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Impact of gas stoichiometry on water management and fuel cell performance of a sulfonated Poly(Ether Ether Ketone) membrane

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ABSTRACT

Fuel cell tests have been performed on sulfonated Poly(Ether Ether Ketone) (sPEEK) membranes using dry gases. Impact of gas stoichiometry on performance evolution and membrane–electrodes assembly's water distribution optimization (water management) was studied. During the tests, output voltage evolution was recorded as well as impedance spectra, polarization curves and water amount collected at both sides.

Fuel cell performances were observed to be influenced by water management which depends on both operating conditions and membrane intrinsic properties. Increasing either hydrogen or oxygen stoichiometry leads to a decrease of performance. This effect was more pronounced for hydrogen increase (anode). This has been ascribed to a global drying of the membrane along with the appearance of a heterogeneous hydration both through the MEA and along the gas channels.

Cell performance characterization during the membrane lifespan was mainly based on Electrochemical Impedance Spectroscopy measurements and showed that water distribution heterogeneity increased with operating time for sPEEK membrane, leading to a drop of performance. This was mainly ascribed to the drying of the gas inlet and the increased hydration at the gas outlet. These behaviours were not observed for the better performing Nafion, which underlines the impact of membrane water transport properties on fuel cell performance.

1. Introduction

In the next decades fuel cells will play a major role in clean power production as a secure and sustainable energy [1]. Researches on various fuel cell technologies using different electrolytes, like alkaline fuel cells (AFC), solid oxide fuel cells (SOFC), proton exchange membrane fuel cells (PEMFC), have reached a high level of development. This diversification offers numerous applications in non polluting systems, from automotive to stationary and portable applications. Their advantages are their high efficiency, the absence of noise pollution and first of all their "zero emission" potential. However, fuel cells as clean energy delivery systems still have to deal with durability and cost issues [2,3].

For PEMFC, the membrane electrodes assembly (MEA) is the active core of the fuel cell in which the electrochemical reactions take place. It consists of a polymer membrane sandwiched between two electrodes (anode and cathode). Hydrogen is supplied at the anode where it is oxidized and oxygen is supplied at the cathode side where it is reduced. The main role of the membrane is to carry protons from the anode to the cathode (where water is produced). It must be at the same time an electrical insulator and a gas separator. State of the art membranes usually consist of a hydrophobic polymer backbone with acid groups (for proton conductivity) distributed either directly on the backbone, or on side chains. As the proton conductivity strongly depends on the water content of the polymer [4], water management is essential for the enhancement of fuel cell performance. During fuel cell operation a lot of water being produced at the cathode side, a high water concentration gradient appears across the membrane and water diffuses from cathode to anode due to capillary forces. This is called back-diffusion [5]. On the other hand, water is dragged by the moving protons from anode to cathode, the so-called electro osmosis drag [6]. These phenomena are illustrated on Fig. 1. Water management is a key point for PEMFC when trying to improve both its performance and durability. For a given membrane a better water management can be achieved by choosing the proper operating parameters.

Abbreviations: AFC, alkaline fuel cells; BPSH, Bi Phenyl Sulfone H-form; EIS, Electrochemical Impedance Spectroscopy; MEA, membrane–electrodes assembly; OCV, Open Circuit Voltage; PEMFC, proton exchange membrane fuel cell; PVDF, PolyVinyliDene Fluoride; RH, relative humidity; R_{ohm}, ohmic resistance; R_{elec}, electrodes resistance; SOFC, solid oxide fuel cell; sPEEK, sulfonated Poly(Ether Ether Ketone).

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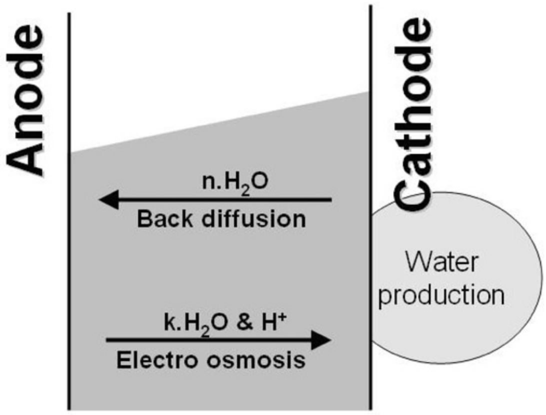

Fig. 1. Schematic representation of water flows across membrane in a PEMFC.

For PEMFC, the reference membrane is Nafion, a perfluorosulfonic polymer. However, despite its good properties up to 80 °C, a loss of its mechanical properties at higher temperatures prevents future development aiming to increase fuel cell efficiency through a working temperature increase. To overcome this issue, researches have been focused on sulfonated aromatic polymers. Despite a lower conductivity at low relative humidity (RH) [7,8] and a limited lifetime attributed to a chemical degradation [9,10], sulfonated aromatic polymers are particularly promising. They offer better thermo-mechanical [11] and permeation [12,13] properties in addition to a lower cost [14,15].

In order to improve both performance and durability, it is possible to adjust many parameters like operating temperature, gas relative humidity, pressure and flow (generally referred as gas stoichiometry). Many studies about operating conditions impact on fuel cell efficiency have been already performed for Nafion [16–18] but this type of information is still very scarce for aromatic polymers. Alberti et al. [7] showed that both Nafion 117 and sulfonated Poly(Ether Ether Ketone) (sPEEK) membranes can exhibit good proton conductivity (up to 50 mS cm^{-1}) at high temperature (150 °C) and RH (75%). Jiang et al. [19] studied for sPEEK membrane the impact of current density, temperature and relative humidity on water management and thus fuel cell performance. They showed that at high current density, back-diffusion effect is not sufficient to counter electro osmosis drag, leading to a drying of the anode side, and therefore a higher membrane resistance and a loss of the fuel cell performance. This phenomenon decreases when the temperature is increased, as water diffusion coefficient increases with temperature. They also found that fuel cell performance decreases for low gas RH as the ionomer membrane dries out.

Our study is focused on the impact of gas stoichiometry on water management and hence fuel cell performance of sPEEK membrane when using dry gases. Water management is studied by collecting water on anode and cathode sides. Performance is evaluated through polarization curves recording. Their evolution at a fixed current density is analysed thanks to Electrochemical Impedance Spectroscopy (EIS) which gives information about hydration homogeneity on the whole active surface area. sPEEK results are then compared to those obtained for Nafion for two operating conditions i.e. for the best and the worst conditions found for sPEEK.

2. Experimental

2.1. Membranes and MEAs

We studied sPEEK E-750 from Fumatech and Nafion NRE 212 from DuPont. The thickness of both membranes was about 50 μm and their ionic exchange capacity (IEC) was respectively of 1.35 and 0.9 mequiv. g^{-1}. Membranes were pretreated before use: sPEEK was immersed at room temperature in H_2SO_4 1 M for 4 h and then washed 3 times in ultrapure water at room temperature; Nafion NRE 212 was immersed at 70 °C in HCl 1 M for 2 h and then washed 3 times in ultrapure water at 70 °C.

Table 1
Gas flow rates corresponding to the chosen stoichiometry at 0.4 A cm^{-2}.

Stoichiometry anode/cathode	H_2 flow rate (N ml min^{-1})[a]	O_2 flow rate (N ml min^{-1})
1.5/1.5	21	11
1.5/3	21	22
3/1.5	42	11
3/3	42	22

[a] N ml min^{-1} stands for normalized flow rate to standard conditions of pressure and temperature.

MEAs were assembled by hot pressing the membrane between two electrodes “E-TEK ELAT® GDE LT120EW” (Pt loading 0.5 mg cm^{-2}) in two steps: 1 MPa for 3 min 30 s then 6 MPa for 3 min 30 s at 135 °C. After being hot-pressed, the MEA was placed into 5 cm^2 single cell fixtures. Airtightness was insured using 270 μm thick Viton gaskets. The single cell was made of two graphite monopolar plates with a single machined serpentine channel. Both channels width and depth are 1.4 mm whereas ribs width is 0.8 mm.

2.2. Fuel cell tests

In situ tests were carried out on a Bio-Logic FCT 150-S commercial bench. Cell temperature, current density as well as gas flow, pressure and relative humidity both at the cathode and anode sides were controlled. Two types of tests were performed: “ageing tests” where fuel cell performance of sPEEK and Nafion membranes (and associated MEAs) were studied; and “hydration tests” where drying was simulated at one or both electrode sides on sPEEK.

2.2.1. “Ageing tests”

In situ ageing tests were performed at 80 °C. Dry hydrogen and oxygen, absolute pressure of 2 bar, were applied in co-flow configuration (with H_2 and O_2 inlets both at the bottom of the fuel cell). Usually use of dry gases in fuel cells is motivated by the increased simplicity and efficiency of the system. In this study dry gases are provided to the fuel cell mainly to amplify the impact of operating conditions on the MEA hydration, enhancing the difference of gas hydration between the inlet and outlet. MEA is therefore drier near the gas inlet, whereas it is more hydrated near the outlet due to water production. The co-flow configuration also amplifies this phenomenon. Current density was constant and set to 0.4 A cm^{-2}.

To study their impact on performance, gas flows were controlled to keep a constant stoichiometry of either 1.5 or 3. In the following, a stoichiometry of 1.5 or 3 will mean that an excess of 50% or 200% of gases is provided to the fuel cell, compared to what needed to produce the collected current. Indeed, a stoichiometry set to 1 leads to flooding as all gases are consumed and therefore cannot push away produced water. It would be more correct to speak of gas flows instead of stoichiometry, but this misuse of language is convenient considering the overall reaction of the fuel cell $H_2 + (1/2)O_2 \rightarrow H_2O$ and is commonly used in the literature [18,20,21].

Correspondences between applied stoichiometries and gas flow rates at 0.4 A cm^{-2} are indicated in Table 1:

2.2.2. “Hydration tests”

“Hydration tests” were performed at 80 °C. Hydrogen and oxygen, absolute pressure of 2 bar, were applied in co-flow configuration with H_2 and O_2 inlets both at the bottom of the fuel cell. Current density was varied from 0.1 to 1.0 A cm^{-2} in order to vary both the amount of produced water and the electro-osmosis dragging force. Gas flow rates and RH were chosen in order to induce drying at one or both electrode sides. For all configurations,