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Influence of different Micro Porous Layers on electrochemical performance of PEMFCs

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Abstract

In this paper the investigation on the rheological, morphological and electrical behaviour of the addition of carboxymethylcellulose (CMC) in two different inks (used to coat a Micro Porous Layer or MPL) was studied. For the sake of comparison two inks with and without the CMC and the same amount of PTFE (12wt%) were prepared. The presence of CMC drives to a different rheological curve with respect to that obtained for standard composition ink and, in particular, to a general increase in viscosity and to a more shear-thinning behaviour.

Two Gas Diffusion Layers (GDLs) were obtained by coating via doctor blade technique the MPLs onto the carbon cloth. Hydrophobicity and morphology of the MPLs coatings were assessed by contact angle measurements and SEM analyses.

The two GDLs so obtained, were also tested in a single Polymer Electrolyte Membrane Fuel Cell and its performances evaluated. The membrane electrode assembly was made of Nafion® 212 with Pt load 0.3/0.6 mg cm^{-2} (anode/cathode). The cell testing was run at 60°C and 80°C, fed with 80%RH hydrogen and air at two different RHs (60 and 100%). PEMFC performances in the various configurations were assessed by polarization and power curves.

Introduction

The success and diffusion of proton exchange membrane fuel cells (PEMFC) is related to their capability to show optimal performances with H_2/O_2 system at high current density. However, when air is used as oxidant, some problems are found due to mass transport limitations that can be bypassed when Gas Diffusion Layer (GDL) is used. GDL is a critical component of a PEMFC because it has the function to transport the reactant gases effectively to the anodic and cathodic catalysts, to drain out the liquid water that is formed during operation, to conduct electron with low resistance and to keep the membrane in wet conditions at low humidity. Accordingly, the performance of the PEMFC is strongly influenced by the GDL properties such as porosity and water management. Porosity and both hydrophobicity and hydrophilicity are fundamentals to ensure the good operation of the system [1]. Summarizing, the ideal GDL should have: bending stiffness, good gas diffusion properties, graded porosity, good permeability, appropriate contact angle, electronic conductivity, stability and durability, compressibility and elasticity at different operating conditions. At present, GDLs are made of macroporous materials such as carbon paper or carbon cloth, 100 – 400 μm thick that can effectively handle gas permeability. To improve water management the co-presence of hydrophobic micropores is required .This is accomplished by coating a thin micro-porous layer (MPL) onto the GDL surface; such a layer also improves the smoothness of the GDL surface allowing a better contact with the catalytic layer [2]. In the common practice MPL almost consists of a mixture of Carbon Black (CB) and polytetrafluoroethylene (PTFE). MPL layer is coated onto the GDL substrate via paint-, roll- or blade coating techniques using a water dispersion of carbon black and PTFE particles in presence of a non-ionic surfactant such as Triton X-100 [3]. It is evident that rheological behaviour and the stability of the suspension are fundamental parameters to asses homogeneity, loading and thickness of the final MPL layer; however, these parameters are controlled by the composition of the slurry that, in some case, it is hardly to be properly tuned; thus the addition of a rheology and stability controller, such as polysaccharides has been proposed [4,5].

1. Scientific Approach

The use of pseudo-plastic shear thinning slurries is usually proposed for laboratory and industrial applications [4-7], when considering blade coating. Thus, in this work, water and PTFE contents were selected according to literature indications for GDLs and doctor-blade applications, moreover the use of a rheology controller was also taken in account [7,8]. In the industrial practice, among different polysaccharides, carboxymethylcellulose (CMC), a molecular chain derived from cellulose [4], is one of the most used viscosity controller in water-based systems for coating processes. CMC is a polysaccharide that, working on the colloidal forces, increases the viscosity of the aqueous phase, suppressing the tendency of the solid particles to aggregate thus inhibiting the collisions between them that would lead to flocculation [7]. Despite of positive effects on rheology behaviour, it is hardly to predict the effect of CMC on the final coated layer, for instance thickness, surface homogeneity and electrical properties. This last point has to be carefully considered because of the thermal treatment that is required for coating consolidation; indeed, it must be performed at temperatures lower than 370°C to avoid PTFE decomposition [9]. According to this, in this work the effect of the addition of CMC to the carbon slurry was investigated. Two inks,

with and without CMC addition, were prepared and deposited via doctor blade on a commercial carbon cloth substrate. In both samples PTFE/CB = 12% (w/w) was set to reply the composition of a sample already studied in a previous work [9]; while, the CMC-containing sample was obtained by adding 2 % (w/w) of CMC.

A commercial carbon cloth SCCG5 P10 (by SEAL SpA) was used as GDL.

2. Experiments

Slurries were prepared according to the procedure described in [5] (Figure 1).

In a typical experiment, carbon black powder, Vulcan XC72R (CB in the following), was mixed with an appropriate amount of 60 wt% PTFE emulsion and Triton X100 as a surfactant (T in the following) using deionised water (W) as solvent. According to Figure 1 a mixture of W, CB, T was prepared by mixing with an UltraTurrax T25 homogenizator for 10 minutes at 8000 rpm; subsequently CMC (Lamberti Company) was added and yet mixed at the same rate; finally, the PTFE emulsion was added and the slurry stirred for 10 minutes at 500 rpm.
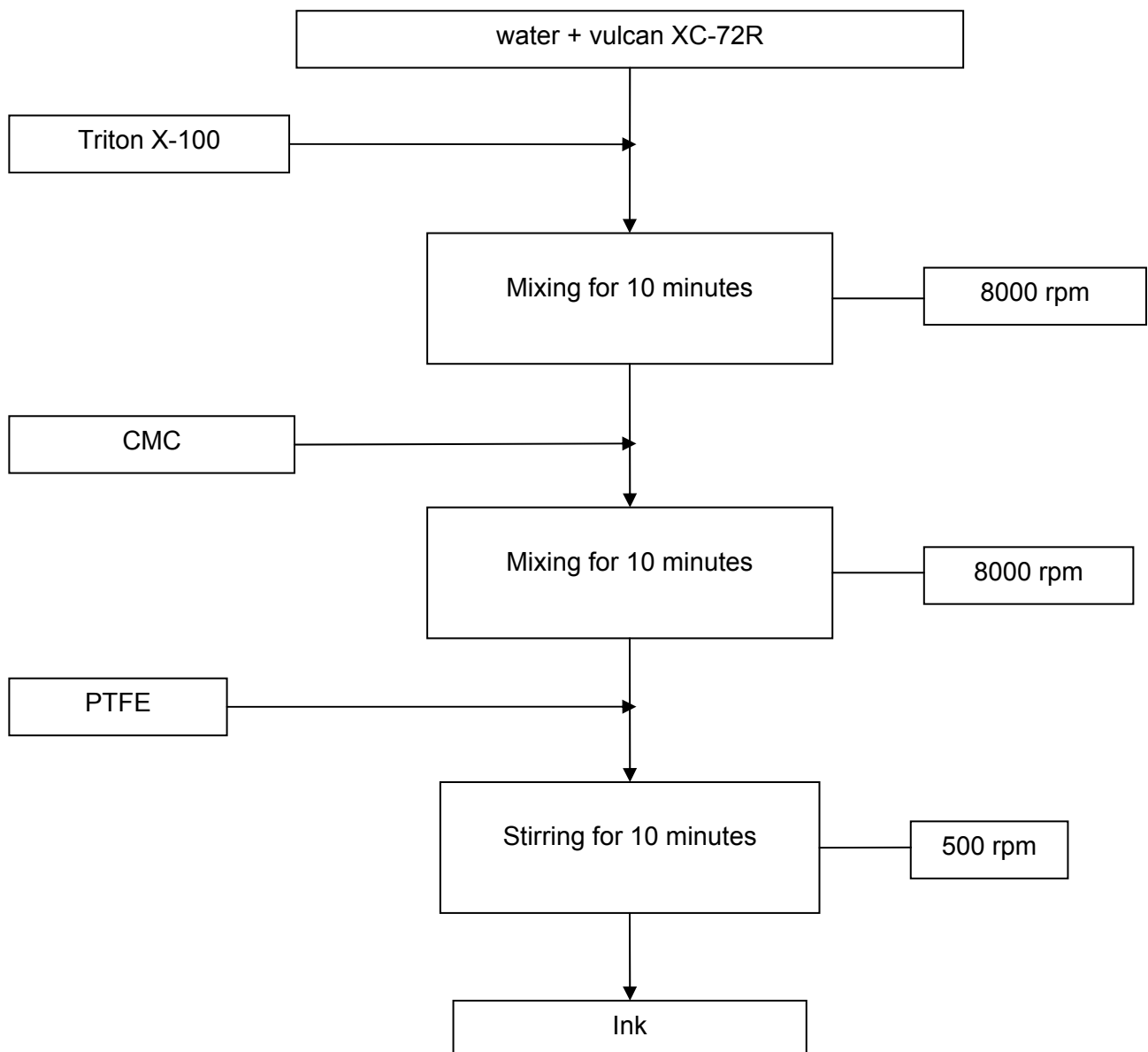

Figure 1. Scheme of the adopted preparation procedure

Using this procedure two inks were prepared (Table1), one with (in the following CMC12) and one without (in the following STD12) CMC. Label of the samples and ratios between the components are reported in the Table 1.

Table1. Inks composition

Sample	CB/T [w/w]	CB/W [w/w]	PTFE/CB [w/w]	CMC/W [w/w]
CMC12	5.6	0.13	0.12	0.02
STD12	5.6	0.13	0.12	-

The rheological behaviour of the inks was analysed at 20°C with a rotational rheometer (Rheometrics DFR 200) equipped with a 40 mm parallel-plates geometry, with a gap between the plates of 0.5 mm. Viscosities were investigated in the shear rates range $10^{-3} \div 10^3 \; s^{-1}$.

Immediately after preparation (in the following t = 0), the slurries were deposited onto the substrate via the doctor-blade technique using a lab-scale commercial equipment (K CONTROL COATER). A linear velocity of 0.042 m/s and a 40 µm gap were selected, corresponding to a shear rate of about 100 s^{-1}. The coated samples were calcined up to 350 C for 30 min with dwelling time at intermediate different temperatures (90°C, 120°C and 280°C) [9].

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

Contact angle measurements were performed to estimate the hydrophobicity of the surface. Drops of volumes $V = 9 \times 10^{-9} \; m^3$ were chosen. Top and side shots of the drop were acquired by means of the videocamera and transferred to the PC. The acquired pictures were processed, using the instrument software, to extract drop contour and apparent contact angle. The drop shape was detected by the contrast (bright-dark difference) of the drop to his surrounding. The contact angle of sessile drops was calculated according to Young-Laplace equation.

Electrochemical performances of the two GDMs were tested in a single cell experiment. The bipolar plates have a single serpentine at the anode and a triple one at the cathode; the active area was 25 cm^2; the MEA was assembled using Nafion 212 membrane, whose thickness was 50 µm and the catalyst layer was coated directly onto the membrane (i.e. catalyst coated membrane, briefly CCM) with a platinum loading of 0.3 mg cm^{-2} at the anode and 0.6 mg cm^{-2} at the cathode. Hydrogen and air were used as the anodic and cathodic feedings, respectively. The experimental set-up was properly designed: (i) flow rates were controlled and detected by a calibrated flow meter; (ii) the degree of humidity and the inlet gas temperature were controlled by external humidifiers and temperature controllers.

Two different cell temperatures (60 °C and 80 °C) were adopted for the experiments, which were carried out under the flow rates regime of 0.20–1.00 NL min–1 (H$_2$/air); only one humidity condition was employed for the hydrogen flow (80% RH), while two different humidity conditions were adopted for the air feeding: 60 and 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, one point per second 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 artifacts due to transient phenomena.

3. Results

In order to investigate the rheological behaviour and the stability with time of the inks the rheological measurements where performed at t=0 h that means immediately at the end of the mixing reaction (Figure 2a) and at t=48 h that means upon in-pot ageing for 48 h (Figure 2b)

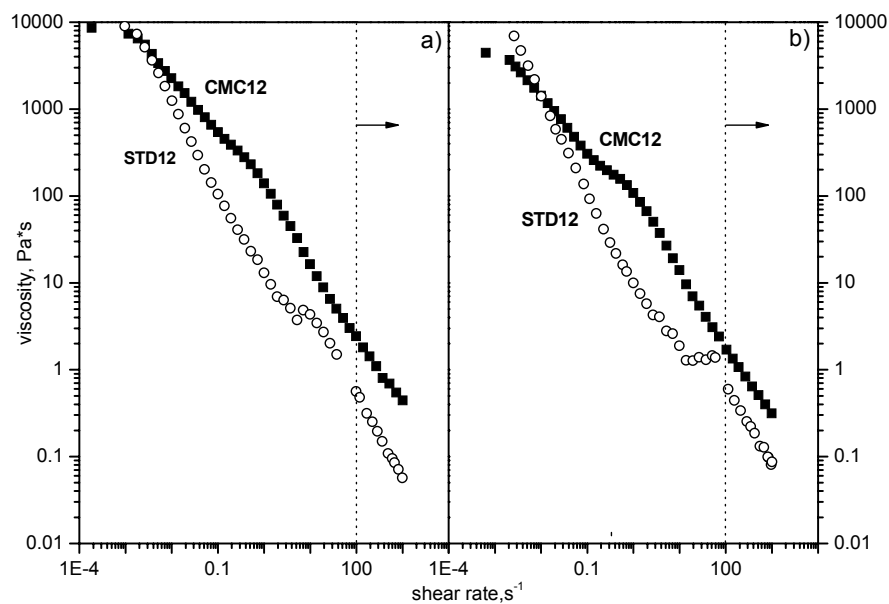**Figure 2 Comparison between rheological curves of the inks with and without CMC a) at t=0 h and b) at t=48 h.**

At t=0 (Figure 2a), both the samples show a pseudo-plastic and shear-thinning behaviour that is the more appropriate for doctor blade deposition. However, the addition of 2% of CMC results in a more shear-thinning sample. CMC also affects viscosity values that are higher for the CMC-containing sample in all the investigated range of shear rate; for instance, at 100 s^{-1}, η= 0.54 Pa s and η= 2.5 Pa s are measured for STD12 and CMC12, respectively. Furthermore, the presence of an inflection point is observed in both the curves that could be ascribed to instability of the ink due to re-aggregation of the dispersed carbon particles. In CMC12 sample the inflection point is smoother and shifted at shear rates far from those proper of doctor blade technique [7]. Considering that the CMC addition should favour the carbon dispersion, it can be hypothesized that CMC effectively affects the stability of the slurry. This effect also persists with ageing time (Figure 2b); indeed, the flow curve of CMC12, upon 48h of ageing time, is practically overlapped to that measured at t=0: the shear-thinning character is preserved and the inflection point, even more pronounced, is still far from the operating range of doctor blade (> 100 s^{-1}).
SEM micrographs of the coatings surfaces upon thermal treatment are reported in Figure 3. The surfaces of both samples are quite homogeneous and characterized by the presence of cracks.
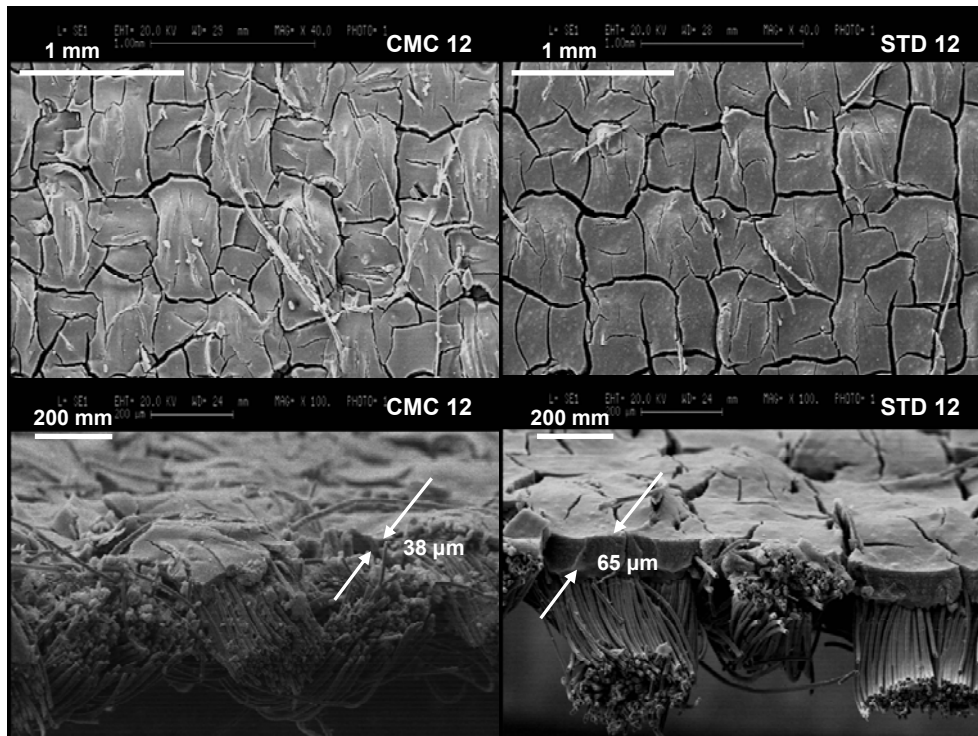
Figure 3. SEM images of surfaces and sections of substrates coated with (CMC12) and without (STD12) CMC.

However, at the surface of the CMC12 sample some fibres of the carbon cloth substrate are still evident suggesting that a thicker coating than in STD12 was deposited; this is confirmed by the images of the cross section of the samples. MPL thickness of CMC-containing sample, even difficult to be measured, is about 35-38 μm, while thickness of STD12 is about 50-70 μm. It is reported by Sullivan et al. [10,11], who studied the rheological behaviour of CMC and polyacrylamide solution, that, using the same experimental conditions, thicker layers are obtained with newtonian fluids than using non-elastic or weakly elastic shear-thinning ones. Accordingly, the deposition of CMC12 ink, more shear- thinning than STD12, resulted in a thinner layer. The contact angle measurements, that give an indication of the hydrophobicity of the samples, are reported in Figure 4.
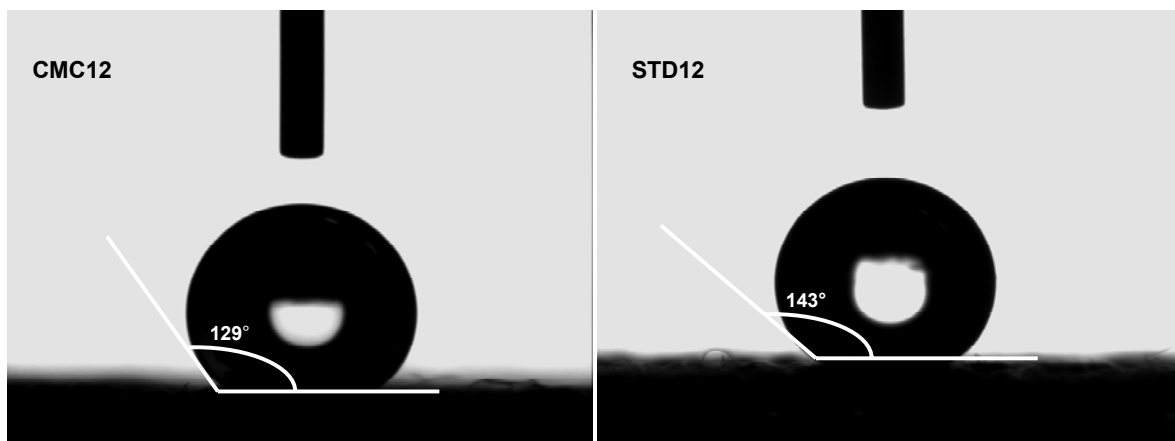

Figure 4 Contact angle measurements

Average values of 143° and 129° were found for CMC12 and STD12 sample, respectively, indicating that sample CMC12 is less hydrophobic than STD12.

The contact angle value of the GDL without any MPL deposition is 123°, thus a very low improvement of the hydrophobicity of the system have been obtained in CMC12 sample. The lower hydrophobicity of CMC12 can be due to many effects related to thermal treatment. Among others, those which are more likely to affect the hydrophobicity could be: the presence of residues of decomposition of CMC, due to the fact that the final temperature of the thermal treatment (350°C) is too low to totally decompose CMC, and/or the formation of additional porosity; indeed, CMC is commonly applied as pore former.

The steady-state current density-potential curves of the PEMFC assembled with the two different types of GDLs are all reported in Figure 5.

By comparing the polarization curves of samples CMC12 and STD12, a significant improvement in the electrical performance of the sample with the CMC12 occurs only when the cell operates at low humidity (RH 80-60) and high temperature (T80) on the entire range of current density (CD) investigated, Figure 5C. Instead, at low temperature the best performances of the CMC12 sample are confined just to the region of low CDs (Figure 5A). On the contrary, at high humidity (RH 80-100), the presence of CMC in the formulation of the ink appears to be detrimental in the management of water that results in poor electrical performances and sudden voltage drop, Figure 5B and 5D.
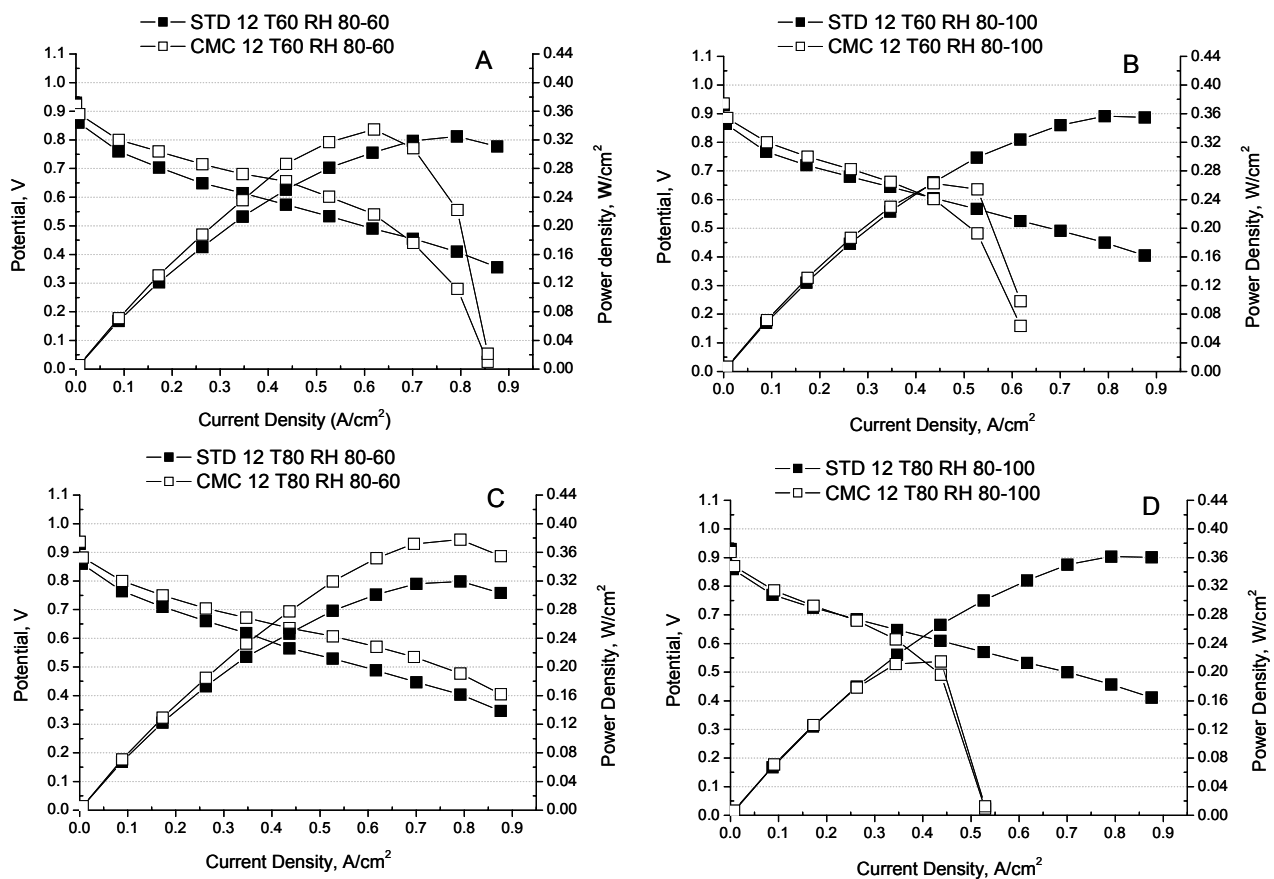

Figure 5. Polarization curves of samples CMC12 and STD12
(A) T60 RH 80-60; (B) T60 RH 80-100; (C) T80 RH 80-60; (D) T80 RH 80-100

In conclusion, the addition of CMC results in an improved control of the ink rheological behaviour, due to a positive stabilization effect on the slurry dispersion. However, because

of a possible incomplete CMC decomposition during thermal treatments of the MPLs, the hydrophobicity of the samples is insufficient to guarantee a proper water management. This effect becomes particularly evident when the cell mounting this GDL (CMC12) is operated at high RH. The operating cell temperature mitigates only partially this effect. More appropriate compositions and thermal treatments might allow overcoming these drawbacks.

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