32, 20133 Milano Italy.
[b] Politecnico di Milano - Dipartimento di Energia, via Lambruschini, 4, 20156 Milano, Italy.
*paola.gallo@polimi.it

In the present work two different hydrophobic agents (i.e. a Perfluoropolyether derivative, PFPE, and a Polytetrafluoroethylene, PTFE) were used to treat the surface of a carbon cloth gas diffusion layer (GDL) . Commercially available products were used in both cases, namely Fluorolink® P56 (supplied by Solvay Solexis s.p.a., Italy) for PPFE and Algoflon® D 1214X (supplied by Solvay Solexis s.p.a., Italy) for PTFE. The behaviour of the PFPE-based hydrophobic coating was compared with that of a standard PTFE one. The properties of a GDL coated with about 1 % wt of PFPE were analysed and compared with those of a 10 % wt PTFE coated GDL. Wettability of the PFPE- and PTFE-based surfaces were analysed by means of contact angle measurement. A simplified axisymmetric drop shape analysis technique was used on sessile drops. Static contact angles and contact angle hysteresis were evaluated at ambient temperature, at 60 °C and at 80 °C. Drop evaporation at the three temperatures was also evaluated. Both the surfaces were found to be highly hydrophobic.
The obtained GDLs were used in a single fuel cell and tested in a lab scale. The cell testing was run at two temperatures (60 °C and 80 °C) with a relative humidity (RH) of the feeding gases of 80/100 %, Hydrogen/Air, respectively. The new PFPE coating sensibly improved the cell performances, and this effect was more evident at 60 ° C than 80 °C.

1. Introduction

A fuel cell (FC) is an electrochemical device, which can produce electricity without the emissions common to combustion processes (Bertei et al. 2009); the main benefits of FC include for example the highest energy efficiency (50–60 %) in the conversion of fuel (typically H_2 and air) to energy (Ismail et al. 2012) and environmentally friendly emissions (water) (Carrette et al., 2001).
Polymer Electrolyte Membrane or Proton Exchange Membrane (PEM) Fuel Cells are nowadays the best choice for portable applications, small-scale distributed power generation and automotive applications.
The membrane electrode assembly (MEA) is the heart of the cell; it is made of a *proton exchange membrane* and two electrode (i.e. anodic and cathodic layers) (Barbir, 2005). Inside the cell the MEA is typically inserted into two bipolar plate (BP). Moreover, a gas diffusion layer (GDL) is inset between the BP and the MEA (Lister and McLean, 2004).
The GDL is a crucial component; it has an important role in the water management, particularly at higher current density when the cell produces a lot of water (Cindrella et al., 2009). Furthermore, it must control the transportation of reactant gases from the flow field to the catalyst layer (so it has to be porous) which has to be homogeneous (Kimball et al., 2010), it has to transport electrons from the bipolar plate to the catalyst (electrically conductive) (Wilde et al., 2004), to conduct heat from the catalyst to the cooling channels in the bipolar plate (thermally conductive) (Nitta et al., 2008) and to manage the removal of reaction products (both liquid and gas) from the catalyst (hydrophobic) (Stampino et al., 2011). Carbon fiber-based materials, i.e. carbon clothes and carbon papers, due to their high porosity and electric conductivity are the best choice to be used inside the cell (Stampino et al., 2008). An important properties

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of GDLs is the hydrophobicity, as it should avoid flooding in their porous microstructure. Typically, the GDLs, both anodic and cathodic side, are coated with an hydrophobic agent, usually a fluoropolymer such as polytetrafluoroethylene (PTFE) dispersions (Ismail et al., 2010). These coatings usually consist in dipping or spraying technique followed by a heat treatment at around 350 °C.

The aim of the present work was to investigate the behaviour of perfluoropolyether (PFPE) derivatives as alternatives to standard fluoropolymer i.e. PTFE. Several grades of PFPE are available in form of aqueous dispersions, and allow for an easy processing without the need of using high temperature thermal sintering treatment typical of PTFE. The focus of the present work was put not only onto the electrochemical performances, but also onto the results of contact angle measurements, particularly the attention was to the experiments at 60 °C and 80 °C, in order to correlate the properties of the coatings to the electrical performances.

2. Experimental

2.1 Sample preparation

The Gas Diffusion Layer (GDL) used in this study is a commercial carbon cloth (SCCG 5N purchased by SAATI S.P.A. Italy) (Fracas et al., 2008). The two hydrophobic agents used are commercially available products (Fluorolink® P56 and Algoflon® D 1214X from Solvay Solexis s.p.a., Italy). The former (P56) is an anionic, segmented polyurethane with high molecular weight, while the latter is an aqueous polytetrafluoroethylene (PTFE) dispersion.

The two dispersion were diluted with distilled water up to concentrations ranging from 1 % to 10 % wt, for P56 and PTFE respectively. The GDL was then dipped in the fluorinated dispersions for 10 minutes. The treated samples were roll squeezed, then put in oven at a temperature of 150 °C, for 30 minutes,for the GDLs treated with perfluoropolyether, and at a temperature of 350 °C, for 30 minutes, for the one treated with PTFE.

2.2 Contact Angle Measurements

A home-made rig was used, whose cores are a SLR digital camera Nikon D90 with a AFS 60 mm F2.8 Macro lens, to acquire the side views of the drops, as described in Guilizzoni (2011), and a PID-controlled heating systems, to perform measurements at the desired surface temperature (Guilizzoni and Sotgia, 2010). The acquired drop images were transferred to a personal computer and the contours of the drop and of the base surface were extracted by image processing. As the investigated surfaces showed a fairly isotropic surface texture, a simplified axisymmetric drop shape analysis technique (del Río and Neumann, 1997) was then used to fit the numerical solution of the Laplace-Young equation (Rotenberg et al, 1983) to the experimental drop contour. No simpler approach could be considered reliable on highly hydrophobic surfaces (Extrand and Moon, 2010). Full details about the measurement technique can be found in (Guilizzoni, 2011). Static θ and advancing θ_{ADV} contact angles were measured using “as placed” drops (with nominal volumes of 13 μL and 120 μL respectively) and following the model by Tadmor (Tadmor and Yadav, 2008), which exploits the contact angle dependence on the drop volume to determine the dynamic contact angles. Receding contact angles θ_{REC} were estimated by an inverse use of such model: given the measured θ and θ_{ADV}, θ_{REC} becomes the only unknown in the equations. As the investigated surfaces are rough, apparent contact angles were measured.

2.3 Single cell Polarization Measurements

Electrochemical performances of the GDLs were tested in a single cell (Fuel Cell Technologies). The BPs have a single serpentine at the anode and a triple parallel serpentine at the cathode side. The GDLs were placed at the anode and cathode side clamping the screws of the cell at a torque of about 10 Nm. The compression of GDLs was fixed at 70 % of the original thickness (about 380 μm) and kept constant with an uncompressible glass fiber gasket. The MEA was assembled using a Nafion®212 membrane with a thickness of 50 μm and an active area of 25 cm^2; the catalyst layer was coated directly onto the membrane with a platinum loading of 0.3 mg cm^{-2} at the anode (A) and of 0.6 mg cm^{-2} at the cathode (C). Pure hydrogen and air were fed at the anode and cathode, respectively. The flow rates were 0.2 NL min^{-1} of hydrogen and 1.0 NL min^{-1} of air, corresponding to a stoichiometric ratio λ = 1.2–2.0 A/C at 1 A cm^{-2}, and were controlled and detected by a calibrated flow meter. The degree of humidity and the gas temperature were controlled by saturators and temperature controllers: the temperature of the cell was kept at 60 °C and 80 °C, the relative humidity of reactants was kept constant both for anode and cathode. In particular, at the anode it was set at 80 % RH, while at the cathode at 100 % RH. An electronic load (RBL488-50-150-800) was connected to the cell, which measures and controls the voltage, the current and the generated electric power. Polarization curves were recorded under galvanostatic conditions in the current density range from OCV to 0.87 A cm^{-2}, with steps of 0.085 A cm^{-2}, and at each step the resulting potential was recorded (galvanostatic mode, 420 s per step, 1 pt per s recorded). Potential values plotted in the steady-state polarization curves result from the averaging of the last 300 pts recorded at each step in order to minimize experimental artefacts due to transient phenomena.

3. Results and Discussions

3.1 Contact angle Results

Surface samples were analyzed at different temperatures equal to 20 °, 60 ° and 80 °C. Figure 1 shows a 120 μl drop resting on the GDL-P56 (a) and on a GDL-PTFE (b); some fibers protruding from the surfaces can be noticed. The results in terms of static and dynamic contact angles are reported in Figure 2. At ambient temperature the differences between the advancing and the static contact angles are comparable to the measurement uncertainty. That is why at 20 °C only static contact angles are shown in Figure 2. Such low contact angle hysteresis joined with the high values of the contact angles should indicate a wetting behaviour of the Cassie-Baxter type (Cassie and Baxter, 1944), due both to the surface roughness and to the protruding fibers (Wang et al, 2007). At ambient temperature the wettability of both surface was very low, very near to the range of super-hydrophobicity. Given the uncertainty in the measured values, which in most cases is in an underestimation direction (Extrand and Moon, 2010), it seems likely that such range may also be entered. As for comparison between the two surfaces, their wettability appears to be almost equal. Some points (not reported in the figure) of the GDL-P56 showed higher contact angles (around 160°), but they appeared to be isolated values, more likely due to favourable local pinning phenomena than to a uniform and reliable surface characteristic. Eötvös numbers of the drops on the two surfaces are also equal within the experimental uncertainty, and a further confirmation came from a preliminary investigation of the roll-off angles: the two samples were both fixed to a metal support, two equal drops were deposed on them, then the support was progressively tilted. During repeated tests the drops always rolled away from the surface almost together. No measurement of such angle was performed, thus such test is only interesting as a relative comparison.

When temperature is increased, the static contact angle decreases for both surfaces, in agreement with recent literature analyses (Berim and Ruckenstein, 2011), and the contact angle hysteresis increases too. This may be explained as a shift from a Cassie-Baxter wetting behaviour at 20 °C towards a Wenzel wetting behaviour (Wenzel, 1936) at 60 °C and 80 °C, due to the change in water surface tension and in the liquid-surface chemical interactions. The decrease is sharp between ambient temperature and 60 °C, while the value remains almost constant when temperature is further increased to 80 °C. Comparing the two surfaces, the GDL-P56 shows a slightly higher decrease of contact angle with temperature.

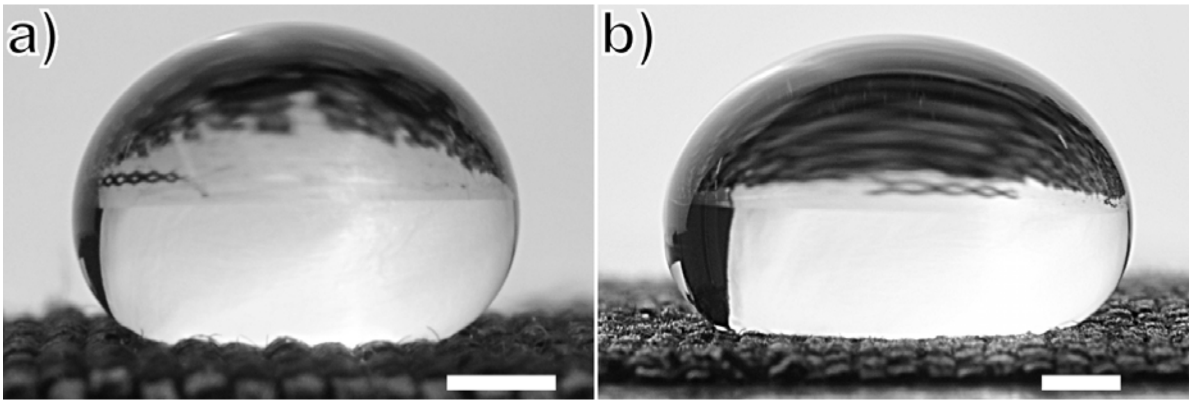
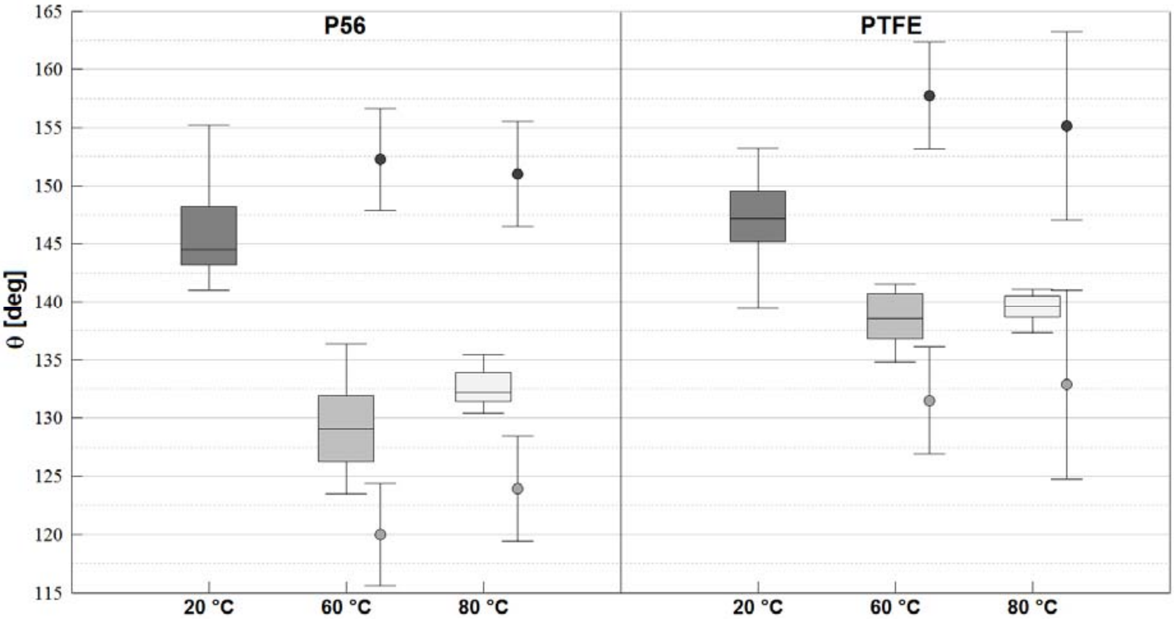


Figure 1: a) Drop resting on the GDL-P56, b) Drop resting on the GDL-PTFE. T = 20 °C, white bars represent 1 mm.



3.2 *Figure 2: Static (boxplots) and dynamic (advancing and receding, shown as median values ± standard deviation) contact angles on the investigated surfaces, at T = 20 °C, 60 °C and 80 °C.*Polarization Results

The perfluoropolyether derivative was described in details in the literature (Trombetta et al. 2005). The hydrophobic PFPE chains were made water-reducible through functionalization with ionic side or end groups. In spite of this, it has been shown that the PFPE derivative has good film forming properties and effectively make hydrophobic the treated surfaces, which become predominantly fluorinated.

Only high values of relative humidity of gases (i.e. RH 80-100 % H_2-Air) were tested in the present work, in order to assess the effectiveness of the two different hydrophobic polymers used to coat the GDL. Besides, these conditions should assure that the membrane was fully humidified. By a first analysis of the experimental results, it can be stated that the addition of PFPE polymer, in the amounts of 1 % wt, positively influences the cell performances at all current density values, as reported in Figure 3, with respect to PTFE which is in the amount of 10 % wt.

Particularly, the beneficial effect of PFPE is more evident when operating at 60 °C; indeed the assembly with the PFPE-treated GDL sensibly improves the cell performances; this effect is even more marked in the high current density region, where the cell is more stressed as the amount of water generated by the cathodic reaction is maximum. In terms of power density GDL-P56 is superior to GDL-PTFE; the peak value is about 0.40 W/cm^2 for GDL-P56 while GDL-PTFE gets only 0.28 W/cm^2.

At 80 °C the effect of perfluoropolyether is more controversial. Also at this working temperature the PFPE based system performs better than PTFE, but the improvement is not so evident. Again, the power density of GDL-P56 is superior to GDL-PFTE; at 80 °C the peak value is about 0.40 W/cm^2 for GDL-P56, while for GDL-PTFE the value is 0.37 W/cm^2. Usually, the slope of the polarization curve in the quasi-linear central region is known to be strictly correlated to the FC ohmic resistance, which is mainly due to membrane resistance, bulk resistance of GDLs and contact resistances between different elements of the assembly.

It is clearly evident that at 60 °C the polarization curve of the cell assembled with GDL-P56 shows a higher slope than the PTFE's slope, confirming a lower overall cell resistance mounting P56 treated GDLs. This effect is mitigated at 80 °C, where all the polarization curves have quite the same slope. Moreover, taking into account the results of contact angle measurement, and particularly the effect of temperature, it can be observed that the GDL-P56 showed a slightly higher decrease of contact angle with temperature, affecting probably the cell performances.

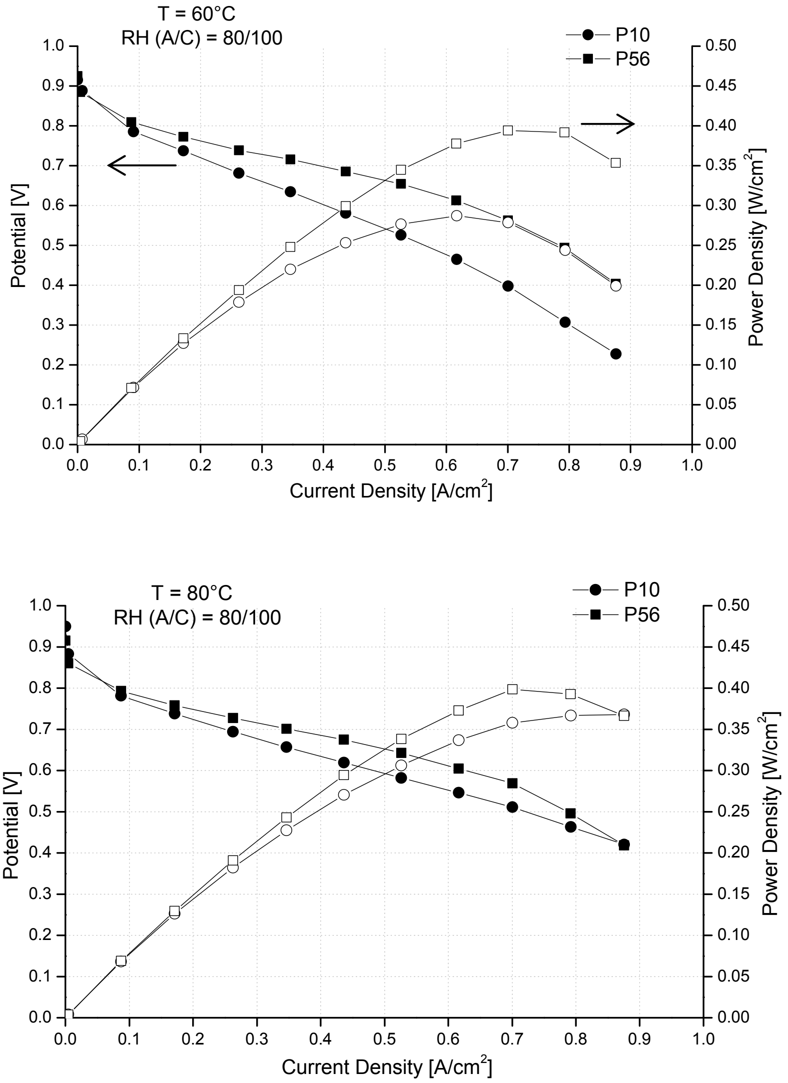


Figure 3: Fuel cell performance: at 60 °C (a) and at 80 °C (b) at high cathodic humidity.

4. Conclusion

As the most common way to characterize the wettability, and consequently the hydrophobicity, of a surface is the measurement of the contact angle, in the present work, a set of experiments were assessed in order to evaluate its variation and to estimate the efficiency of two different coatings. The results highlighted the very high hydrophobicity of the prepared surfaces at room temperature, which is fairly conserved at 60 °C and 80 °C too, even if at the highest temperatures a change in the wetting behavior may take place. No major difference was observed between the two surfaces, even if the GDL-P56 showed a slightly higher decrease of contact angle with temperature, which is likely to affect the cell performances.

Further investigation by means of electrochemical impedance spectroscopy are reported in Gallo Stampino et al. 2012.

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