

Formulation and Properties of Different Microporous Layers with Carboxymethylcellulose (CMC) Composition for PEM-FC

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Inks formulation to deposit microporous layers (MPL) for polymer electrolyte membrane fuel cells (PEM-FCs) application were studied. The effect of the addition of carboxymethylcellulose (CMC) on slurry rheological behaviour and on final morphological, electrical and wettability properties of the so-obtained MPLs were assessed. For this purpose different formulation, namely with and without CMC, were compared. The presence of CMC resulted in a general increase of slurry viscosity and stability. Wettability analyses for surface characterization were performed by means of contact angle measurements applying the sessile drops technique. 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. The presence of residual amounts of CMC, not fully decomposed upon MPL thermal treatment, affected negatively the final MPL characteristics in terms of hydrophobicity.

Fuel cell assemblies using MPLs with and without CMC showed different electrochemical performances in terms of I-V curves and impedance spectra. CMC-containing MPLs showed electrochemical performances that were influenced by the CMC content: more CMC induced a decrease in power density. However, CMC-based MPLs exhibited lower ohmic resistances.

1. Introduction

In the last decade, fuel cells (FCs) have attracted scientific community attention for use as alternative power sources. A number of studies have been reported on different kinds of fuel cells such as Solide Oxide FCs (SOFCs) (Sieniutycz S. 2011), Direct Methanol FCs (DMFCs) (Ismail A., 2012) and Polymer Electrolyte Membrane FCs (PEMFCs) (Venturelli et al. 2009). In particular, PEMFCs have already been used in some mobile and stationary applications due to low related emissions and high power densities reached. Several works have been performed in order to develop new materials and technological solution to improve PEMFC performances. It has been evidenced that water management in the cell, and particularly at the cathodic side, is crucial for the performances (Ahmed et al. 2008).

Water management can be effectively performed by the use of a Gas Diffusion Medium (GDM). This fundamental cell component consists of a macroporous carbon cloth or carbon paper substrate called Gas Diffusion Layer (GDL) coated with a carbon layer, the so-called microporous layer (MPL). One of the main property required to MPL is hydrophobicity. Moreover, the presence of MPL coating also improves the smoothness of the GDL surface, allowing a better contact with the catalytic layer, and electrical conductivity (Ji and Wei, 2009). Recently, MPLs were proposed to reduce mass transport limitations in PEMFCs, which are due to water flooding, and to improve performances, especially in the high current density region (Tseng and Lo, 2010). Liquid water is generated at cathodic side by the oxygen reduction reaction and it is also supplied to the cell by external humidifiers to maintain the proper membrane wetness. An accumulation of liquid water could result in diffusion limitations, in fact, the rise of mass

transfer resistances due to the blocking of porosity by water presence will result in the decrease of reactant gases supply, thus in a worse cell performance. Instead if the electrolytic membrane is dehydrated, the performance of the fuel cell would decrease because ionic conductivity of the proton membrane is strongly dependant on water content (Peighambardoust et al., 2010).

Thus, GDM composition and properties have to be tuned in order to guarantee the correct balance between external water by humidifiers and internal generated water. GDLs substrates are typically coated with water-based dispersions of carbon black and a polymer such as PTFE that acts both as binder of carbon particles and hydrophobic agent; the binding effect is obtained by thermal treatment up to polymer sintering (Park et al., 2012). However, conflicting results on the influence of the PTFE content in the MPL are reported: the suggested PTFE content ranges from less than 5 % to more than 40 % in the MPL layer. The MPL is usually coated on the GDL by means of various techniques, like painting, rolling, spraying, screen printing (Lee et al., 2004), and the blade-coating technique. Blade-coating implies the use of highly viscous inks (Stampino et al. 2009), spread by a blade onto the substrate: the ink viscosity, the coating speed and the distance between the blade and the substrate are responsible for the thickness and homogeneity of the final MPL (Latorrata et al., 2012). Due to the requirements on both rheological behaviour and stability, MPL slurries generally have complex formulations (Tracton, 2005).

To fulfill the cited requirements the use of CMC as viscosity and stability controller is reported in many fields of application (Benyounes et al., 2010). CMC is a natural polysaccharides that, acting on the colloidal forces, increases the viscosity of the aqueous phase and suppress the aggregation and the flocculation of solid particles. Furthermore, CMC solutions show a shear thinning behaviour which is suitable for blade-coating application (Sullivan and Middleman, 1986). Moreover, CMC is a hydrophilic molecule, thus its presence in the final MPL layer, possibly due to its incomplete decomposition upon thermal treatment could not be necessary detrimental. In fact, in view of its hydrophilic nature, it could act as a water reservoir in order to prevent dehydration of the ionic conducting membrane even in conditions of low relative humidities (RHs) of the supplied gases. In this work, the use of CMC in the MPL ink formulation and its effect on the rheological properties and on the electrical performances of a single PEMFC are reported. CMC based slurries were prepared on the basis of the procedure described in . Three inks were prepared, two containing CMC and one without CMC as a reference. The PTFE content was fixed at 12 % w/w that was found to be a reasonable compromise between hydrophobicity and electrical performances (Latorrata et al, 2012). The rheological behaviour of the inks was evaluated and the blade-coating technique was employed to coat GDLs. The deposited layers were characterized by contact angle measurements to evaluate the surface wettability and optical and SEM images were used to evaluate the surface morphology. Electrochemical tests were performed under two operating temperature, namely 60 °C and 80 °C, and two relative humidity (RHs) conditions (80-60 and 80-100 %, Anode-Cathode).

2. Experimental

Commercial carbon clothes GDLs (SCCG5 P10, SAATI Group), hydrophobised with polytetrafluoroethylene (PTFE), were used as substrates. Inks were prepared according to the procedure described elsewhere (Latorrata et al, 2012). In order to investigate the effect of CMC addition, two different CMC-water ratios were employed (i.e. 0.25 % wt and 1.0 % wt), while PTFE content was set to 12 % wt of CB. In the following, these inks will be identified as CMC-0.25 and CMC-1.0, while the reference sample will be identified as CMC-0. The inks were coated and treated as reported in Stampino et al. (2009). All the inks were analysed by a rheological point of view as described in A Cambridge Stereoscan 360 scanning electron microscope (SEM) was used for the morphological analyses. In order to assess the hydrophobicity of the surfaces, samples were analyzed at r.t. (i.e. room temperature), 60 °C and 80 °C by means of the experimental setup and procedures described in Guilizzoni and Sotgia (2010) for heating system and in Guilizzoni (2011) for the image acquisition chain. The sessile drop technique was used, which is still the most common approach despite the many issues, both conceptual (Extrand and Moon, 2010) and experimental (Hoefnagels et al., 2007), that affect such kind of measurement on highly hydrophobic and very rough surfaces. Drops having a nominal volume $V_S = 13 \mu\text{L}$ ($1.3 \cdot 10^{-8} \text{ m}^3$) were used for static contact angle tests. Much larger drops, having a nominal volume $V_L = 120 \mu\text{L}$ ($1.2 \cdot 10^{-7} \text{ m}^3$), were used to estimate the advancing and receding contact angles, following a slightly modified version of the model proposed by (Tadmor and Yadav, 2008). The surface samples were fixed to rigid metallic supports by double-sided tape to minimize warping or other deformations.

The electrochemical performances of the three GDMs were tested in a single cell assembly. The active area was 25 cm²; Nafion™ 212 membrane was used and the catalytic platinum loading was 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. Flow rates were controlled and detected by a calibrated flow meter; humidity and the inlet gas temperature were controlled by external humidifiers and temperature controllers. Experiments were carried out at two different cell temperatures (60 °C and 80 °C) under the flow rates regime of 0.20/1.00 NL min⁻¹ (H₂/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), for measuring voltage, current and generated power, was connected to the cell. Polarization curves were recorded under galvanostatic conditions in the current density (CD) range from OCV to 0.87 A/cm², with steps of 0.085 A/cm².

3. Results

In order to investigate the effect of CMC in the inks formulation, rheological measurements were performed. All the samples are pseudo-plastic and shear-thinning (Figure 1), which makes them suitable for blade coating applications. The presence of CMC improves the shear-thinning behaviour and stabilises the rheological one. Addition of CMC, indeed, results in a more regular rheological curve: smoother inflection points are observed in the CMC-containing samples (Figure 1). A positive stabilization effect on the rheological behaviour is clearly evident upon CMC addition to the formulation. The presence of CMC possibly prevents re-aggregation or separation of the dispersed carbon particles during measurements, thus resulting in more stable slurries for all the range of the applied shears. This effect is much more evident at high shear rates (> 100 s⁻¹), those of interest for blade-coating application, where the slurries undergo high shear effects. SEM micrographs of the coatings surfaces upon thermal treatment are reported in Figure 2 together with that of the uncoated GDL(a). No positive effect of CMC addition is found on coatings homogeneity: traces of the original substrate microstructure are somewhat evident and cracks at the surfaces are always distinguishable. In addition to that, CMC is a hydrophilic molecule, it adsorbs large water amounts thus it undergoes a marked swelling effect. Upon thermal treatment, water is eliminated and a marked volume contraction of the final layer occurs, conversely it does not when the CMC-free sample is fired. FTIR measurements are in progress to better clarify this point. Surface hydrophobicity was evaluated by apparent contact angles measurements, analysing both the shape of the drops and the contact angles at different temperatures, namely r.t., 60 °C and 80 °C. Figure 3 shows a drop resting a) on CMC-0, b) on CMC-0.25 and on c) CMC-1 surfaces. In agreement with SEM analysis, the MPL layer does not ensure a complete coverage of the GDL structure and drops lay on an irregular surfaces that are characterized by cracks and, in some case, by protruding fibres. In particular this picture is more evident in CMC-0.25 sample. Despite of the irregularity of the surface quite good hydrophobic behaviour is found for all the samples (Figure 4). At r.t., the water repulsion behaviour of the surfaces is very good, extending, for all of them, up to the boundary of super-hydrophobicity.

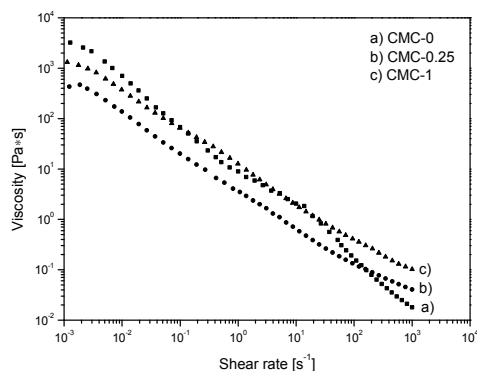


Figure 1: Rheological behaviour of: a) CMC-0, b) CMC-0.25 and c) CMC-1, as prepared;

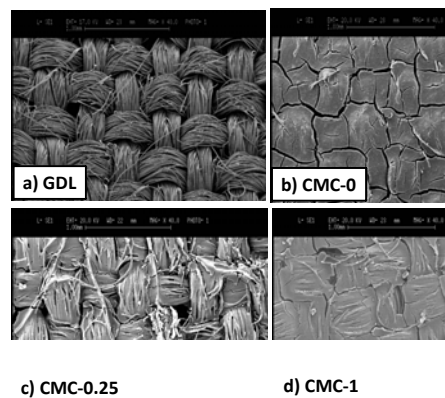


Figure 2: SEM micrographs (40x) of the uncoated GDL and the coated samples (b-d)

Given the uncertainty in the measured values, generally speaking they are underestimated (Extrand and Moon, 2010) (Extrand and Moon, 2010), thus a super-hydrophobic nature could be accounted for all the samples. The high scattering of the data may be caused by the cited incomplete and not uniform facing of the GDL. Unevenness in the deposition or simply the fast sample wear could be charged of these defects. The presence of residual CMC fragments due to an incomplete decomposition cannot be discarded too. Indeed, even the similar average wettability of the CMC-0.25 and CMC-1 is the result of points with different water repulsion behaviour, some of them are near the medium hydrophobicity.

When the temperature is increased, the static contact angle decreases for all the surfaces and the contact angle hysteresis increases. A shift from a Cassie-Baxter wetting behaviour (Cassie and Baxter, 1944) at r.t. towards a Wenzel wetting behaviour (Wenzel, 1936) at 60 °C and 80 °C seems likely. A progressive decrease of contact angle on increasing the temperature is observed for CMC-0 and CMC-1, with the larger decrease between 60 °C and 80 °C. The contact angle decrease observed for this samples could be explained with changes in the surface where re-orientation of the long polymer molecules could happen (Tavana et al. 2007). An effect of liquid adsorption at the surface could be also taken into account (Tavana et al., 2007), particularly on porous surfaces as the investigated ones: once the surface is heated, it dehydrates, so that it is particularly suited towards water adsorption (Diaz et al., 2010).

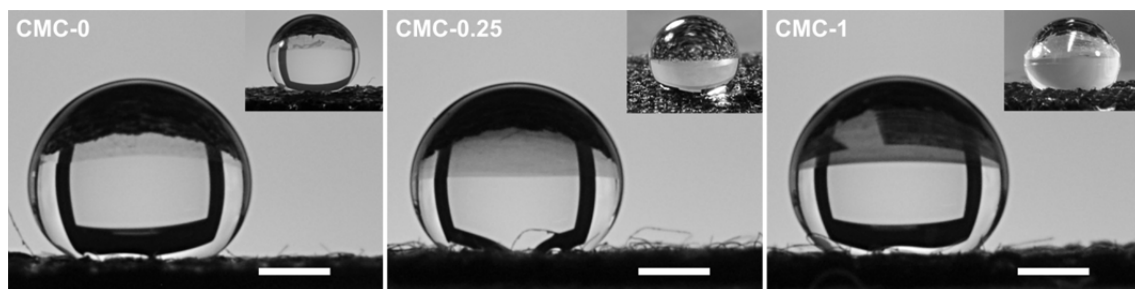


Figure 3: Drop resting on a) CMC-0, b) CMC-0.25 and c) CMC-1 surfaces, at $T = 20^{\circ}\text{C}$. Main panels show side views for contact angle measurement, inset shows inclined perspectives. White bars represent 1 mm.

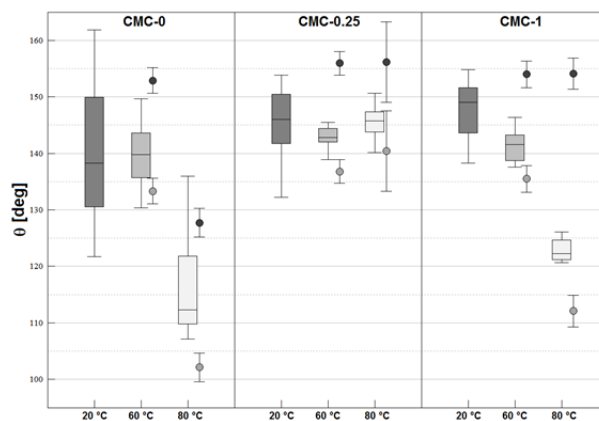


Figure 4: Static (boxplots) and dynamic (advancing and receding, shown as median values \pm standard deviation) contact angles on the investigated surfaces, at $T = 20$ °C, 60 °C and 80 °C.

Generally, it can be noticed that ohmic resistance decreases when, keeping temperature fixed, RH increases, due to a better membrane hydration and consequently a higher proton conductivity. When RH is constant, even an increase of temperature leads to a similar behaviour because of the same beneficial effect on the membrane conductivity. Moreover, the presence of CMC is effective in reducing ohmic resistance, above all for the sample CMC-1: a higher content of CMC makes the system able to hydrate membrane much more, as reported in Latorrata et al. (2012). Figure 5 shows the polarization and power density curves obtained for the fuel cell assembled with the three different GDMs in each operating condition. The fuel cell assembled with the samples without CMC shows the best performances in all the employed conditions in terms of maximum power density reached. CMC-0.25 exhibits performances comparable to the best ones only in the low and

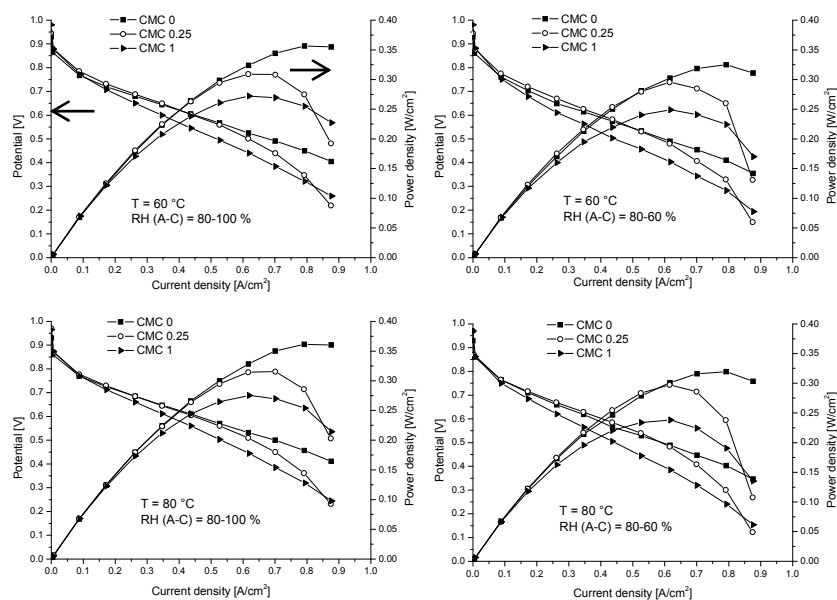


Figure 5: Polarization and power density curves measured for the three different fuel cell assemblies in each employed operating condition

in the medium current density region, while at high current densities it shows a sudden voltage drop; for CMC-1 such a trend is more dramatically highlighted. This behaviour could be ascribed to an ineffective water management of the CMC-based GDMs due to CMC hydrophilic feature: residual CMC pieces could

remain in the MPL bulk and adsorb the water produced by cathodic reaction that could cause channels flooding, thus reducing voltage values at high current density (i.e. when more water is generated).

4. Conclusions

Carbon slurries suitable for blade coating applications can be obtained with and without CMC in the inks formulation. However, CMC improves the shear-thinning behaviour and stabilises the rheological curve even at low content possibly preventing re-aggregation and separation of the dispersed carbon particles. No positive effect of CMC addition is found on coatings homogeneity: traces of the original substrate microstructure are somewhat evident and cracks at the surfaces are always distinguishable.

The high volume contraction in CMC-containing coatings upon thermal treatment are probably responsible for lower MPL thickness and cracks number and dimensions. Despite of the irregularity of the surface, quite good hydrophobic behaviour is found for all the samples. At r.t., the water repulsion behaviour of the surfaces is very good, extending, for all of them, up to the boundary of super-hydrophobicity.

CMC-based MPLs can induce a dramatic voltage drop of a fuel cell running at high current densities because of CMC hydrophilic nature. However, they are able to guarantee a better membrane hydration and consequently reduce ohmic resistances.

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