



Short communication

Surface treatments with perfluoropolyether derivatives for the hydrophobization of gas diffusion layers for PEM fuel cells

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ABSTRACT

In the present work, preliminary results of different hydrophobic surface treatments for gas diffusion layer (GDL) for PEM fuel cells are presented. This hydrophobic coating consists of new perfluoropolyether (PFPE) derivatives, in comparison to standard polytetrafluoroethylene (PTFE) dispersions. Experimental conditions for an efficient coating of fluoropolymers onto carbon clothes were explored by wet chemical methods. The GDLs obtained were tested in a single fuel cell at the 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 coatings measurably improve the cell performances, and this effect is more evident at 60 °C with respect to 80 °C.

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1. Introduction

Fuel cells (FC) are electrochemical devices, which produce electricity through clean chemical reactions without the emissions common to combustion processes; the benefits of FC include high-energy efficiency (50–60%) in the conversion of fuel (typically H₂ and air) to energy and environmentally friendly emissions (water) [1].

At present, the so-called polymer electrolyte membrane or proton exchange membrane (PEM) fuel cells are the best choice for automotive applications [2], for small-scale distributed power generation and also for portable applications [1].

The heart of the PEM fuel cell is the membrane electrode assembly (MEA), which consists of a proton exchange membrane and two catalyst layers (i.e. anode and cathode). MEA is typically sandwiched by two flow field plates that are often mirrored to make a bipolar plate (BP), when cells are stacked in series for greater voltages. Usually, a gas diffusion layer (GDL) is inserted between the BP and the MEA [3,4].

The GDL is a key component because it plays a critical role in the water and reagent gases management of the fuel cell [5]. It must control the homogeneous transportation of reactant gases from the flow field to the catalyst layer (so it has to be *porous*) [6], it must easily transport electrons from the bipolar plate to the catalyst (*electrically conductive*) [7,8], conduct heat from the catalyst to

the cooling channels in the bipolar plate (*thermally conductive*) [9] and it must manage the removal of reaction products (liquid and gas) from the catalyst (*hydrophobic*) [5,6,10].

Most of these requirements are met by carbon fiber-based materials, i.e. carbon clothes and carbon papers, due to their high porosity and electric conductivity. Moreover, GDLs, must be made hydrophobic in order to avoid flooding in their porous microstructure. Usually, both anode and cathode GDLs are coated with an hydrophobic agent, typically a fluoropolymer such as polytetrafluoroethylene (PTFE) [11,12] or fluorinated ethylene propylene (FEP) [13] dispersions. These conventional treatments usually involve dipping or spraying technique followed by a heat treatment at around 350 °C [14]. Several articles in the literature concern the use of PTFE and FEP coatings, and it was found that the optimal amount is around 10–15 wt% [5,13,14].

Moreover, some works reports on the hydrophobic properties of GDLs hydrophobized by plasma treatment with fluoruous gases [15]. The hydrophobic properties are largely improved but obviously this is a more expensive method than standard wet chemical processes like dip coating [15].

The aim of the present work was to investigate the behaviour of perfluoropolyether (PFPE) derivatives as alternatives to standard fluoropolymer. 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. To the best of the author's knowledge PFPEs derivatives have not been used for application on GDL, but they are commonly exploited to impart water repellence and soil release to different substrates like paper, textiles, and stones [16–18]. Particularly, in

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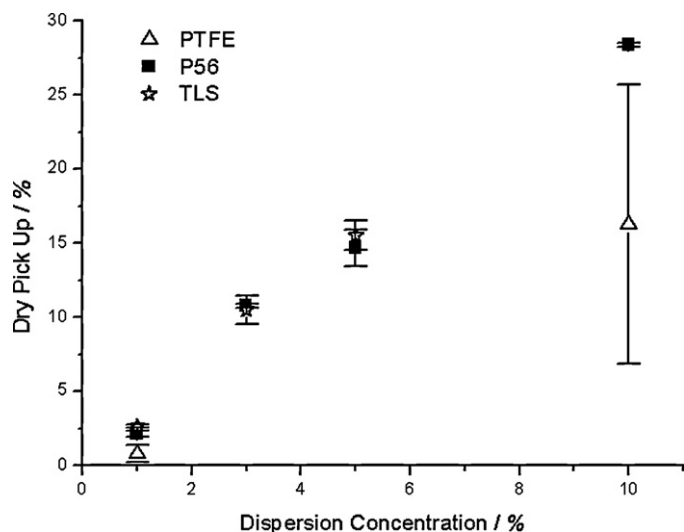


Fig. 1. Dry pick up of GDL coated with different fluorinated derivatives at increasing dispersion concentrations.

the present work, only the hydrophobic effect onto the substrates was investigated, the three samples tested are not coated with the microporous layer, as the key point of the present paper is to evaluate only the hydrophobicity of the carbon clothes coated with different fluoropolymers.

2. Experimental

2.1. Preparation of gas diffusion layers

The gas diffusion layer (GDL) used in this study is a commercial carbon cloth (SCCG 5N purchased by SAATI S.P.A., Italy) [19]. The perfluoropolyether derivatives used are commercially available products (Fluorolink® P56 and Fluorolink® TLS 5007, from Solvay Solexis s.p.a., Italy). The former perfluoropolyether (P56) is an anionic, segmented polyurethane with high molecular weight, while the latter (TLS) is a phosphate ammonium salt with lower molecular weight. It was also used an aqueous polytetrafluoroethylene (PTFE) dispersion (Algoflon® D 1214X, Solvay Solexis s.p.a., Italy) for benchmarking purposes.

PFPE dispersions were diluted with distilled water up to concentrations ranging from 1 to 10 wt%. The GDL was then dipped in the fluorinated dispersions for 10 min. The treated samples were

roll squeezed, then put in oven at a temperature of 150 °C for the GDLs treated with perfluoropolyethers, in order to obtain the complete dry off the water, and at a temperature of 350 °C for the one treated with PTFE.

The dry pick up values were calculated from the sample's weight percentage difference before dipping and after heating procedures.

2.2. Contact angle measurements

Static contact angles with bi-distilled water were measured according to the sessile drop technique with a OCA 20 Dataphysics instruments. Values were averaged from at least 20 measurements for each sample.

2.3. Morphological analysis

Microscope analyses were performed using a scanning electron microscope (SEM) Cambridge Stereoscan 360 to evaluate the different morphology of samples.

2.4. Single cell polarization measurement

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 screw 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 cm²; 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 $\lambda = 1.2$ –2.0 A/C @ 1 A cm⁻², and were controlled and detected by a calibrated flow meter.

In the present experimental work the *I*–*V* curves were made at constant flow rate both for H₂ and air, and the cell was operated at ambient pressure. 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,

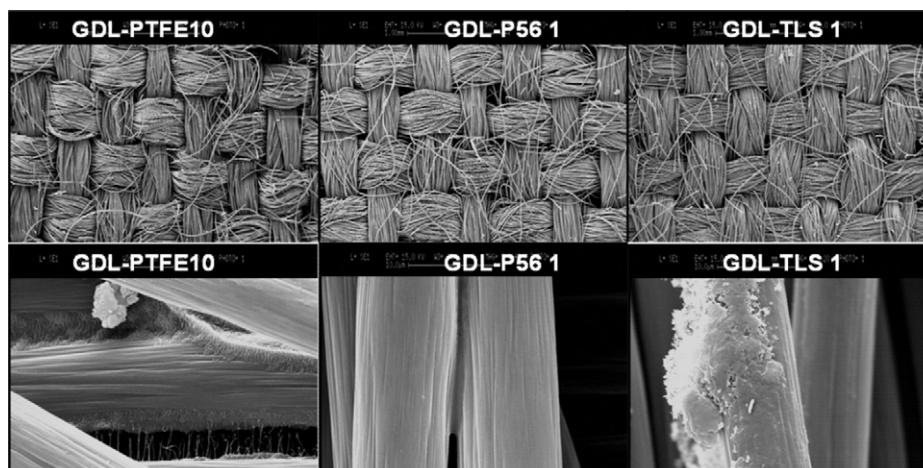


Fig. 2. Microscopical analysis of the three samples analyzed: GDL-PTFE 10, GDL-P56 1 and GDL-TLS 1.

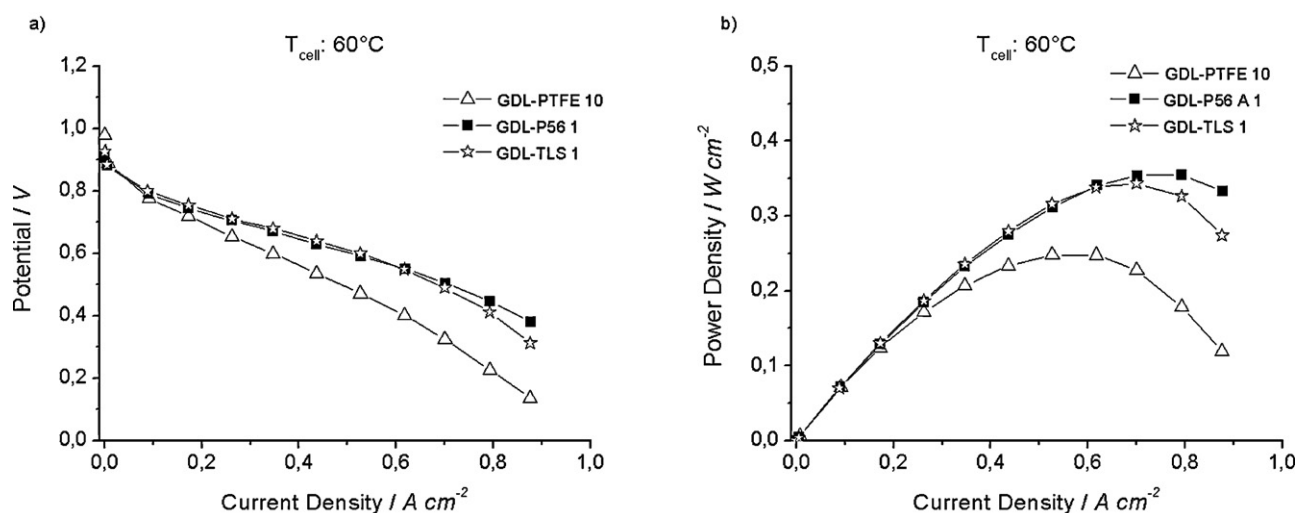


Fig. 3. Polarization (a) and power density (b) curves of single cell assemblies mounting three different GDLs (GDL-P56 1, GDL-TLS 1 and GDL-PTFE 10) at 60 °C and RH 80/100 air/H₂.

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

The two perfluoropolyether derivatives were described in details in the literature [16,17]. 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 derivatives have good film forming properties and effectively make hydrophobic the treated surfaces, which become predominantly fluorinated [18]. The GDL samples coated with PFPE dispersions show (Fig. 1) a high dry pick up value and an overall good reproducibility of the application. A linear correlation between the fluorinated dispersion concentration and dry pick-up after coat-

Table 1

Contact angle measurements of GDL coated with different fluorinated derivatives.

Sample name	Contact angle (°)	St. deviation
GDL-PTFE 10	147.3	4.31
GDL-P56 1	147.3	4.37
GDL-TLS 1	144.0	5.16

ing can be observed. On the other hand the carbon cloth samples treated with PTFE show a lower pick-up and lower reproducibility.

Three different samples were selected for contact angle measurement and for the fuel cell testing: a GDL coated with an aqueous dispersion of PFPE polyurethane (P56) at 1 wt% (*GDL-P56 1*) and a GDL coated with an aqueous dispersion of phosphate (TLS) at 1 wt% (*GDL-TLS 1*); for sake of comparison, as reported by literature [5], a GDL coated with an aqueous dispersions of polytetrafluoroethylene 10 wt% (*GDL-PTFE 10*) was included in the experiments.

As-received GDL shows an immeasurably low contact angle value due to its porous microstructure. Some contact angle measurements for selected coated samples are presented in Table 1. As observed the application of PFPE dispersions at 1 wt% makes the

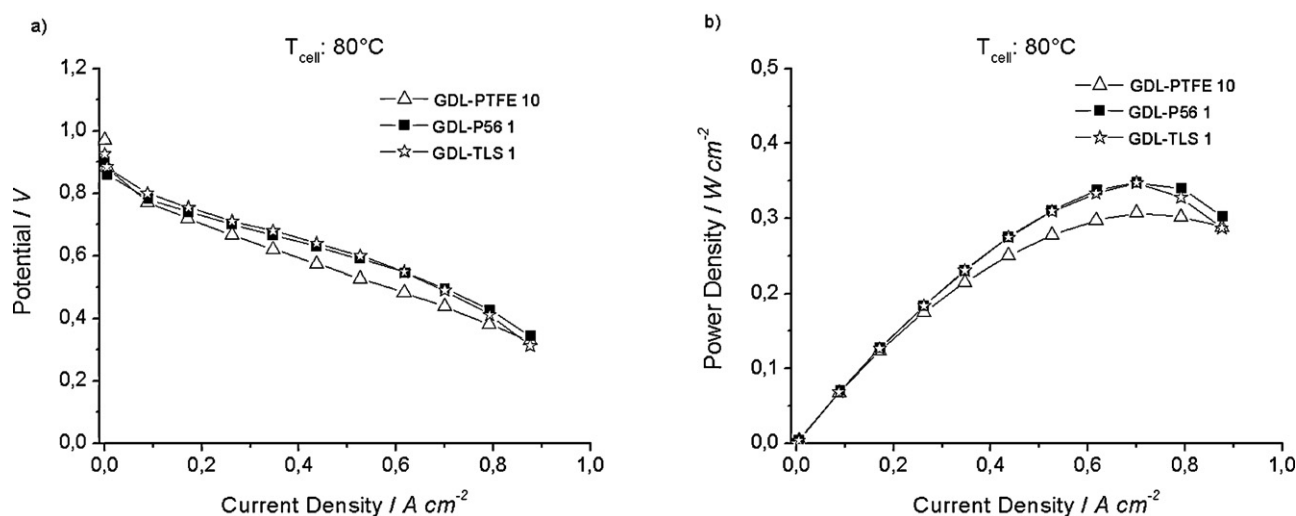


Fig. 4. Polarization (a) and power density (b) curves of single cell assemblies mounting three different GDLs (GDL-P56 1, GDL-TLS 1 and GDL-PTFE 10) at 80 °C and RH 80/100 air/H₂.

GDL surface very hydrophobic, in quite the same way of PTFE coated samples.

The three GDLs were observed with the electronic microscope in order to identify the presence of the polymeric agglomerates among the carbon fibres. In Fig. 2 are shown the carbon fibres of GDL treated with different polymer. It is possible to observe the presence of polymer onto the carbon fibres in the samples considered. Some polymer agglomerates were found in GDL-PTFE 10 and GDL-TLS 1 while GDL-P56 1 seems to present a more uniform distribution.

In order to assess the effectiveness of the GDLs hydrophobic treatments only high values of relative humidity of gases (i.e. RH80–100% H₂–Air) were adopted in the present work. Moreover, these conditions should assure that the membrane be fully humidified. Analyzing the experimental results, it is worth noting that the addition of different PFPE polymers, even in as small amounts as 1 wt%, positively influences the cell performances at all current density values, as reported in Figs. 3 and 4.

Particularly, when operating at 60 °C, the assembly with the PFPE treated GDL measurably improves the cell performances; this effect is even more evident in the high current density region, where the cell is more stressed and the amount of water generated by the cathodic reaction is maximum. In terms of power density GDL-P56 1 and GDL-TLS 1 are superior to GDL-PTFE 10; the peak value is about 0.35 and 0.34 W cm⁻² for GDL-P56 1 and GDL-TLS 1, respectively, while GDL-PTFE 10 gets only 0.25 W cm⁻².

At 80 °C the effect of perfluoropolyethers is more controversial. Also at this working temperature the PFPE based system performs better than PTFE, but the enhancement is less evident. Again, the power density of GDL-P56 1 and GDL-TLS 1 are superior to GDL-PTFE 10; at 80 °C the peak value is about 0.34 W cm⁻² both for GDL-P56 and GDL-TLS, while for GDL-PTFE 10 the value is 0.30 W cm⁻².

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.

At 60 °C the polarization curve of the cell assembled with GDL-PTFE 10 shows a lower slope than the two PFPE's slopes, that is indicative of an higher overall cell resistance mounting PTFE treated GDLs. This effect is mitigated at 80 °C, where all the polarization curves have quite the same slope.

We can assume that at 60 °C the PFPE probably shows a better water management during the cell operation preventing both the drying of the membrane and the flooding of the GDL at the cathodic side.

4. Conclusive remarks

In this work some preliminary data about the use of perfluoropolyether derivatives as hydrophobic surface treatments for GDL were presented. It was interesting to observe that the application of a small amount of PFPE (1 wt% of PFPE to coat GDLs, with respect to the 10 wt% of PTFE) allowed for a clear improvement in electrochemical performances. Moreover, the application procedure of PFPEs seems quite simple and user-friendly, showing a very good dry pick-up even at low dispersion concentration, and being quite effective even without the high temperature sintering cycle typically needed for PTFE coatings. More work is however needed to further improve the performances and optimize the composition (i.e. average molecular weight and functionalities) of the perfluoropolyether derivatives.

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