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Effect of different substrates, inks composition and rheology on coating deposition of microporous layer (MPL) for PEM-FCs

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ABSTRACT

The rheology of microporous layer (MPL) inks for polymer electrolyte membrane fuel cell (PEM-FC) applications was investigated, and its effect on thickness and morphology of final layer, prepared via doctor-blade technique, was examined. The effect of the carbon black (CB) on slurry viscosity was studied in the range CB/water = 0.11/0.17 (g/g) as well as the effect of surfactant and PTFE (Teflon®) addition. Slurry viscosity is mainly determined by the CB/water and CB/surfactant ratios, while PTFE addition has minor influence. Viscosities in the range 0.05–0.06 Pa s (at shear rate 100 s^{-1}) were found to be appropriate for coating deposition. Two substrates of different morphology, a carbon cloth (CC) and a woven non-woven (WNW), were coated with slurries of different composition but showing the same rheology. Notwithstanding the use of slurries with the same rheological behavior, different MPL coating thicknesses were obtained. This suggested that the substrate morphology has a non-negligible influence on the final MPL thickness. The MPL layer definitely increased the hydrophobicity, and in some samples the region of superhydrophobicity (contact angle $>150^{\circ}$) was reached. In-plane electrical resistance of gas diffusion layers (GDLs), i.e. substrate coated with MPL, was measured and it was found that the two different substrates have no influence on it (about 0.8 Ω). FCs assembling different GDLs showed different electrochemical performances in terms of I–V curves: MPLs coated onto WNW gave somewhat higher power densities (0.40 W/cm^2 at 0.5 V).

1. Introduction

Polymer electrolyte membrane or proton exchange membrane (PEM) fuel cells are electrochemical devices that produce electricity through the direct electrochemical oxidation of a fuel (usually hydrogen) and reduction of atmospheric oxygen without combustion, thus avoiding the related emissions [1]. The heart of a 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 between two flow field plates, often mirrored to make a bipolar plate (BP) when cells are stacked in series. One of the main problems of a PEM-FC is the water management; the excess water produced at the cathode side can result in flooding of the electrode, then water hinders the transport of reactants and therefore decreases the cell performance. For this reason a gas diffusion layer (GDL) is inserted between the BP and the MEA. At present, GDLs are made of porous carbon paper or carbon cloth, wet-proofed with PTFE (Teflon®) and coated with a thin microporous layer (MPL) consisting of a mixture of carbon powder and PTFE. After the introduction of the MPL, Pt-based catalysts can be either supported on the MPL surfaces or on the membrane surfaces (MEA). The microporous layer and the catalyst may have a complex composition and they are usually coated on the hydrophobic side of the GDL by various techniques, like painting [2], rolling, spraying, screen printing [3], and the so-called doctor-blade technique [4]. This technique implies the use of highly viscous inks, spread by a blade onto the substrate. The ink viscosity, the coating speed and the distance (gap) between the blade and the substrate are responsible for the thickness and homogeneity of the final MPL. Furthermore, a possible influence of the substrate nature (cloth or paper) has to be considered. As far as we know, the effect of different substrates on the thickness and microstructure of the deposited MPL has not yet fully investigated. It was found [3] that techniques that allow the preparation of more porous structures lead to better performances due to better gas permeability, but could lack in water management control. Different approaches have been proposed for the correct balance of the gases and water transport, like modifying the pore structure and the hydrophobicity with different PTFE loadings [5] or using MPLs with graded porosity [6]. The influence of the PTFE content in

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the microporous layer has been investigated by different authors [2,7–12] but conflicting results are reported: the suggested PTFE content ranges from less than 5% to more than 40% in the MPL layer.

In this study two different commercial substrates, i.e. a carbon cloth and a woven–non-woven, were considered as support for the MPL. An optimized composition, having an appropriate rheology was selected for doctor-blade deposition and the final coatings were investigated by SEM and contact angle measurements.

The comprehension of the effect of the ink components and rheology on the physico-chemical properties of the MPL coating as well as of the nature of the substrate surface is addressed.

The electrical characterization of all the prepared GDLs was made by impedance spectroscopy, while only selected coated samples were tested in a single FC assembly (25 cm^2 active area). The final goal is the correlation of the properties of the MPL with the electrochemical performance of the PEM-FC.

2. Experimental

2.1. Preparation

Two commercial substrates were considered, a carbon cloth (SEAL SCCG5N) and a carbon woven–non-woven (SIGRACET 10CA), identified as CC and WNW, respectively. Both substrates are 400-μm thick and PTFE treated (about 10 wt%) to increase their hydrophobicities.

Carbon powder, Vulcan XC72R (CB in the following), 60 wt% PTFE emulsion, TritonX100 surfactant (T in the following) and deionized water (W in the following) were used to prepare the inks for the microporous layer (MPL). Carbon powder, surfactant, PTFE and water were mixed with UltraTurrax T25 for 15 minutes, and then the so-obtained ink was mixed with a magnetic stirrer for one hour. The effect of the components on slurries viscosity was investigated considering the ranges CB/W = 0.11/0.17 (g/g), CB/T = 5.81/7.91 (g/g) and PTFE/CB = 0.12/0.39 (g/g).

The slurries were deposited onto the substrates via doctor-blade technique using lab-scale commercial equipment K CONTROL COATER. A linear velocity of 0.0625 m/s and a 40 μm gap were selected, corresponding to a shear rate of about 170 s^{-1}. The coated samples were calcined up to 370 °C for 30 min.

2.2. Characterization

2.2.1. Rheology

The rheological behavior of the inks was analyzed at 20 °C with a rotational rheometer (Rheometrics DFR 200) equipped with a 25 mm parallel-plate geometry, with a gap between 0.5–1.0 mm. Shear rates between 10^{-3} and 10^{3} s^{-1} were investigated.

2.2.2. Microstructure and morphology

A Cambridge Stereoscan 360 scanning electron microscope (SEM) was used for the morphological analysis of the samples. SEM analyses were carried out both onto the surfaces and the fracture surfaces of the samples that were gold coated to prevent charging effects.

2.2.3. Contact angle

The experimental tests were carried out by experimental set-up and procedures developed at the "Multiphase Thermo-Fluid Dynamics Laboratory" of the Department of Energy, Politecnico di Milano [13]. The system, located on an anti-vibrating optical bench, (Newport, SA Series, 1.2 m × 0.80 m) is equipped with a high precision metering pump (Cole–Parmer Instrument Company, model AD74900) completed by a microsyringe (Hamilton) that supplies drops of controlled volume on the surface samples. Photographs were taken using a high-resolution digital video/still camera (Canon, model DM-XM2, maximum resolution 1488 × 1128). The camera is equipped with three single-element close-up lenses (Hoya) for a total power of +7. In a typical test, the surface sample is placed under the syringe and a drop of fixed volume is dropped on it. Drops of volumes $V = 13 \times 10^{-9}$ m^3 were chosen. Top and/or side shots of the drop were acquired by means of the videocamera and transferred to the PC. *Ad hoc* software was developed, within the Matlab® programming environment, to process the acquired pictures, extracting drop contour and apparent contact angle (Fig. 1). First of all, images were pre-processed to correct the distortions resulting from the use of close-up lenses and high levels of zoom. The drop contour extraction can be done filtering the difference between an image with the drop and an image of the background only. Once the drop contour has been extracted, it is fitted using three methods: a 7th-degree polynomial, a cubic spline, an approximate drop contour equation [14]. Then, the apparent contact angle is extracted from each fitting curve. The three methods were compared using: test images found on the World Wide Web, computer generated images and images of drops on smooth HDPE (high density polyethylene) surfaces, for which contact angle values are available in the literature [15–18]. The total uncertainty, in the range of high hydrophobicity and superhydrophobicity, can be estimated to be within ±4° and this can be considered satisfactory.

2.2.4. Electrical characterization

The in-plane electrical characterization of GDLs was made by using a Frequency Response Analyzer FRA (Solartron 1260). Measurements were carried out using the 4-terminal technique, this was made necessary because of the very low impedances of these materials, at room temperature. The cell used in the experiments was developed *ad hoc* for GDLs; experimental set-up is reported in Fig. 2. All the impedance spectra were obtained over a frequency range of 0.5 Hz/1.0 MHz at fixed current amplitude of 10 mA. GDLs resistances were deduced by interpreting the experimental impedance spectrum with an equivalent circuit made of a resistance and an inductance in series.

2.2.5. Single cell polarization measurement

A single cell (fuel cell technologies) was used for all the steady-state polarization measurements. This kind of cell has a single

Figure 1. Extraction of the drop contour and contact angles.

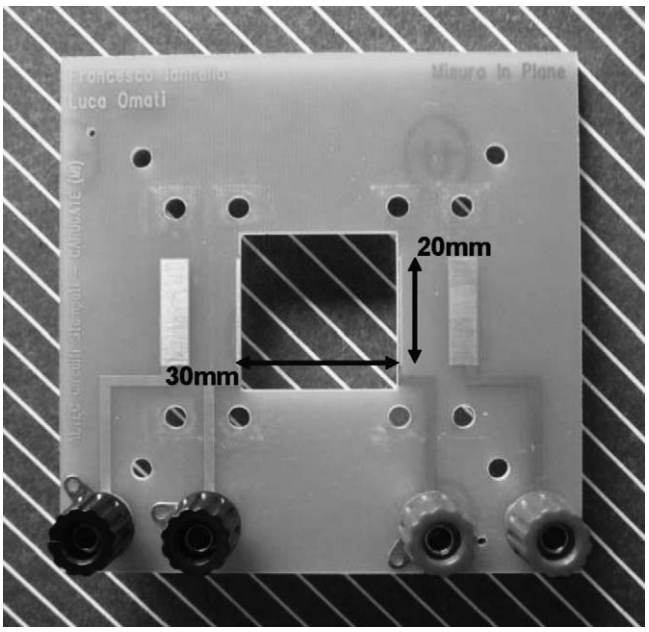

Figure 2. Cell used in the experiments, developed *ad hoc* for GDLs.

serpentine at the anode and a triple one at the cathode. The MEA was assembled using a Nafion112 membrane with a thickness of 50 μm and an active area of 25 cm^2; the catalyst layer was coated directly onto the membrane (i.e. catalyst coated membrane, briefly CCM) with a platinum loading of 0.5 mg cm^{-2} for both the anode and the cathode. To test the cell the experimental set-up was properly designed. Hydrogen and air were used as the anodic and cathodic feedings, respectively. The flow rates 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 333 K. The same operating temperature was adopted for all experiments and temperature controllers were used to keep it constant as much as possible. Connected to the cell there was an electronic load (RBL488-50-150-800) which measured and controlled voltage, current and electric power generated; to obtain a polarization curve (I–V) the cell voltage was changed from OCV to 0.3 V, with steps of 0.05 V, and at each step the resulting current were recorded.

3. Results and discussion

The use of pseudo-plastic shear thinning slurries is usually proposed for laboratory and industrial applications [19], when considering blade coating. Thus, water and PTFE contents were selected according to literature indications for GDLs and doctor-blade applications [12,19].

The ink compositions considered in this work are reported in Table 1, in terms of weight ratios among the components. First, the effect of CB, T and W on the slurry rheology was investigated (*ink 1–ink 3*). In Fig. 3a the flow curves of the slurries in which no PTFE was added (*ink 1–ink 3*) are reported. It is evident that *ink 1* and *ink 3* are pseudo-plastic and shear thinning as desired, while in *ink 2* the pseudo-plasticity is less evident, at least for the investigated range of shear rate.

Table 1
Compositions of different inks prepared throughout this work (CB = carbon black; T = tritonX100; W = water; PTFE = teflon).

	Ink 1	Ink 2	Ink 3	Ink 4 (12%)	Ink 5 (40%)
CB/T (g/g)	5.81	7.91	5.63	5.60	5.90
CB/W (g/g)	0.11	0.17	0.17	0.17	0.17
PTFE/CB (g/g)	–	–	–	0.12	0.39

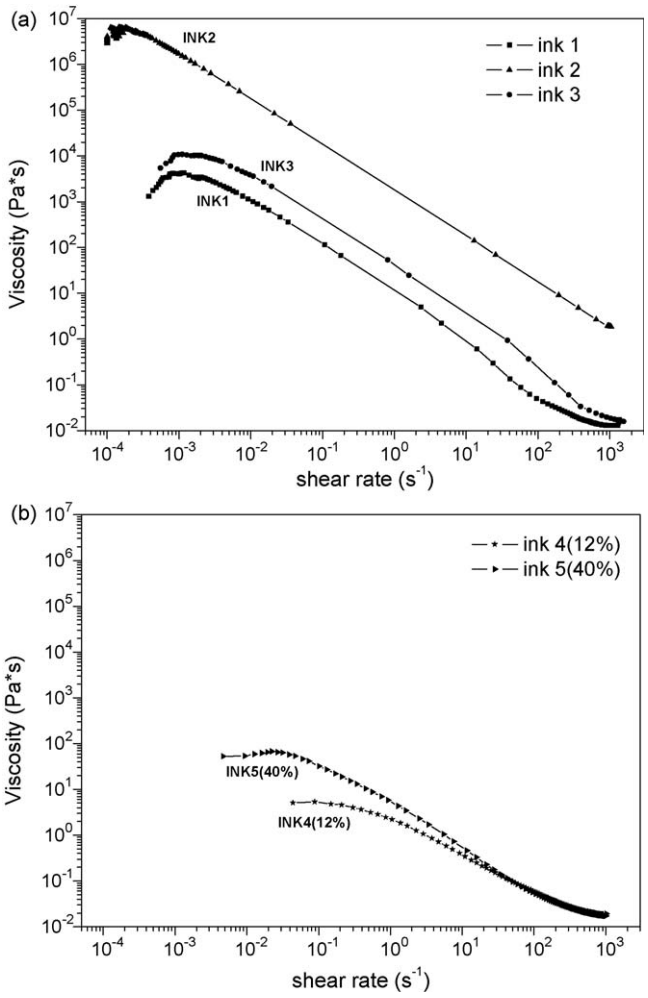

Figure 3. Rheological curves of the inks (compositions as Table 1); (a) inks without PTFE and (b) inks with PTFE.

Furthermore, *ink 2*, that contains the smallest amount of surfactant (CB/T = 7.91 g/g), shows a very high viscosity. At shear rate 110 s^{-1}, typical of blade coating process, the viscosity of *ink 2* is 10 Pa s to be compared with 0.1 Pa s of *ink 3* (CB/T = 5.63 g/g). This outcome is not surprising, because a lower amount of surfactant results in poor carbon dispersion.

On the other hand, at fixed CB/T, an increase of the amount of water results in a decrease of the viscosity: at shear rate 110 s^{-1} the viscosity of *ink 3* (CB/W = 0.17 g/g) is 0.1 Pa s to be compared with 0.04 Pa s of *ink 1* (CB/W = 0.11 g/g).

In conclusion, the starting composition of the inks to be coated onto the chosen substrates was driven by the following considerations: ink 2 was discarded because it is not shear thinning in the range of interest, i.e. shear rate in excess of 100 s^{-1} [19], while *ink 1* was discarded because of its lower viscosity.

In Fig. 3b the flow curves of the slurries based on *ink 3* composition in which PTFE was added are reported. According to literature [12], two amounts of PTFE content were selected: 12 wt%, *ink4* (*12%*), and 40 wt%, *ink5* (*40%*), with respect to CB (Table 1).

PTFE addition results in slurries with the same rheological behavior of *ink 3*, i.e. pseudo-plastic and shear thinning, but with lower viscosity (Fig. 3b). Yet, there is no effect of PTFE loading; indeed, the flow curves of *ink4* (*12%*) and *ink5* (*40%*) are totally

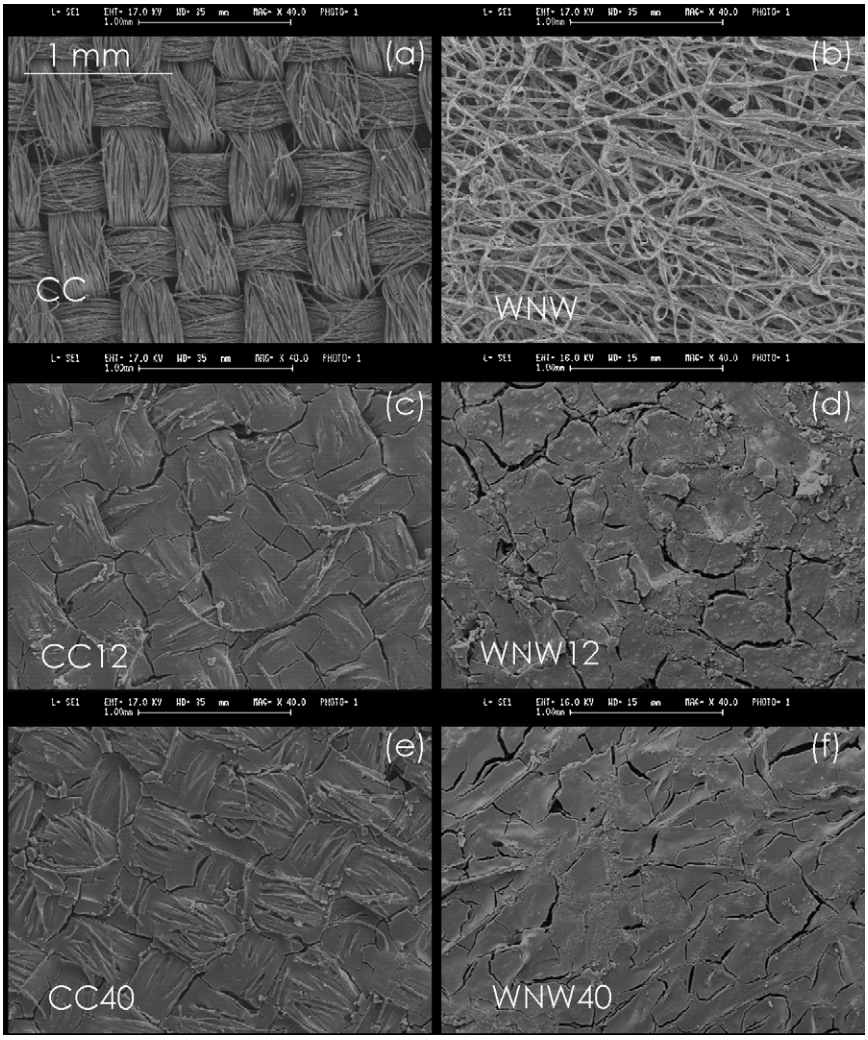

Figure 4. SEM images of the surfaces of CC (a, c, e) and WNW (b, d, f) samples with and without MPL.

overlapped in the range of interest, despite the large difference in PTFE content, i.e. 12 and 40% wt/wt, respectively.

In view of this PTFE effect on viscosity values, the composition of *ink 3* apparently was the best choice for this application. Thus, both slurries, i.e. *ink4* (*12%*) and *ink5* (*40%*), were deposited via doctor-blade on the two substrates (CC and WNW); the GDLs so obtained are labeled: CC12 and CC40, substrate carbon cloth coated with *ink4* (*12%*) and *ink5* (*40%*), respectively; WNW12 and WNW40, substrate woven non-woven coated with *ink4* (*12%*) and *ink5* (*40%*), respectively.

SEM micrographs of the surface of the substrates as received and of the coatings upon thermal treatment are reported in Fig. 4. In the case of CC, the coating results quite homogeneous, but it follows the warp and weft thread of the original cloth (Fig. 4c and e); on the contrary, in the case of the WNW, the MPLs have a less smooth surface, but no trace of the original substrate microstructure is evident. The cracking detected on the surface of WNW samples, and in minor extent also on CC ones, is probably due to shrinkage during thermal treatment. This phenomenon could be limited by properly tuning the operating conditions; thus, studies are in progress to further investigate these aspects.

MPL thickness of samples prepared with WNW substrate (WNW12 and WNW40) was very uniform (about 35 μm) and the amount of PTFE had no effect on it (Fig. 5a and b). On the contrary, the thickness of the layers coated on the cloth substrate (CC12 and CC40) varied in the range around 10–100 μm, being ruled by the path of warp and weft thread (Fig. 5c and d); also in this case, on the average no difference was detectable between samples CC12 and CC40. It is reported in the literature that for shear thinning fluids, with viscosity similar to those here studied, the thickness of the final film depends only on rheology and not on geometry or gap of the doctor-blade equipment [20]. Accordingly, the constancy in coating thickness, observed for the samples prepared using the same substrate, is a consequence of the comparable viscosity values of the two different slurries (about 0.04 Pa s at 110 s^{-1}), while the difference in thickness between the two substrates can be mainly ascribed to their different morphology.

3.1. Contact angle

In view of the isotropic surface roughness of the substrates the drop could be considered axisymmetrical with very good approximation.

As the investigated *MPL surfaces* have in general to be considered as rough, the static apparent contact angle was analyzed. No contact angle hysteresis was evaluated for the present study. If the surface is suitable, it can be characterized (in terms both of profile and of roughness) by means of the "surface analyzer" (SM Sistemi di Misura s.r.l., model RT80); for *MPL surfaces*, this is not possible because the probe of an analyzer would damage the MPL itself.

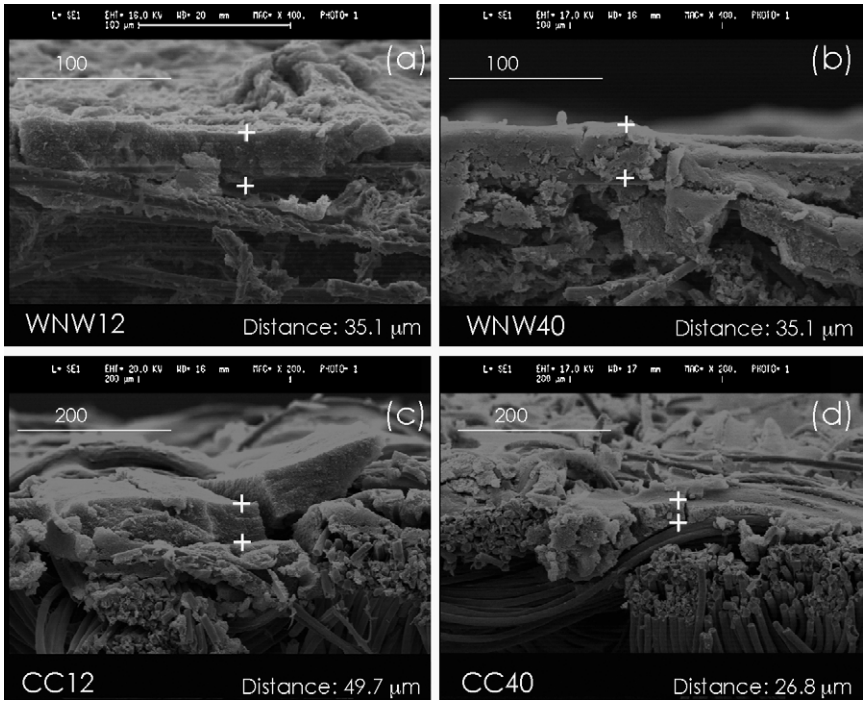

Figure 5. Cross section SEM images of WNW (a, b) and CC (c, d) samples.

Repeatability analyses were first of all performed, using different surface samples for each type. Some samples showed higher dispersion (up to 5.2° std. dev.), other were more uniform, but the mean values (average and median) had differences within ± 2°. Once the repeatability was checked, one sample for each kind was analyzed, deposing and analyzing a minimum of ten drops on it.

The main statistical parameters of the results on each sample were calculated. The median and the arithmetic average values were practically coincident; the first was chosen as a mean value, because it is less sensitive to "extreme" values with respect to the arithmetic average and it helps to identify outliers. Fig. 6 shows the results of the comparison among the different types of GDL/MPL.

It can be noticed how the data dispersion on many of the samples is higher than in the case of smooth surfaces. In particular, this is due to the inhomogeneous surface of the coated sample, deriving from the slight non-planarity and *GDL texture*. The latter effect is also responsible for the significant influence of the substrate even after the deposition of the MPL.

The differences are not only in the values, but also in the trend. Upon increasing PTFE content in the MPL, the increase in contact angle on CC substrate is less than linear. On the other hand, WNW GDL shows almost unchanged contact angle values when coated with 12% PTFE (WNW12), but a very sharp increase with the 40% PTFE (WNW40). In any case, the WNW GDL is the substrate which offers the best performances. In particular, WNW40 reached the region of superhydrophobicity (contact angle larger than 150°).

On the other side, the behavior of the CC GDL is less performing, but more regular when applying MPLs with increasing PTFE loadings.

3.2. Electrical characterization

As shown by the SEM images (Fig. 4), the presence of the MPL smoothes down the GDL surface and reduces the roughness; as a consequence, the in-plane resistance slightly improves (Fig. 7), decreasing from 0.86 Ω in the CC (or WNW) to 0.73 Ω in the CC12

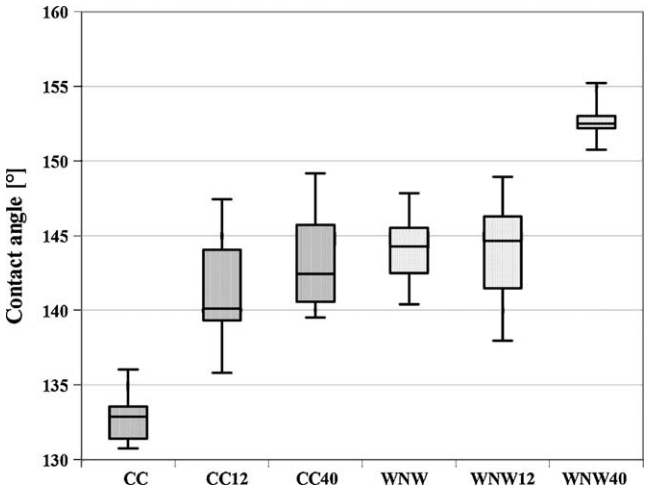

Figure 6. Results of the contact angle analysis on the six investigated surfaces.

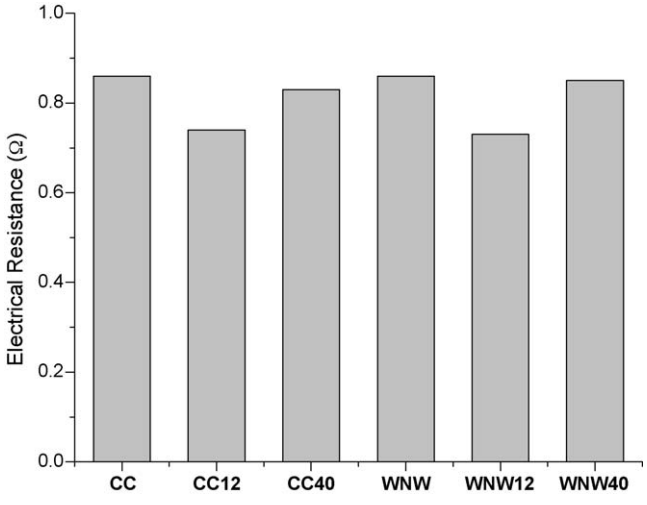

Figure 7. Electrical in-plane resistance of all samples.

(or WNW12). As expected, high PTFE loadings in the MPL worsen again the in-plane resistance, which comes back to about 0.85 Ω (CC40 and WNW40).

Because the two substrates, i.e. WNW and CC, have the same in-plane resistance, it is reasonable that the addition of the MPL has the same effect on this property irrespective of the substrate itself, and so it is (Fig. 7). Considering that the lowest in-plane resistance is displayed by samples WNW12 and CC12, the fuel cell polarization analysis was performed using these two GDLs.

The steady-state current-potential curves (I–V) of the cell with the two GDLs are shown in Fig. 8a and b. The measurements were carried out under three different cathode relative humidity conditions: RH 100/100, 100/80 and 100/60 at the anode and cathode, respectively.

For the CC12 (Fig. 8a) it is evident that humidity conditions do not affect the cell performances (the polarization curves are almost overlapping in the whole current density range) as far as cathode RH is higher than 80%, while a small deterioration of the cell performance can be observed at 60% RH. In the case of WNW12 (Fig. 8b) no effect of RH on cell performances is observed.

In terms of power density WNW12 is superior to CC12 (about 0.40 W/cm^2 vs. 0.35 W/cm^2 peak value), although at high current density CC12 seems to perform well.

The cell configuration being identical in all the polarization analyses apart from the GDLs, it is quite obvious to ascribe to the GDLs any difference in performance. Moreover, because the in-plane resistances of WNW12 and CC12 are almost identical, the better electrochemical performance of WNW12 is likely due to lower contact resistances [21] between the catalyst layer coated onto the membrane and the MPL coated onto the GDL.

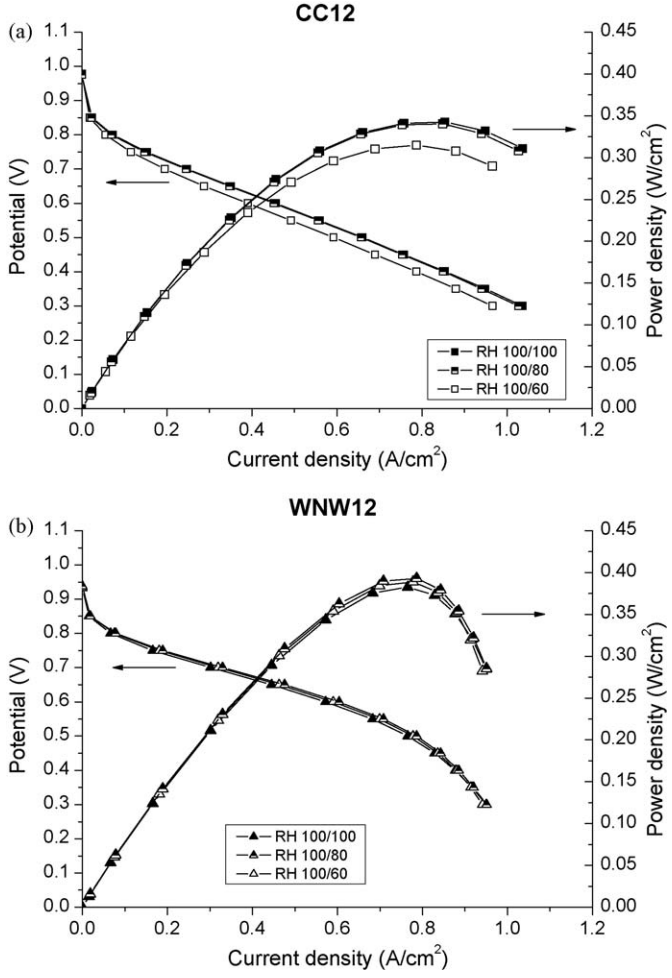

Figure 8. Polarization curves of cell assemblies with different samples: (a) CC12 and (b) WNW12.

4. Conclusions

1. The rheological behavior of the inks investigated in this work is suitable for coating deposition on the selected substrates via doctor-blade. Slurry viscosity is mainly determined by the CB/W and CB/T ratios; PTFE addition does not affect the rheological behavior, but slightly decreases the viscosity.
2. Notwithstanding the same rheological behavior of the PTFE-containing ink4 (12%) and ink5 (40%), the thickness of the MPL coated onto the WNW and CC GDLs is different; thus, the substrate morphology has a non-negligible influence on the final MPL thickness.
3. Contact angle measurements evidenced that the layers are hydrophobic and that the coating with the MPL definitely increased the hydrophobicity. In particular, the effect of the amount of PTFE is very positive and, for the highest CB/PTFE ratio (WNW40), the region of superhydrophobicity (i.e. contact angles exceeding 150°) can be reached.
4. The substrate does not affect the in-plane resistance of different GDLs having the same composition. However, WNW12 and CC12 have slight different electrochemical performances; being the cell configuration identical apart from the GDL, only the contact resistances could be responsible for this behavior.

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