Design of properties and performances of innovative gas diffusion media for polymer electrolyte membrane fuel cells

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ABSTRACT

Gas diffusion medium (GDM) is a crucial carbon-based component for water management in polymer electrolyte membrane fuel cells (PEMFCs). GDM consists of a macro-porous substrate, which is usually a carbon cloth or carbon paper, coated with a thin micro-porous layer (MPL). Traditionally, PTFE is used as hydrophobic agent and binder. In this work, three different GDMs were prepared using fluorinated polymers (polytetrafluoroethylene-co-hexafluoro-propylene (FEP), polytetrafluoroethylene-co-perfluoroalcoxy vinyl ether (PFA) and a fluorinated polyurethane based on perfluoropolyether blocks (PFPE)) in order to replace conventional PTFE as hydrophobic agent, which was used as reference. Inks composition and rheological behaviour were fixed in order to apply the blade coating technique for MPL deposition. These polymers allowed to decrease temperature during thermal treatments with respect to the one necessary for treating PTFE-based MPLs. Moreover, superhydrophobic layers were obtained for all the samples and the final electrical performances of the whole fuel cell system were improved with respect to the ones reached with PTFE-based samples. In particular, FEP allowed to reduce significantly mass transfer resistances in the operating conditions of the fuel cell.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are electrochemical devices that produce electricity through the direct electrochemical oxidation of a fuel (usually hydrogen) and the reduction of oxygen with high efficiency and low environmental impact. Moreover, PEMFCs are capable of producing high power densities and undergoing rapid changes in load; thus, they are regarded an alternative power source for both automotive and stationary applications [1–5].

PEMFCs performances and costs mainly depend on the membrane electrode assembly (MEA), composed by the polymer electrolyte membrane and the two catalytic layers (i.e. anode and cathode). Between the MEA and bipolar plate, where serpentines with the flow field lie, the so-called gas diffusion medium (GDM), fundamental to the proper working of the fuel cell (FC), is inserted. It plays an important role in determining the electrochemical performance of the device since it has to guarantee a proper transport of water. An efficient water management is a key factor to obtain enough power, to prevent degradation of materials and to avoid flooding of the electrodes during operation of a PEMFC. Indeed both deficiency and excess water would cause severe problems to power generation. Water deficiency would result in reduction of ionic conductivity of the membrane as well as it would drive to severe contact resistances between the membrane and the catalyst layer; on the other hand, excess water would cause diffusive limitations thus reducing catalytic sites for electrochemical reactions and hindering reactants transport to the electrodes [6–10]. It has been demonstrated that GDM is able to manage water efficiently depending on composition and properties such as thickness, porosity, hydrophobicity and permeability [11]. An optimal GDM reduces flooding under high relative humidity (RH) conditions and prevents membrane dehydration under low RH conditions [10,12–14].

GDM consists of two main components, a gas diffusion layer (GDL), which can be a macro-porous carbon-fibre, carbon-cloth or woven-non-woven substrate and a micro-porous layer (MPL) which is a carbon layer.

Gas diffusion layer (GDL) can remove reaction products (exhausted gases and water) from the catalyst layer and it can favour heat removal from the MEA. Moreover, it can guarantee

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a good contact between bipolar plates and MEA. In this respect, GDL characteristics, such as electronic and thermal conductivity, porosity, hydrophobicity, compressibility and elasticity, play a crucial role in determining the water management efficiency during PEMFC operations [9,15–18]. MPL is directly coated onto GDL surface and it consists of carbon particles and of a hydrophobic agent, namely PTFE. Due to its micro-porosity it improves capillary pressure, thus the water removal capability. Many studies have demonstrated that a MPL coated onto the GDL is effective in improving water management, thereby getting better electrical performances [7,9,10,12,14,16,19,20].

A more hydrophobic MPL would allow a faster water removal process at the cathode side [21]. A typical MPL formulation mainly contains carbon black (CB), polytetrafluoroethylene (PTFE), both as binder and hydrophobic agent. CB is dispersed using proper solvents and dispersants, then a PTFE suspension is added. The resulting ink is deposited onto one side of the GDL substrate pretreated with PTFE. A subsequent thermal treatment of the formed GDM is required to evaporate the solvent and the surfactant and to induce the polymer spreading onto the carbon, called in the literature sintering [11].

The effect on water management of the different MPL components has been extensively investigated during the last decade [9,11]. Nature and loading of the carbon powder, wettability, thickness and porosity of the layer surface were suggested to be responsible for the final MPL properties. Much less attention has been paid on the nature of the hydrophobic agent, keeping PTFE as the best choice for that purpose for many years. Only few works have dealt with the use of different polymers such as fluorinated ethylene propylene (FEP) [22,23] and polyvinylidene fluoride (PVDF) [24–27].

Some of us have recently reported the beneficial effects of the use of perfluoropolyether derivatives for hydrophobic surface treatments of GDLs [28].

In the present study, three different fluorinated polymers were tested in order to replace PTFE: perfluoroalcoxy (Teflon® PFA), fluorinated ethylene propylene (Teflon® FEP) and a fluorinated polyurethane (Fluorolink® P56, Solvay) based on perfluoropolyether (PFPE) blocks [29–33] were applied to make both GDLs (i.e. the substrate) and MPLs (i.e. the coated layer) hydrophobic.

Different formulations were prepared and the effect of the polymers nature on the rheological behaviour of the ink was studied in order to apply doctor blade technique for coating deposition. The influence of the polymer nature on the final GDLs and MPLs properties, such as contact angle values and morphology, was studied with the final target to evidence a relationship between GDM composition and electrochemical behaviour of the running fuel cell.

2. Experimental

2.1. Preparation

Commercial carbon cloths (S5, from SAATI, Italy) were used as GDLs.

Commercial aqueous dispersions of polymers as hydrophobic agents were used for polymers raw materials: a high molecular perfluoropolyether (PFPE) Fluorolink® P56 from Solvay Solexis, fluorinated ethylene propylene (FEP) and perfluoroalcoxy (PFA) both from DuPont.

Before coating deposition, the surfaces of the bare GDLs were hydrophobized by soaking in a solution of the selected fluorinated polymer for 20 min. Subsequently they were heated in air for 30 min up to 150 °C, 260 °C and 305 °C to melt and to make PFPE, FEP and PFA fibrous, respectively [34].

Table 1
Inks composition in terms of significant ratios. Ink based on PTFE refers to sample prepared in [13] in which surfactant was Triton X-100.

Sample name	CB/H$_2$O (w/w)	Polymer/CB (w/w)	CB/IPA (w/w)	CB/Triton (w/w)
ink-PTFE	0.13	0.12	–	5.6
ink-PFA	0.13	0.12	5.6	–
ink-FEP	0.13	0.12	5.6	–
ink-PFPE	–	0.12	7.72	–

Highly conductive graphitic carbon black (CB, Cabot Vulcan XC72R) with high surface area was used for MPL preparation. Isopropyl alcohol (IPA), supplied by Sigma–Aldrich, was used as solvent and dispersant. Slurry composition and experimental procedures were selected according to a procedure previously reported [13].

In a typical experiment, CB was slowly added to a solution of the polymer dispersion and IPA (Triton X-100 in the reference ink preparation based on PTFE [13]) in deionized water. The mixture was vigorously stirred and homogenized by a high shear mixer (UltraTurrax T25) at 8000 rpm for 10 min.

The final inks compositions are reported in Table 1; the selected formulation would guarantee a proper rheological behaviour of the ink when used in blade coating procedure.

Indeed, the obtained inks were deposited onto the hydrophobized GDL substrate via the blade coating technique, using a lab-scale commercial equipment K-101 Control Coater. A linear velocity of 0.0154 m/s and a 40 μm gap, corresponding to a shear rate of about 350 s^{-1}, were adopted.

Finally, to remove water and IPA and to sinter the fluorinated polymer, the coated samples were heated in air up to 150 °C, 260 °C and 305 °C (30 min) for PFPE, FEP and PFA, respectively. Reference samples based on PTFE were treated at 350 °C [13].

2.2. Characterization

X-ray diffraction (XRD) analysis of the fluorinated polymers was performed using a Bruker-D8 Advance instrument. Spectra were recorded under the following experimental conditions: Cu Kα radiation, 2θ range = 20–80° 2θ, step scan = 0.02° and time per step = 12 s. The crystallinity degree was estimated by XRD pattern using the following equation:

$$x_c = \frac{I_c}{I_c + I_a}$$

where I_c is the diffracted intensity of the crystalline peak at about 18° 2θ and I_a is the diffracted intensity of the amorphous halo at about 16° 2θ.

DSC thermograms of the fluorinated polymers were recorded in air using a Mettler Toledo 823e instrument, temperature range: r.t. – 400 °C and heating and cooling rates 10 °C/min.

The rheological behaviour of the inks was tested at 20 °C by means of a rotational rheometer (Rheometrics DFR 200) equipped with a 40 mm parallel-plates geometry, with a gap between the stationary plate and the movable one of 1 mm. Dynamic viscosities were investigated in the shear rates range 10^{-3} to 10^3 s^{-1}.

Contact angles were measured with a modified axisymmetric drop shape analysis technique [35] using "as placed" sessile drops [36], i.e. gently deposited drops on a fixed surface with no vibration or other disturbances. A high precision metering pump with suitable syringes was used to generate drops of controlled volume and side views of such drops were taken using a diffuse 800 W light and a SLR digital camera with a 60 mm F2.8 Macro-lens. The side shot of the deposited drop were processed with the technique described in [37,38]: the numerical integration of the axisymmetric Laplace-Young equation in dimensionless arc-length coordinates was fitted