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Innovative Gas Diffusion Media for PEM Fuel Cells Based on a Fluorinated Polyurethane as Hydrophobic Agent

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The present work focuses on the use of an alternative polymer (Fluorolink® P56, a commercially available, anionic, segmented polyfluorourethane with high molecular weight) to be used as hydrophobic agent in GDMs production for PEMFCs. Prepared samples were physically evaluated by static contact angle, SEM analysis, porosimetry and finally tested in a single lab-scale fuel cell in order to assess electrochemical performances.

In a typical experiment, carbon black (CB), Fluorolink P56 (two different concentrations) and isopropyl alcohol were mixed at 8000 rpm by using an Ultra Turrax homogeneizator. Inks produced were blade coated on hydrophobized commercial GDLs (SAATI Group). Then the samples were treated for 30 minutes at 150 °C in order to remove the wetting medium and to make the polymer fibrous. The layers based on Fluorolink P56 showed good surface uniformity and a superhydrophobic behavior (i.e. mean contact angle higher than 150°). Electrochemical tests, performed at 60 °C and 80 °C and low (60%) and high (100%) relative humidities, demonstrated that innovative GDMs are able to guarantee higher power density values in certain operating conditions and very low overall ohmic resistances, even though some critical issues still remain in diffusion limitations at high current densities, when more water is generated.

1. Introduction

The world energetic dependence on non-renewable energetic sources is a continuously arising and up-to-date problem. Pollution and global warming are the most remarkable effects connected to fossil fuels employment (Sieniutycz, 2011). Fuel cells have been widely accepted as the most likely alternative energy source for nowadays (Niya and Hoorfar, 2013). In particular, Proton Exchange Membrane Fuel Cells (PEM-FCs) are very promising devices thanks to their high energy concentration, great portability and quick starting time for both portable (Markotter et al., 2013) and non-portable (Ang et al., 2010) applications. The electrolyte used in the device is a polymeric membrane and it is usually composed by fluorinated compounds; Nafion®, which was developed by Dupont in 1970s, is a very popular compound for that kind of applications (Peighambardoust et al., 2010).

Many studies pointed out the crucial role of Gas Diffusion Media (GDM) in the cell assembly. Placed strictly in contact with cell electrodes, the GDM is composed by a Gas Diffusion Layer (GDL) and a Micro-Porous Layer (MPL), usually coated above it. The key role of the diffusion layers consists in an optimization of reactants feeding on the catalyst layer and in the subsequent removal of reaction products. Both MPL and GDL are specifically designed in order to properly manage water produced during cell running. In order to do that, those layers are usually made hydrophobic by using fluorinated polymers. Polytetrafluoroehylene (PTFE) is a very well-known hydrophobic agent; several studies have been performed in order to understand cell performance dependence on both MPL and GDL polymer content, fixing the optimal value in the range of 20% (Ismail et al., 2013).

The aim of this work is to investigate the possibility to use an alternative fluorinated polymer as hydrophobic agent for GDM production, instead of PTFE. The latter, as previously said, is a widely used

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polymer for GDM treatments, but it shows issues concerning the amount of polymer needed to achieve good electrochemical performance.

2. Experimental

A PTFE based GDM (assumed as standard for performance evaluation, GDM STD) was produced on the basis of a patented procedure (Lee et al., 2009). At first, carbon black (CB, Vulcan XC-72 R), surfactant (T, Triton X-100) and wetting medium (W, distilled water) were weighted and strongly mixed at 8000 rpm for 10 minutes by using Ultra Turrax (IKA, T25 homogeneizator). Then, the PTFE polymer emulsion (DuPont) addition was performed under magnetic stirring at 500 rpm for 10 minutes, obtaining a dispersed ink. Blade coating technique was used in order to leave an ink layer of the thickness needed (40 μm) on a commercial carbon cloth GDL substrate, made hydrophobic with PTFE (SCCG5 P10, SAATI Group). The speed of the lab-scale coater (K Control Coater) was set on 0.042 m/s, corresponding to a shear rate of about 100 s^{-1}. Samples were treated at 350 °C for 30 minutes in order to remove the solvent and to bind the polymer (Latorrata et al., 2012).

In order to produce slurries based on the polyfluorourethane polymer (Fluorolink® P56, Solvay Solexis, PFPE in the following), a new and simplified procedure was assessed; it consisted in a 10 minutes high-shear mixing of CB, PFPE and isopropyl alcohol (IPA) by Ultra Turrax. The two Fluorolink P56® based inks were blade coated setting speed at 0.154 m/s, corresponding to a shear rate of about 350 s^{-1}, on a GDM made hydrophobic using the same polymer. For the substrate production, the untreated carbon cloth GDL was made hydrophobic by dip-coating in a water-Fluorolink P56 emulsion and a subsequent heat treatment for 30 minutes at 120 °C. After slurry deposition, samples were treated at 120 °C for 30 minutes in order to remove the solvent and to bind the polymer.

In Table 1, a brief summary of GDM components concentration used in ink formulation is proposed.

Table 1: Inks composition (Note: all the numbers refers to w/w ratio)

Sample	CB/W	CB/T	CB/IPA	Polymer/CB
GDM STD	0.13	5.6	-	0.12 (PTFE)
GDM PFPE-12	-	-	7.72	0.12 (PFPE)
GDM PFPE-6	-	-	7.72	0.06 (PFPE)

Prepared inks were characterized in terms of rheological properties by using a lab-scale rheometer (Reologica Intruments AB, Stresstech 500). Applied shear rate was varied between 10^{-3} s^{-1} and 10^{3} s^{-1}, measuring the corresponding dynamic viscosity values.

Being GDM hydrophobicity a crucial feature for device performance enhancement (Barbir, 2005), static contact angle (CA) analyses were performed on prepared samples by using a OCA 20 Dataphysics Instrument.

The morphology of the samples was observed with a Stereo Zoom Microscope (Olympus SZ40).

Polarization curves were obtained by testing samples in a single fuel cell connected to an electronic load (TDI Power, RBL488 50-150-800). A commercial catalyst coated membrane (CCM, provided by Baltic Fuel Cells) was used during the tests. The electrode Pt loading amounted to 0.3 mg/cm^2 on the anode side and to 0.6 mg/cm^2 on the cathode side respectively. The active area was 23 cm^2.

Each sample was tested under a variety of operative conditions. Temperature was set at two different values (60 °C and 80 °C). Relative humidity level (RH) was held constant (80%) at the anode side and varied (60% and 100%) at the cathode side. Following, conditions will be displayed with a compact format (for instance T60 RH 80-100) where the first number refers to the temperature (i.e. T60 equals to 60 °C) while the second and the third number refer to anodic and cathodic relative humidities, respectively. Tests were performed using different input flow rates (0.2 NL/min for hydrogen and 1 NL/min for air).

Tests were performed in galvanostatic condition, from Open Circuit Voltage condition (OCV) to high current density values (1.13 A/cm^2), with steps of 0.09 A/cm^2.

Allowing to deeply investigate materials properties, electrochemical impedance spectroscopy (EIS) is a non-invasive diagnostic technique widely used in Fuel Cell performance evaluation. Using this technique it is possible to obtain microscopic information about the system and to determine all the typical potential losses associated with the device operating. In addition to that, electrochemical parameters of the device can be identified using suitable equivalent circuit models (Yuan et al., 2010).

Measurements were made by using a Frequency Response Analyzer (FRA, Solartron 1260) connected to an electronic load. Tests were carried out evaluating the device response, in terms of potential, to a sinusoidal alternate current perturbation input, with a signal amplitude of 200 mA (Wagner and Gulzow, 2004). Results were obtained in a frequency range between 0.5 Hz and 1 kHz.

Impedance spectra were obtained for each current density value set, form OCV to 1.13 A/cm^2. For the sake of brevity, only spectra recorded at 0.37, 0.56, and 0.76 A/cm^2 will be reported in the following, being those values depictive of the device behaviour at low, medium and high current densities, respectively.

3. Results

Rheological characterization results of produced inks is shown in Figure 1.

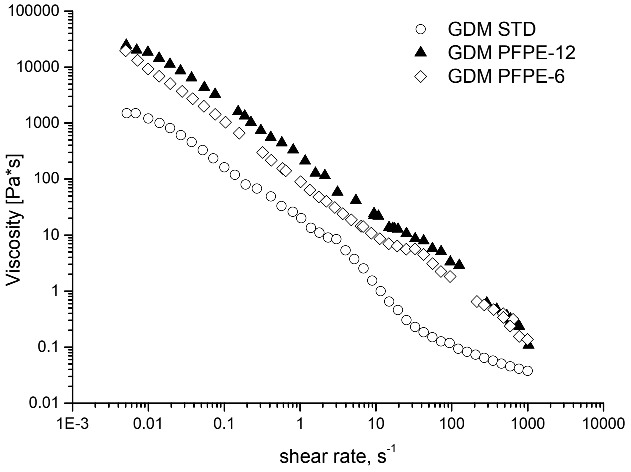

Figure 1: Results of rheological analysis of the three inks prepared.

As reported in literature, a shear-thinning slurry is needed in order to control layer thickness using blade coating technique (Greener and Middleman, 1974). From rheological analysis results reported in Figure 1, it is clear how all samples have a viscosity-shear rate dependence typical of shear-thinning pseudoplastic fluids, as desired for deposition (Sullivan and Middleman, 1986). The change from PTFE to PFPE leads to higher viscosity values and a dependence on polymer content is clear: the higher the polymer content, the higher the viscosity. It has to be noted, anyway, that the change in viscosity may also be caused by the change in slurry formulation, as the PTFE one is based on water and Triton X-100 while only IPA was used for PFPE based GDMs. IPA-based inks rheological curves also show a remarkable discontinuity in the 100-200 s^{-1} range, likely due to solvent evaporation.

Results obtained in terms of static contact angle (CA) are reported in Table 2. Each sample was evaluated before cell testing (BCT) and after (ACT), for both anode (ACT-A) and cathode side (ACT-C).

Table 2: Summary of the detected contact angles

Sample	BCT	ACT-A	ACT-C
GDM STD	145.2 ± 4.1	145.7 ± 1.8	146.5 ± 2.3
GDM PFPE-12	148.1 ± 3.9	150.3 ± 2.3	146.4 ± 5.3
GDM PFPE-6	150.8 ± 1.8	147.1 ± 5.3	148.9 ± 2.8

PFPE hydrophobic properties have already been investigated for GDL production, as reported in literature (Stampino et al., 2013). Contact angle values reported in Table 2 confirm the polymer as a good water management agent also for MPLs, as all samples display a good water repellant behaviour. In average terms and taking in account measurement uncertainty, materials based on the new polymer have similar hydrophobic behaviour to PTFE, near to superhydrophobicity (the CA threshold value for super-hydrophobicity is set at 150°). Moreover, no apparent correlation can be identified for CA values before and after cell testing, as all samples preserve their water repulsion properties.

Results of surface characterization performed by optical microscopy (OM) are reported in Figure 2. A magnification (40x) of the MPL surfaces is shown in order to have an overview of surface homogeneity for prepared samples.

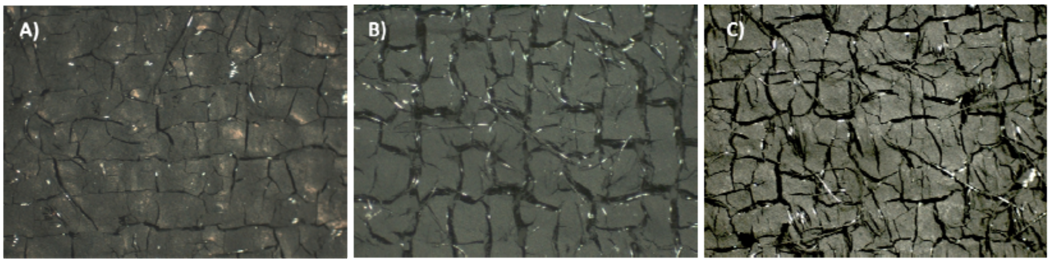

Figure 2: OM images of MPL surfaces: A) GDM STD, B) GDM PFPE-12 and C) GDM PFPE-6

OM analysis shows a different crack morphology for MPL surfaces based on different polymers; GDM PFPE-12, which contains a higher amount of PFPE displays thicker cracks while the PTFE based sample appears to be more homogeneous. On the other hand, GDM PFPE-12 and GDM PFPE-6 display several similarities as far as surface roughness and uniformity, pointing out a similar behaviour and good reproducibility of surface morphology.

Electrochemical properties assessment of prepared materials was performed by means of EIS and by evaluation of polarization curves obtained in galvanostatic condition. Hereafter polarization curves will be reported first. A direct comparison between the performance of the different samples in the different operative conditions is proposed in Figure 3.

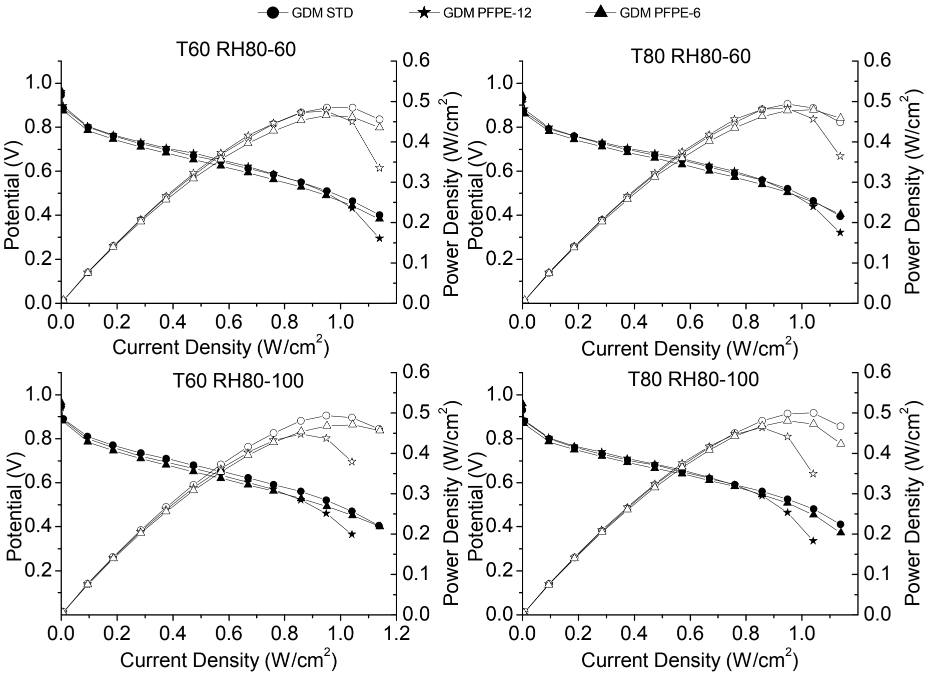

Figure 3: Polarization curves at 60 °C and 80 °C with different RH condition (80-100 and 80-60)

Polarization curves show how GDM PFPE-6 and GDM STD samples reach almost the same performance. At the same time, GDM PFPE-12 points out worse results with slightly lower values in terms of power density reached at lower current density values. Polarization curves recorded for GDM PFPE-12 are clearly affected by problems in terms of water management. As a matter of fact, the potential losses rapidly increase starting from medium current density values, highlighting problems linked to water production especially at high cathodic relative humidities, where water management problems are enhanced.

All samples were characterized in terms of voltage losses and electrochemical parameters by using EIS. Impedance spectra collected at the previously introduced operative conditions are reported in Figure 4.

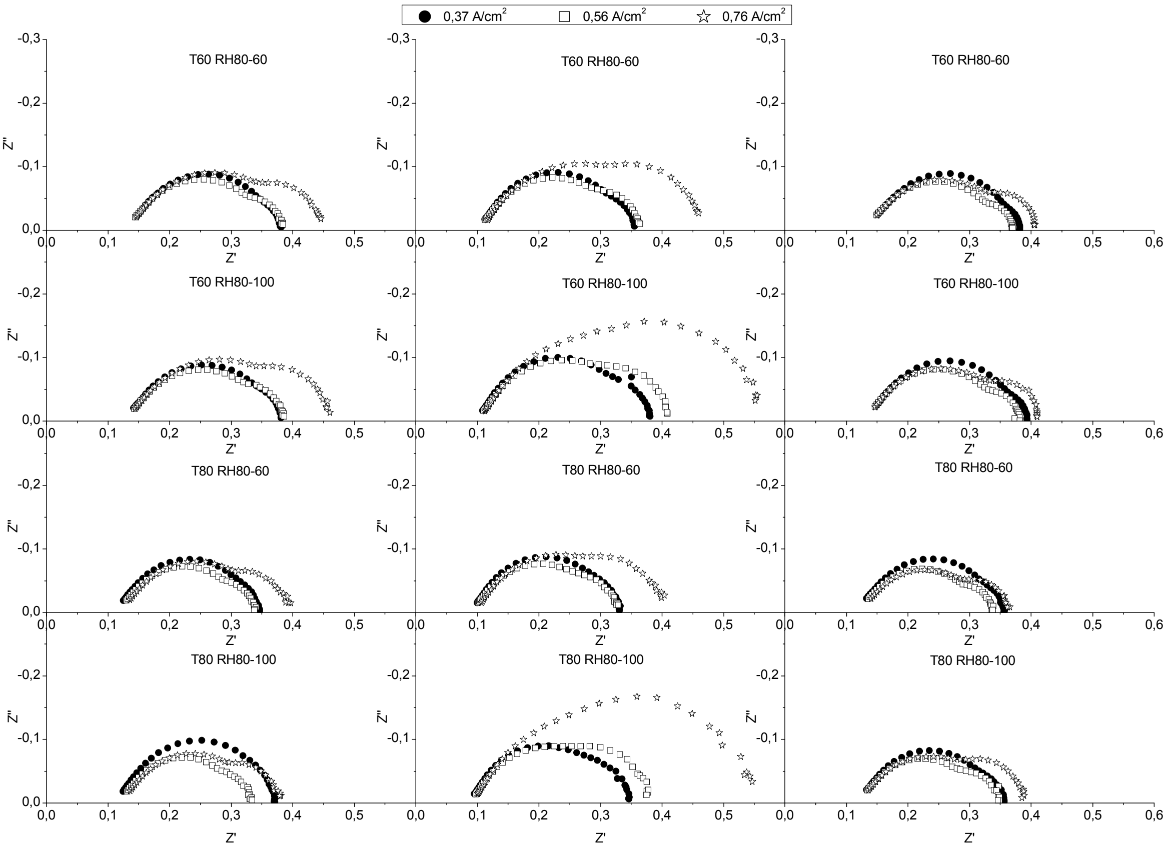

Figure 4: EIS spectra for samples GDM STD (left column), GDM PFPE-12 (central column) and GDM PFPE-6 (right column) recorded at 0.37, 0.56 and 0.76 A/cm^2 at different temperature/relative humidity conditions

Impedance spectra show similar values in terms of ohmic resistance (high-frequency real impedance) for samples GDM STD and GDM PFPE-6, while values are lower for GDM PFPE-12, where a decrease in the parameter is remarkable probably because of a smoother MPL surface related to the higher amount of polymer in the formulation. Those considerations are supported by optical microscope images (Figure 2) where the presence of GDL carbon wires on MPL surface can be detected for sample GDM PFPE-6.

All samples gradually display an increase in terms of concentration losses (i.e. diffusive limitations) as pointed out by the presence of a second semicircle in impedance spectra, especially at higher current density values, where water management properties of samples are crucial (Yuan et al., 2010).

The biggest semi-circles obtained with GDM PFPE-12 point out a non-optimal water management by the diffusion media, likely because of the reach of the maximum in MPL polymer content. In fact, as reported in literature, a maximum is reached in the power density-polymer content relation (Park et al., 2008). Further experiments should be planned employing intermediate polymer concentrations, in order to corroborate this hypothesis.

4. Conclusions

In this work, Fluorolink® P56, a commercially available, anionic, segmented polyfluorourethane with high molecular weight, was evaluated as alternative compound for Gas Diffusion Media production. Good results were obtained in terms of hydrophobicity, as almost no changes in contact angle values occurred by changing the polymer used.

The new preparation procedure developed, with the introduction of isopropyl alcohol in ink formulation, led to higher values in terms of viscosity.

Though the hydrophobicity target has been reached, no improvement in electrochemical performances has been reported. On the other hand, the use of half the amount of PFPE (6%) with respect to PTFE (12%) allowed to reach almost the same performance. At the same time, heat treatment process takes place at lower temperature (120 °C instead of 350 °C).

Further investigations need to be accomplished in order to deeply understand polymer concentration influence on device performance.

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