Membranes for direct methanol fuel cell applications: Analysis based on characterization, experimentation and modeling

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Abstract

A critical analysis is performed about fundamental aspects regarding the direct methanol fuel cell (DMFC) technology, focusing mainly on the proton exchange membrane (PEM). First, the basic DMFC operation principles, thermodynamic background and polarization characteristics are presented with a description of each of the components that comprise the membrane electrode assembly (MEA) and of the DMFC test system usually used for DMFC research. Next, the paper focuses

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particularly on the PEM development chain, performing an overview of the research progress regarding this DMFC component. Specific efforts are devoted to research aspects related with the membrane preparation, characterization, DMFC tests and modeling. Apart from this, recent achievements at our research groups regarding the PEM development for DMFC applications are emphasized.

1. Introduction

In the last two decades, the interest in the fuel cell technology has increased dramatically. Earth environmental issues related with atmospheric pollution, green house effects and global warming are the main driving forces [1]. In contrast to the environmental and efficiency limitations associated to thermal processes that are commonly used for producing energy from fossil fuels, fuel cells have potentially higher efficiencies (non-dependent on the *Carnot* cycle) with absence of local gaseous pollutants, such as sulfur dioxide and various nitrogen oxides, along with striking simplicity and absence of moving parts [1,2].

Nowadays, after many years of research and development, there are several fuel cell systems near commercialization [3]. The possible applications of this technology range from stationary power production (megawatts), down to portable systems to supply portable electric equipments, such as notebooks, cellular phone and video cameras (watts). In between these two extremes lies the application for transportation, with almost all major car manufacturers now having their own research programs [3].

While hydrogen is the best fuel in terms of energy conversion (chemical into electrical), its production, storage and distribution has several problems [4-7]. No efficient and practical method of storing hydrogen for fuel cell applications currently exists [8]. While liquefaction leads to a form of hydrogen that is potentially attractive for use in larger fuel cell systems, the energy density is low due to the ultra-low gravimetric density of the fuel (Table 1). Furthermore, if the energy consumed during the liquefaction process is taken into account, the

Table 1. Energy density of fuels for direct polymer electrolyte fuel cells [7].

Fuel	Fuel cell reaction	Energy Density Wh cm^{-3}
Hydrogen (liq. at -273ºC)	$H_2 + 0.5O_2 \rightarrow H_2O$	2.7
Hydrogen (gas at 20MPa)	$H_2 + 0.5O_2 \rightarrow H_2O$	0.5
Methanol (liq.)	$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$	4.8
Ethanol (liq.)	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	6.3
Ethylene glycol (liq.)	$C_2O_2H_6 + 2.5O_2 \rightarrow 2CO_2 + 3H_2O$	5.9

energy density is lowered still further, by as much as 40% [7]. Another hydrogen storage approach is the application of metal hydrides. However, the reversible storage of hydrogen in metal hydrides has been limited to relatively low achievable specific energy (Wh/g of hydride) [8].

Although less reactive compared to hydrogen, methanol (CH_3OH) is considered to be an alternative fuel due to its high energy density (Table 1), being easier to store and distribute (liquid at atmospheric temperature). Additionally methanol can be easily produced from natural resources (e.g., wood, natural gas, and coal) and is biodegradable. In comparison to other carbonaceous or alcoholic fuels, methanol is known to have the best combination between energy density and rate of electro-oxidation [4]. Methanol can be completely electro-oxidized to CO_2, at temperatures well below 100ºC and, furthermore, it has enough energy density in comparison to that of other fuels (Table 1).

The methanol drawbacks for widespread use in fuel cells systems are the facts of being toxic, causing blindness or even death if swallowed, and flammable, forming explosive mixtures with air and burning without flame. In order to fulfill these health and safety issues, fuel cell developers plan to build up closed systems using diluted aqueous methanol solutions, which decrease significantly the toxic and flammability problems (typically 5 wt.% in water).

Methanol can be used directly in fuel cells, direct methanol fuel cells (DMFC), or indirectly as hydrogen source to polymer electrolyte membrane fuel cells (PEMFC), after reformation. The on-board reforming approach, which involves extensive, multi-step purification of the fuel, after which the resulting hydrogen-rich mixture is supplied to the PEMFC, seems to be quite complex and not a reliable power delivery source over long time applications and reasonably broad conditions of operation [7]. These limitations led the R&D community to the conclusion that DMFC operating at low/medium temperatures (up to 130ºC) is the most favorable option for mobile and portable applications (ranging from mW to W) . Furthermore, since methanol is fed directly as diluted aqueous solution (typically 5 wt.%), it also avoids complex humidification and thermal management problems associated to the hydrogen fuel cells.

In the last years, "heavyweight players" such as Sony, Toshiba, Nokia, Siemens, Motorola and Samsung, among others, are investing serious amounts of money in the development and commercialization of direct methanol fuel cells for portable applications [6]. They believe that the payback will be a next generation power source that revolutionizes the performance and easy-of-use of all sorts of portable electronic equipments – including notebook computers, mobile phones, video cameras, and plenty more besides [7]. Furthermore, some of these companies are talking in terms of months rather than years when it comes to DMFC based products commercialization [9]. In comparison with

the rechargeable battery based on lithium ion polymer, the DMFC has theoretically 10 times more weight energy density [6]. This performance translates into larger conversation times for mobile phones, longer times for use of notebook computers between replacement of fuel cartridges and more power available on these devices to support consumer demand. Another advantage regarding consumer convenience is the instantaneous refueling of the DMFC in comparison to the rechargeable batteries that require hours for charging the depleted power.

2. Basics of the DMFC

The basic DMFC is comprised by two electrodes, anode and cathode, and a solid electrolyte in between [4]. The usually applied catalysts in DMFC anode and cathode catalyst layers are Pt/Ru ($\sim$2 mg/cm^2) and Pt ($\sim$0.1 mg/cm^2), respectively. As for electrolyte, the DMFC uses a proton exchange membrane (PEM) that electronically isolates the anode from the cathode and enables the transport of protons. Although the thermodynamic characteristics are similar to the hydrogen reaction, especially in terms of reversible oxidation potential, the methanol electro-oxidation reaction is a slow process, as it involves the transfer of six electrons to the electrode for complete oxidation to carbon dioxide. The involved reactions are the following:

Anode reaction: $CH_3OH + H_2O \xrightarrow{\text{Pt/Ru}} CO_2 + 6\,H^+ + 6e^-$ (1)

Cathode reaction: $\frac{3}{2}\,O_2 + 6\,H^+ + 6\,e^- \xrightarrow{\text{Pt}} 3\,H_2O$ (2)

Overall reaction: $CH_3OH + \frac{3}{2}\,O_2 \longrightarrow CO_2 + 2\,H_2O$ (3)
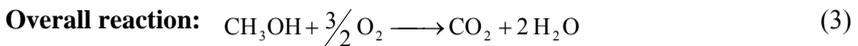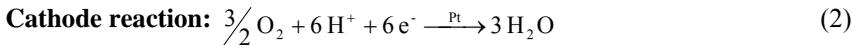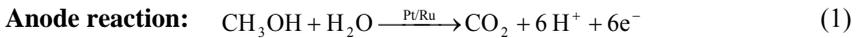
The basic operation principle of the DMFC is shown in Figure 1. At the anode, methanol and water are supplied and converted to carbon dioxide, protons and electrons. Currently most of the systems described in the open literature involve a liquid methanol-water feed, although in some platforms the methanol is supplied to the DMFC anode as vapor. The produced electrons from the anode reaction are subsequently transferred via the external circuit (which includes a load), where they can perform electric work. On the other hand, protons are transported to the cathode side through the PEM. At the cathode, the protons and electrons reduce oxygen (from air) to form water.

2.1. Thermodynamic backgroung

In an electrochemical cell, operating at isothermal conditions, if the enthalpy energy of both anode and cathode reactions could be fully converted into electric work, the enthalpic cell voltage, U_H, obtained would be:
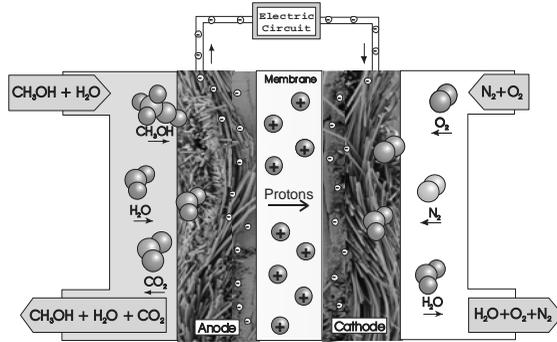
Figure 1. Sketch of the DMFC illustrating the mass transport of the different species.

$$U_H = -\frac{\Delta H_R}{zF} \tag{4}$$

where z is the number of electrons involved in the electrochemical reaction (6 electrons for the DMFC), F is the Faraday constant (96484.6 C mol^{-1}) and ΔH_R the overall reaction enthalpy at standard conditions (Table 2).

Table 2. Thermodynamic data and overall enthalpic and reversible voltage for the direct methanol fuel cell reactions (standard conditions, P = 1 atm and T = 298.15K; Anode: methanol oxidation reaction; Cathode: oxygen reduction reaction) [10].

Reaction	ΔH_R [kJ mol^{-1}]	ΔS_R [J mol^{-1}·K^{-1}]	ΔG_R [kJ mol^{-1}]	U_H [V]	U_{rev} [V]
Methanol oxidation	110.69	-79.11	134.28	-0.19	-0.23
Oxygen reduction	-857.49	-97.98	-828.28	1.48	1.43
Overall Cell	-746.80	-177.09	-694.00	1.29	1.20

However, according to the second law of thermodynamics, if an electrochemical cell operates reversibly (concerning the energy conversion) [1], there will be a variation of the system entropy (released heat). Thus, the maximal electric work of an electrochemical cell is obtained from the Gibb's free energy variation, ΔG_R, and the maximal fuel cell voltage, U_{rev}, is obtained as follows:

$$U_{rev} = -\frac{\Delta G_R}{zF} = -\frac{\Delta H_R - T\Delta S_R}{zF} \tag{5}$$

where T is the system absolute temperature and ΔS_R is the variation of the system entropy for standard conditions (Table 2).

Since not all the fuel chemical energy in a DMFC is converted into electric work, the thermodynamic fuel cell efficiency is limited by the fuel intrinsic properties. Therefore the maximum thermodynamic efficiency that can be achieved by a DMFC electrochemical cell can be obtained by the following equation:

$$\eta_{th} = \frac{U_{rev}}{U_H} = \frac{\Delta G_R}{\Delta H_R} \tag{6}$$

From the data presented in Table 2, the maximal thermodynamic efficiency of 92.9% for the DMFC (at standard conditions) can be obtained.

2.2. Polarization behavior

The classical experimental procedure to evaluate the performance of a fuel cell is to measure the stationary current-voltage behavior (Figure 2). The S-shape curve, which is typical for a fuel cell system, reflects the different limiting mechanisms occurring during the operation of the fuel cell [5]. From Figure 2, it can be observed that at zero current, the cell presents the maximum experimental voltage value (open circuit voltage, OCV). The DMFC experimental open circuit voltage differs from the reversible DMFC voltage due, essentially, to fuel losses (methanol crossover form the anode to the cathode) [11]. The transport of methanol from the anode to the cathode is associated to the problematic high permeability of PEM towards methanol. The permeated methanol reacts with oxygen at the cathode side forming a mixed potential that decreases the open circuit voltage. This DMFC limitation will be further discussed in the following sections.

For low current densities, the cell voltage loss is mainly influenced by the kinetic limitations of the reactions involved at the anode and cathode (Figure 2). The so-called activation polarization, ΔU_A, is mainly due to the energy reaction barrier (mostly the methanol electro-oxidation reaction), which must be overcome in order to the electrochemical reaction occur. For the DMFC, the methanol oxidation is one of the most limiting aspects due to the poor electro-oxidation kinetics [4-7]. Indeed, an overall of six electrons are formed (Eq. 1); consequently many surface-bound reaction intermediates can be expected [5]. At high current densities, mass transport limitations dominate the process, increasing the potential loss due to cell fuel or oxidant starvation, ΔU_C (Figure 2). For a certain current (limiting current) the cell voltage drops to zero. In

The figure shows a current-voltage curve. Labels on the y-axis (Voltage, V) and x-axis (Current, A). Labels include:

- Enthalpic cell voltage: $U_H = -\dfrac{\Delta H_R}{zF}$
- Reversible cell voltage: $U_{rev} = -\dfrac{\Delta G_R}{zF}$
- Open circuit cell voltage: U_{cell}
- $\left|\dfrac{T\Delta S_R}{zF}\right|$
- ΔU_A
- ΔU_B
- ΔU_C
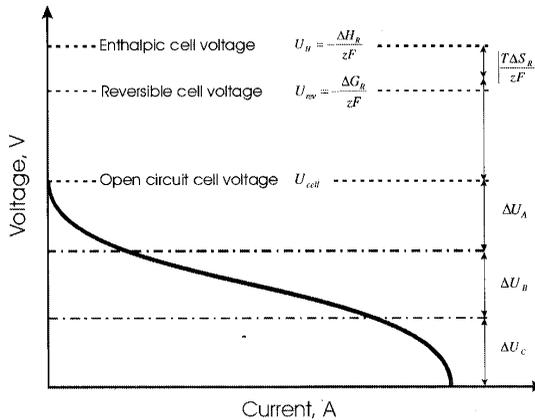
Figure 2. Typical current-voltage behavior of a DMFC.

between A and C regions, it lies the so-called resistance polarization region, ΔU_B, in which the voltage variation shows more or less an ohmic behavior (Figure 2). This potential loss is mainly associated with the transport of electrons and protons through the electrodes and electrolyte, respectively. The electrodes usually have low resistance for the transport of electrons. However, the proton exchange membrane has much higher resistance for the transport of protons (ionic resistance) from the anode to the cathode, being the dominant factor in the ohmic voltage loss [5].

2.3. Membrane electrode assembly

The membrane electrode assembly (MEA) consists in the association of anode and cathode catalyst layers, ion-exchange polymer membrane and anode and cathode electrode backing/gas diffusion layers (Figure 3) [1]. The functions of the three basic components are intimately related, and the interfaces formed between them and with the plates flow fields are critical for maximum fuel cell performance [12].

The diffusion layers are made of a carbon cloth that plays a key role on the transport of species and MEA structure integrity (Figure 3) [4, 5, 12]. The porous backing, apart from allowing the transport of methanol and oxygen to the anode and cathode catalyst layers, respectively, also allows the conduction of electrical current out of the cell and provides the MEA's mechanical stability by holding the catalyst porous film-like structure [12]. Also, the carbon cloth structure allows the effective reactions products transport, carbon dioxide and water at the anode and cathode, respectively, in order to prevent
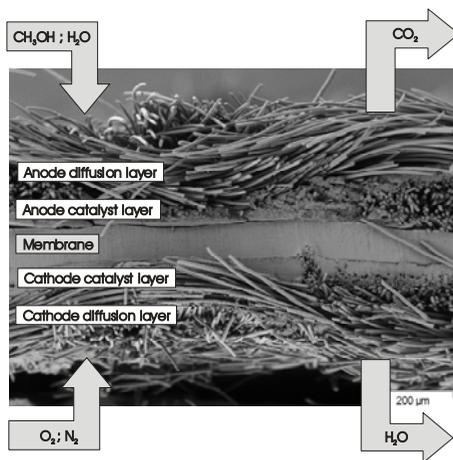
Figure 3. Scanning electron micrograph of a MEA.

the blockage of the transport paths in the electrodes. Usually, the diffusion layers are hydrophobized with polytetrafluoroethylene (PTFE) to prevent the flooding of the carbon cloth channels and to promote the gas transport [4].

On the other hand, the catalyst layer is where the chemical reactions are promoted. The catalyst layers have a film-like structure (Figure 3) consisting of the following materials: 1) carbon black particles (usually Vulcan XC72) as electric conductor and catalyst support (if the catalyst is used as supported); 2) PTFE as hydrophobic element that also provides mechanical stability (holding the carbon particles) and 3) an ionomer (usually Nafion®) to promote the proton transport to the electrolyte and contact between electrodes and electrolyte polymer [4, 5, 12]. The catalyst can be used either unsupported or supported in carbon particles. It should have a high active surface area, poisoning-proof towards carbon monoxide and high dispersion. It is well known that the electro-oxidation, in Pt-based catalysts, of low molecular weight organic molecules, such as methanol, gives rise to the formation of strongly adsorbed CO species in linear or bridge-bounded form [4]. Accordingly to much work dedicated to the electro-oxidation of methanol, the most successful results up to date have been achieved using a binary alloy of platinum with ruthenium (Ru) [4]. The success of this alloy can be explained by the bifunctional effect of the Pt-Ru catalyst for DMFC [13]. The dehydrogenation steps take place at Pt surfaces sites, whereas Ru sites assume the role of providing the oxide/hydroxide species required to complete the oxidation of surface CO [13]. It is worth noting that the rate of methanol oxidation at Pt-Ru is strongly dependent on the temperature, with high

performance being obtained near and above 100ºC [14]. On the other hand, just like in a hydrogen fuel cell, the cathode reaction in a DMFC requires platinum to act as oxygen reduction electrocatalyst.

Finally, the proton exchange membrane plays a decisive role in the DMFC by isolating electronically the anode from the cathode, preventing the loss of methanol and oxygen and, mainly, enabling the transport of protons from the anode to the cathode. A critical analysis of the PEM characteristics for DMFC applications will be further discussed in detail.

2.4. DMFC test system

The research and development of direct methanol fuel cells requires intensive experimental work [15]. An experimentation platform should allow a wide range of parameters variation and ensure enough reproducibility. A simplified flow sheet of a DMFC test facility is presented in Figure 4. In this case, a tank is used to store the aqueous methanol solution (usually 1.5 M). A speed adjusted pump sucks the aqueous anode feed and pumps it into the closed circuit. A density meter enables the evaluation of the mixture density in order to verify the methanol concentration loss during DMFC operation. Usually the anode feed tank has a total volume higher than 2 liters in order to prevent the excessive variation in methanol concentration during one day experiment (less than 5%). To ensure the supply of aqueous methanol solution in liquid phase at temperatures higher than the methanol boiling point (64.7ºC), the feed tank is pressurized with nitrogen. The feed tank pressure is controlled to adjust pressure fluctuations caused, for example, by the production of carbon dioxide at the anode side, using a venting valve (V1).

The oxidant gas supply to the cathode can be either pure oxygen or air. A flow meter controller is used to maintain the constant gas flow. A further option is the possibility of humidifying the cathode gas inlet. This can be achieved by bubbling this gas stream through a heated water container, the humidifier. Humidity control is obtained by regulating the temperature of the humidifier (temperature controller, TC). At the exit of the cathode a needle valve provides the required pressure ratios in the cell (V2). For the determination of the methanol crossover at the cathode outlet, the CO_2 concentration is measured using an IR sensor [15].

For adjusting the electronic load of the cell and for measuring the current-voltage behavior, an electronic load is integrated in the DMFC flow sheet. This load can be operated potentiostatically or galvanostatically. The cell current is measured by a shunt, which is a precisely defined resistance that enables a certain voltage drop, proportional to the cell current. A more detailed description of a fully automatic DMFC test facility is described elsewhere [15].
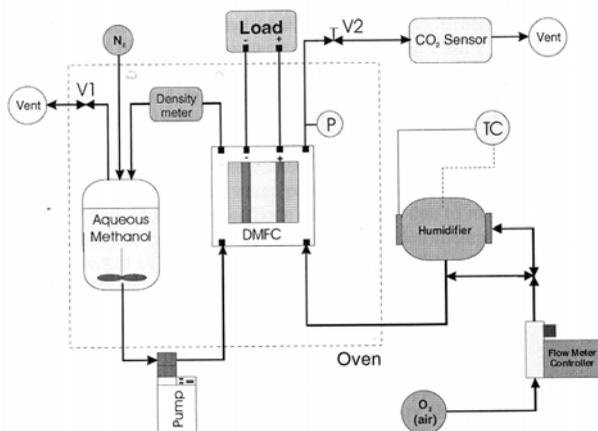
Figure 4. Simplified flow sheet of a direct methanol fuel cell test facility.

3. R&D regarding proton exchange membranes

The research and development of novel proton exchange membranes is known to be one of the most challenging aims regarding the direct methanol fuel cell technology [4-7, 16]. Usually mentioned as the heart of the DMFC, the membrane should ideally combine high proton conductivity (electrolyte properties) and low permeability towards DMFC species (barrier properties). Additionally, it should have a very high chemical and thermal stability in order to enable the DMFC operating at up to 150ºC [4-7]. Nowadays, although involving high cost, perfluorinated ion-exchange polymers, such as Nafion[®] from Dupont, are still the most commonly used for DMFC applications (Figure 5) [16]. This kind of membranes combines the extremely high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups [16]. For Nafion[®], excellent characteristics in terms of chemical and thermal stability are ensured by the well known Teflon[®]-like perfluorinated backbone (Figure 5). However, Nafion[®] only has a good proton conductor behavior when swollen in water and, consequently, the sulfonic groups are solvated.
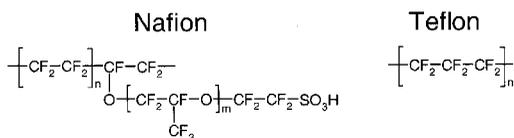
Figure 5. Chemical structure of Nafion[®] and Teflon[®] (PTFE).

In the presence of water, the distinct characteristics of both hydrophilic and hydrophobic characters of Nafion[®] are even more pronounced due to the aggregation of the hydrophilic domains (nano-separation) [16]. Consequently, DMFC species are readily transported across perfluorosulfonic acid membranes (mostly methanol and water) [4, 16-18]. This results in the drawback methanol crossover from the anode to the cathode, which is mostly performed by: 1) diffusion through the water-filled channels within the Nafion[®] structure and 2) active transport together with protons and their solvate water molecules during DMFC operation (electro-osmotic drag). The crossover methanol is chemically oxidized to CO_2 and H_2O at the cathode, decreasing the fuel utilization efficiency and depolarizing the cathode. Apart from this, it can also adversely affect the cathode performance due to the consumption of oxygen by the parasitic methanol oxidation at the cathode catalyst layer, lowering its partial pressure [19]. It is believed that the methanol crossover from the anode to the cathode leads to a DMFC efficiency reduction down to 35% [18]. On the other hand, the high water permeability in perfluorinated membranes can also cause cathode flooding and, thus, lower cathode performance due to mass transport limitations [4]. The loss of oxygen from the cathode to the anode is also detrimental for the DMFC efficiency, although it can be neglected in comparison with the effect of the methanol crossover. In contrast, nitrogen and carbon dioxide mass transfer in the proton exchange membrane does not affect significantly the DMFC performance.

3.1. Novel materials

The key of the PEM research for direct methanol fuel cell applications is to overcome the strong link between proton conductivity and methanol permeability through the development of new materials or modification of the existing ones. The R&D schemes attempted so far have been mostly focused on either modifying the perfluorinated membranes by addition of highly hydrophilic oxides, or varying the polymer nano-pore network structure by modifying the polymers chemical nature [4-7], e.g. the use of SiO_2 entrapped particles in Nafion[®] polymeric structure [20], which work as a physical barrier for methanol crossover. However, as expected, the membrane ohmic resistance increases, depending on the concentration of silica. Other preparation approach proposes the inorganic incorporation of zirconium phosphate in perfluorinated membranes (23wt.%) [21]. This membrane shows lower methanol crossover when compared to recast Nafion[®] modified with SiO_2 (3 wt.%) due to the higher content of inorganic compound (higher diffusion barrier characteristics). Yet, larger ohmic resistances were observed due to reduced proton mobility inside the Nafion[®] channels.

Nowadays, there are several alternative novel materials that show promising properties for DMFC applications. Some of the investigated

membranes so far are: sulfonated poly(ether ether ketone) [22-26], poly(ether sulfone) [27], polyvinylidene fluoride [28], styrene grafted and sulfonated membranes [29], zeolites gel films and membranes doped with heteropolyanions [30]. Apart from enabling different preparation or modification approaches, the characteristics of these novel materials enable completely distinct mass transport mechanisms and much lower costs when compared to Nafion[®]. Non-fluorinated membranes based on sulfonated poly(ether ether ketones) (sPEEK) proved already to have promising characteristics in terms of barrier and electrolyte properties for DMFC applications [22, 26]. The plain poly(ether ether ketone) (PEEK) can be easily made hydrophilic by sulfonation reactions, with the sulfonation degree (SD) controlled by the reaction time and temperature (Figure 6).

PEEK   **sPEEK**
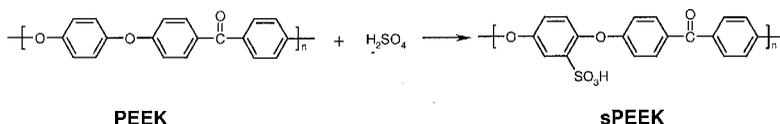
Figure 6. Sulfonation reaction of the poly(ether ether ketone).

The sulfonation degree can optimize the hydrophobic-hydrophilic balance, acting directly on the electrolyte and barrier properties, as well as in the chemical and thermal stability of the polymer [22-26]. Higher sulfonation degrees increase the polymer proton conductivity and tend to improve the DMFC performance. However, the permeability towards methanol also increases concurrently, decreasing the fuel cell overall efficiency [22]. On the other hand, the polymer stability tends to progressively deteriorate with the sulfonation degree. Recently, Li et al. reported better DMFC performances for the sPEEK membranes (SD = 39 and 47%) compared to Nafion[®] 115, at 80ºC [31]. Similar results were obtained by the authors for a sPEEK membrane with SD = 42% and thickness ranging from 25 to 55 μm.

Non-fluorinated PEM properties regarding proton conductivity and methanol permeation can be also improved by the preparation of hybrid or composite membranes incorporating inorganic-ceramic materials [32-42]. For an optimized composition, the hybrid or composite material may have superior performance as compared to the plain polymer [32]. For DMFC applications operating at medium temperatures (up to 130ºC), promising results were obtained by the authors for sPEEK composite membrane with SD = 68% modified with 20.0 wt.% of zirconium phosphate (ZrPh) pre-treated with *n*-propylamine and 11.2 wt.% of polybenzimidazole (PBI) [35, 36]. This membrane proved to have a good balance between proton conductivity,

aqueous methanol swelling and permeability. In addition, DMFC tests for this membrane showed similar current density output and higher open circuit voltage compared to that of sPEEK with SD = 42%, but with much lower CO_2 concentration at the cathode outlet (thus higher global efficiency) and higher thermal/chemical stability.

Another approach is the incorporation of heteropolyacids in plain polymers [40, 41]. Heteropolyacids are well known for being proton conductors when in the crystalline form with a certain number of water molecules in their structure [43-45]. However, it is also well known that these electrolytes usually leach out of the polymer, decreasing the fuel cell performance [43, 46, 47]. Finally, the modification of sPEEK polymer with zirconium oxide incorporated via *in-situ* hydrolysis proved to be very promising for decreasing the hybrid membrane permeability towards methanol (improved barrier properties) and for increasing the chemical/thermal stability of the polymer [37-39]. The drawback of the incorporation of ZrO_2 is the fact that it has also high impact on the proton conductivity, decreasing therefore the fuel cell performance [39].

3.2. Characterization methods

In order to select the proper PEM material for direct methanol fuel cell applications, characterization methods play an important role in DMFC research. Ideally, the obtained characteristics of the specific material should be used as a selection criterion: they should allow researchers to forecast the corresponding DMFC performance [48]. For example, instead of conducting DMFC experiments, which are time and money-consuming, the characterization results should be used to estimate qualitatively the fuel cell performance, for a given PEM membrane [39]. Apart from this, the characterization results should also allow the identification of critical parameters regarding the application of certain materials in DMFC. The various membrane characterization methods normally involved in PEM research for DMFC applications can be classified as: (a) related to electrical or conductive properties; (b) related to the permeation of the DMFC species; (c) related to thermal and chemical stability and (d) related to the membrane morphology and element analysis.

At present, several characterization methods are used to obtain critical parameters for DMFC application [39, 48, 49]. The three most common characterization methods for PEM research for DMFC applications are listed and described bellow.

3.2.1. Swelling measurements

The water or methanol solubility in the membrane is closely related to its basic properties and plays an essential role on its behavior. Proton conductivity

depends to a large extent on the amount of adsorbed water and even the proton transport is influenced by it [50]. On the other hand, the methanol crossover is also associated to higher water concentration in the membrane [51]. Apart from this, the absorbed water also influences the ionomer microstructure, cluster and channel size and modifies the membrane mechanical properties [52, 53]. The membrane properties in terms of swelling are usually evaluated using batch experiments in liquid solutions at room temperature [25, 26, 34-39, 49, 54]. The water or methanol uptake, W_{uptake}, is usually obtained using the following relation:

$$W_{uptake} = \frac{w_{wet} - w_{dry}}{w_{dry}} \tag{7}$$

where w_{wet} is the membrane sample wet weight after a certain time in the solution (up to the equilibrium) and w_{dry} is the initial dry weight of the sample after the drying process (usually in an oven with vacuum).

3.2.2. Conductivity measurements

The proton conductivity of a specific material is strictly related with the ohmic losses associated to the membrane during DMFC operation. The key for PEM research is to develop membranes with improved proton transport properties in order to have a minimum voltage drop, mainly for fuel cells operation at high current densities. This property is usually evaluated by impedance spectroscopy, using a membrane immersed in an acid solution or just hydrated in different values of relative humidity [25, 26, 33-42, 48, 49]. From impedance spectroscopy experiments, the membrane proton conductivity, k_m, is obtained determining the impedance modulus at null phase shift [55] using the following equation:

$$k_m = \frac{d_m}{A \cdot |Z_m|_{\alpha=0}} \tag{8}$$

where d_m is the membrane thickness, A is the contact area membrane/electrodes and $|Z_m|_{\alpha=0}$ is the impedance modulus at null phase shift.

3.2.3. Permeability measurements

The study of the methanol mass transport through DMFC membranes is very common due to its detrimental effect on the DMFC performance as discussed before. Even not accounting for the anode catalytic reaction and the

electro-osmotic drag mass transfer, the permeability is usually evaluated by pervaporation [33-41, 48, 49] and diffusion cell experiments [56-58]. Pervaporation experiments consist on measuring the amount of permeated methanol and water through the membrane for a certain experiment time. The permeability coefficient, P_i, of species i (water or methanol) is obtained from the species flux according to

$$P_i = \frac{J_i \quad d_m}{\gamma_{i,L} \quad X_{i,L} \quad p_i^{sat}}$$ (9)

where J_i is the molar flux, γ_i is the activity coefficient, $X_{i,L}$ is the molar fraction in the liquid phase and p_i^{sat} is the equilibrium vapor pressure of species i.

Apart from studying the liquid species mass transport, nowadays researchers start also to characterize the permeation of gaseous species through the proton exchange membrane [35, 38]. Since the carbon dioxide concentration at the cathode outlet is usually used as an experimental measure of the methanol crossover, its transport through the electrolyte membrane should be also considered. The permeability of the gaseous species is usually evaluated through the pressure rise method, in the presence of water vapor (swollen membrane). As stated in [59], the permeability coefficient of species i can be obtained from pressure rise experiments using the following equation

$$P_i = \frac{V \quad d_m}{R \quad T \quad A} ln \frac{p_{i,F} \quad p_{i,P\,x}}{p_{i,F} \quad p_{i,P\,x+1}} \quad \left(t_{x+1} \quad t_x\right)$$ (10)

where V is the permeate volume, R is the gas constant, $p_{i,F}$ is the species i partial pressure in the feed stream, $p_{i,P}$ is the species i partial pressure in the permeate side and t is the experiment time. The subscripts x and x+1 refer to time instant x and time instant after x, respectively.

Other characterization methods are applied as well to give information on the chemical structure (determination of ion-exchange capacity, IEC, Fourier transform infrared spectroscopy, FTIR, nuclear magnetic resonance, NMR [60-63]), stability (thermo gravimetrical analysis, TGA) and morphology (scanning electron microscopy, SEM, small angle x-ray scattering, SAXS, transmission electron microscopy, TEM).

With respect to the validation of the standard characterization data, results recently published by the authors show a good qualitative agreement between them and the DMFC performance [39]. From this study it is possible to verify that characterization results obtained by impedance spectroscopy, water uptake

and pervaporation experiments can be effectively used as critical parameters for the selection of proton electrolyte membranes for DMFC application purpose [39].

3.3. DMFC tests

DMFC tests can be performed to study the behavior of a certain material as electrolyte for real fuel cell operating conditions [12, 15]. These tests are normally implemented for a certain collection of membranes that have been previously selected based on the characterization methods results previously described. Usually, the experimental operation conditions of the DMFC test cell are selected in order to focus mainly on the membrane properties [15]. As an example, the DMFC test should be performed with a constant cathode flow rate, enough to prevent the electrodes flooding and oxygen starvation. Also, the electrodes used for the MEA preparation should always be the same (usually E-Tek® ELAT electrodes). Low amounts of catalyst in the electrodes are preferred in order to increase the methanol crossover detrimental effect and study the membrane barrier properties for more unfavorable conditions (usually, 1 mg/cm^2 PtRu and 0.4 mg/cm^2 Pt in the anode and cathode catalyst layers, respectively). When preparing the MEA, the pressing conditions are selected in order to enable a good contact between the membrane and electrodes (practically negligible contact resistance).

The recording of the current-voltage and power density characteristics of DMFC is the most important and common fuel cell characterization method (Figure 7) [1-6]. Usually, the DMFC polarization behavior is measured potentiostatically, with voltage steps of 50 mV during 2 minutes (quasi-steady-state conditions), ranging from the open circuit voltage down to 50 mV and back to the open circuit voltage [15]. For a specific material, the characteristic polarization is predominantly controlled by the methanol crossover through the membrane from the anode to the cathode, by the PEM proton conductivity and, finally, by the kinetics of methanol electro-oxidation at the anode catalyst layer [14, 64-71].

Usually, DMFC tests involve also the measurement of the open circuit voltage. The main propose for this measurement is to infer about the cell voltage loss that is essentially due to the methanol permeation from the anode to the cathode. During OCV experiments, the concentration of methanol at the anode-membrane interface is maximal because no methanol is being consumed (no current output). Consequently, the methanol crossover is higher due to a larger mass transfer gradient across the membrane, making the detrimental effect of the methanol crossover more noticeable for OCV experiments [72].

In order to study the DMFC behavior under high load, experimental tests are also performed measuring the current density for constant voltage (CV) experiments, at 35mV. This measurement is performed in order to infer about
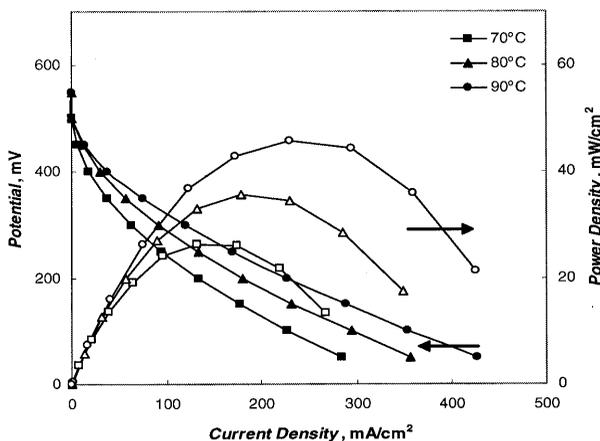
Figure 7. Current-voltage and power density plots of the DMFC using a sPEEK membrane with SD = 42%.

the cell voltage loss associated to the PEM proton conductivity (ohmic losses) and methanol crossover effect for high load conditions. When the DMFC is under load conditions, there will be a consumption of methanol at the anode catalyst layer and, consequently, the methanol mass transfer gradient across the membrane decreases (leading to lower CO_2 concentrations at the cathode outlet).

Since the membrane development involves the characterization of materials with distinct swelling properties and this factor is known to strongly influence the performance of the DMFC, researchers also measure the cell impedance in order to diagnose the membrane state in terms of absorbed water content. The cell impedance measurement is commonly performed at high frequency, such as 10kHz, in order to measure the impedance for null phase conditions (NPAI) [15]. At null phase frequency, the impedance is dominated by the ohmic resistance in the cell and thus by the membrane conductivity and the contact resistances.

3.4. DMFC efficiency

As mentioned before, during DMFC tests, the methanol crossover from the anode to the cathode can be measured by the CO_2 content at the cathode outlet [15]. However, this CO_2 content does not give an absolute amount of the methanol that permeates through the membrane. One must also quantify the CO_2 that permeates through the membrane from the anode to the cathode during fuel cell operation. In addition, it should be expected that the crossover methanol is not completely oxidized to CO_2 at the cathode catalyst layer. A

detailed method for evaluating the absolute CO_2 amount at the cathode outlet due to the permeation of methanol was recently presented by V.S. Silva et al. [36], accounting to the membrane permeability towards CO_2. The effect of the non-converted crossover methanol at the cathode outlet was not considered because from gas chromatography analysis it was verified that the methanol molar fraction is usually less than 0.5% in this stream.

Therefore, from the predicted carbon dioxide molar flow rate due to the parasitic methanol oxidation at the cathode, $N_{CO_2}^{MeOH}$, and assuming the Faraday law, the current density loss due to methanol crossover, I_{MeOH}, can be evaluated through the following equation:

$$I_{MeOH} = \frac{N_{CO_2}^{MeOH} \cdot 6 \cdot F}{A_{cell}} \tag{11}$$

where A_{cell} is the DMFC effective area.

In order to study the ratio of the converted fuel to electric power (anode) to the total amount of converted fuel (anode and cathode), researchers usually calculate the DMFC Faraday efficiency, η_F, using the following equation:

$$\eta_F = \frac{I_{i,cell}}{I_{i,cell} + I_{i,MeOH}} \tag{12}$$

where $I_{i,cell}$ is the DMFC measured current density.

On the other hand, in order to study the fuel cell polarization loss behavior, the potential efficiency, η_E, is also calculated. It is defined as the DMFC cell voltage divided by the reversible cell voltage:

$$\eta_E = \frac{U_{i,cell}}{U_{rev}} \tag{13}$$

in which $U_{i,cell}$ is the measured cell voltage during the polarization curve evaluation.

The global DMFC efficiency, η_{DMFC}, is defined as the product of the thermodynamic efficiency, Faraday efficiency and potential efficiencies (Figure 8) and it is given by the following equation:

$$\eta_{DMFC} = \eta_{th} \cdot \eta_E \cdot \eta_F \tag{14}$$

Since the thermodynamic efficiency of the DMFC is constant and independent of the material, usually PEM researchers neglect this term in the DMFC overall efficiency [4, 22, 36].

3.5. PEM modelling

As mentioned before, in order to infer about the PEM properties and select the proper materials for DMFC applications, researchers usually apply standard characterization methods such as impedance spectroscopy, pervaporation and swelling experiments [39, 48, 49]. The results obtained from PEM characterization allow a qualitative first screening of the membranes properties for DMFC applications [39]. However, the application of standard characterization methods and DMFC tests are not enough to answer some questions, especially in terms of which is the optimal PEM development strategy that should be targeted, having in mind a compromise between proton conductance (electrolyte requirements) and methanol and water transport (barrier requirements). In order to answer these questions, we believe that it is of decisive importance to develop novel R&D tools that could be complementary to the PEM standard characterization methods and DMFC tests [38, 39].
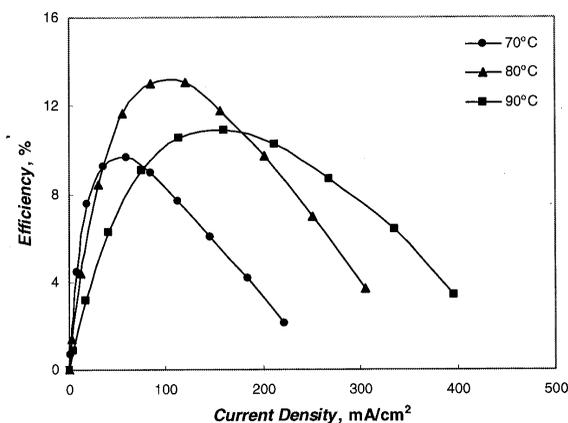
Figure 8. Estimated overall efficiency of the DMFC using a sPEEK membrane with SD = 42%.

Mathematical modeling seems to be very useful for these propose since it allows the prediction of the DMFC performance for distinct materials and operation conditions. Unfortunately, much of the developed DMFC modeling research has focused extensively on Nafion® [73]. These models use data taken from literature that are usually impossible to reproduce by membrane development research groups and, in many cases, these parameters hardly represent the properties of membranes under development. Therefore, the

developed mathematical models have limited usefulness for membrane development proposes regarding direct methanol fuel cells.

Recently, in order to fulfill this lack, the authors reported the development of a semi-empirical mathematical model that enables the prediction of the DMFC performance using inputs obtained by easy-to-implement characterization methods [74]. The applied standard characterization methods were: impedance spectroscopy (proton conductivity), water uptake (water sorption), pervaporation (permeability towards methanol and water) and gas permeation (permeability towards oxygen, nitrogen and carbon dioxide). For PEM development proposes, the present mathematical model proved to be very useful for selecting the right modifications that should be performed in order to prepare optimized materials that can improve the DMFC overall performance [75]. This model will be used by the authors to assist the PEM development and, consequently, to reduce the applied efforts to find the optimal material/conditions for DMFC applications.

4. Conclusions

Nowadays, most of the world energy requirements are obtained by burning fossil fuels in generally low efficiency thermal processes. Associated consequences, such as, atmospheric pollution, global warming, and green house effects are the main driving forces for the development of new power sources and converters. In this regard, it is widely recognized that fuel cells are becoming suitable for replacing common combustion processes in the near future.

Direct methanol fuel cells have good potentialities for portable applications. Devices based on this technology eliminate the need of a complex reformer unit and avoids thermal and humidification problems (simplicity). However, one of the main drawbacks associated to the DMFC is the methanol crossover across the proton exchange membrane (where Nafion$^{®}$ is commonly used). The methanol crossover from the anode to the cathode decreases the fuel utilization efficiency and affects detrimentally the cathode performance. Therefore, the development of new PEMs with improved barrier and electrolyte properties is known to be one of the most challenging aims regarding the DMFC technology.

The present work gives an overview of the PEM development process comprising the following steps: materials preparation, characterization, DMFC test, modeling and simulation. The recent developments achieved by the authors concerning these aspects are emphasized. New materials using poly(ether ether ketone) as matrix polymer, modified inorganically with zirconium oxide or zirconium phosphate pre-treated with *n*-propylamine and polibenzimidazole are mentioned. Membranes with improved relation between barrier and electrolyte properties were prepared, in comparison with that of Nafion$^{®}$. In addition, a research work regarding the characterization methods

validation is mentioned in terms of DMFC qualitative performance prediction. In this study it is shown that impedance spectroscopy (proton conductivity), water uptake (water swelling) and pervaporation (permeability towards methanol and water) can be effectively used as critical parameters for the PEM selection aiming the DMFC application. On the other hand, the importance of developing DMFC mathematical models based on characterization data is emphasized. These modeling tools proved to have a promising potential on assisting the PEM development by answering basic questions concerning novel materials with the best compromise between proton conductance (electrolyte properties) and methanol crossover (barrier properties).

Acknowledgements

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