Investigation of sulfonated polysulfone membranes as electrolyte in a passive-mode direct methanol fuel cell mini-stack

F. Lufrano *, V. Baglio, P. Staiti, A. Stassi, A.S. Aricò, V. Antonucci

CNR – ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via Salita S. Lucia sopra Contesse n. 5 - 98126 S. Lucia - Messina, Italy

ABSTRACT

This paper reports on the development of polymer electrolyte membranes (PEMs) based on sulfonated polysulfone for application in a DMFC mini-stack operating at room temperature in passive mode. The sulfonated polysulfone (SPSf) with two degrees of sulfonation (57 and 66%) was synthesized by a well-known sulfonation process. SPSf membranes with different thicknesses were prepared and investigated. These membranes were characterized in terms of methanol/water uptake, proton conductivity, and fuel cell performance in a DMFC single cell and mini-stack operating at room temperature. The study addressed (a) control of the synthesis of sulfonated polysulfone, (b) optimization of the assembling procedure, (c) a short lifetime investigation and (d) a comparison of DMFC performance in active-mode operation vs. passive-mode operation.

The best passive DMFC performance was 220 mW (average cell power density of about 19 mW cm^{-2}), obtained with a thin SPSf membrane (70 μm) at room temperature, whereas the performance of the same membrane-based DMFC in active mode was 38 mW cm^{-2}. The conductivity of this membrane, SPSf (IEC = 1.34 mequiv. g^{-1}) was 2.8×10^{-2} S cm^{-1}. A preliminary short-term test (200 min) showed good stability during chrono-amperometry measurements.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Portable power is becoming important for many electronic devices, such as notebook computers, personal digital assistants (PDAs), power tools and cellular phones. Currently, these devices are powered by primary and secondary batteries. The power source is often the largest component in the device. The running time and functionality of these electronic devices are often limited by the quantity of energy that can be stored and carried within them. Such aspects represent a limiting factor in efforts towards device miniaturization. Advances in the development of portable fuel cells will have a great impact on the use and development of modern electronic devices. Unlike primary and secondary batteries, in which reactants and products are contained in the battery, fuel cells employ reactants that are continuously supplied to the cell; byproducts are also continuously removed. Methanol, which is characterized by low cost, easy storage and handling, and high-energy density appears well suited for portable fuel cells [1–3].

In practice, fuel cells do not operate as single units; rather, they are connected in series (stack) to achieve suitable potential. For conventional actively driven fuel cells, the most popular means of interconnection are the bipolar plates. These connect one cathode to the anode of the next cell; furthermore, the bipolar plates serve as a means of feeding oxygen to the cathode and fuel to the anode. Usually, this type of fuel cell works with forced airflow on the cathode side and forced fuel flow on the anode side, requiring various auxiliary components and quite a complicated control system. This type of fuel cell does not easily fit the requirements for portable applications. For such applications, the key challenges are to provide acceptable power output and high-energy efficiency under conditions convenient to the user. Desired operating conditions include, for example, an operating temperature near room temperature, no forced airflow, and no recirculation fuel pump. In this concern, the concept of passive-feed direct methanol fuel cells (DMFCs) has recently received significant interest [4–9] because provides unique features for the miniaturization of fuel cell systems. Several designs have been proposed for the development of air breathing fuel cells [10–13]. All these investigations into passive DMFCs were based on membrane-electrode assemblies (MEAs) equipped with Nafion as the electrolyte. Yet, since methanol is rapidly transported across perfluorinated membranes and is chemically oxidized to CO_2 and H_2O at the cathode, there is a significant decrease in Coulombic efficiency, as much as 20% under practical operating conditions. Thus, it is very important to replace conventional membranes with alternative proton conductors, composites, or blend membranes [14–22] that have the capability of inhibiting/reducing methanol transport. These polymer electrolytes should be low cost

* Corresponding author. Tel.: +39 090 624226; fax: +39 090 624247.
E-mail address: lufrano@itae.cnr.it (F. Lufrano).

and have high ionic conductivity and low permeability to methanol. Furthermore, they must be chemically and electrochemically stable under operating conditions. These requirements may be met, potentially, by various classes of solid polymer electrolytes that show promising properties for application in DMFCs. These alternative polymeric membranes, which are currently being investigated in fuel cells, are prepared from thermostable aromatic polymers such as sulfonated poly(aryl ether sulfone)s [23–25], sulfonated polysulfones [26–32], sulfonated polyetherketones [33–36], or sulfonated polyimides [37–39].

Among non-perfluorinated materials, sulfonated polysulfone (SPSf) is interesting because of its low cost, commercial availability, and easy chemical processing. For these reasons, many research groups [26–30], including our own [31,32], are investigating this material. However, to the best of our knowledge there are no studies in the literature on the use of sulfonated polysulfone membranes in passive DMFC stacks. Here, we report on the synthesis of sulfonated polysulfone with two different degrees of sulfonation (57 and 66%), both to provide adequate proton conductivity and low swelling at room temperatures under conditions different from those previously reported [31,32,40]. In fact, in this study, we have shortened reaction time and increased reaction temperature in the synthesis conditions. The sulfonated polysulfone was synthesized by a well-known method using trimethyl silyl chlorosulfonate as a mild sulfonating agent in a homogeneous solution of chloroform [26–32,40].

The influence of the polymer electrolyte properties (degree of sulfonation of the sulfonated polysulfone) and membrane thickness on the behaviour of a monopolar mini-stack operating at room temperature in an air breathing passive mode is reported. The object of this study was to provide new insights into the behaviour of this DMFC mini-stack operating with an alternative non-perfluorinated membrane.

2. Experimental

2.1. Synthesis of SPSf

A commercial polysulfone polymer (Lasulf from Lati SPA Varese – Italy) was used for the sulfonation process which consisted of dissolving 5 or 6 g of polymer in chloroform at room temperature and, subsequently, treating the polymer solution at 50 °C with trimethylsilyl chlorosulfonate (Aldrich) in order to produce a silyl sulfonate polysulfone. The amount of intermediate product was controlled by the molar ratio (2.5) between the sulfonating agent and the polymer repeating unit. Reaction temperature was kept at 50 ± 0.5 °C with a system that condensed the chloroform vapor. Different from previous works [31,32,40] in which the reaction time was 24 h at 25 °C, the higher temperature (50 °C) allowed a reduction in reaction time to 5 and 6 h for the preparation of two different samples. After the first step, the silyl sulfonate polysulfones obtained were treated with a 30 wt% sodium methoxide/methanol solution at 50 °C for 1 h, which is the condition used to cleave the silyl sulfonate moieties, thus producing sodium sulfonated polysulfone. The polymers were precipitated from the solutions in cold ethanol, which had previously been kept at −10 °C. The precipitates were separated from the solvent by filtration, vigorously washed several times with ethanol, and rinsed several times with distilled water. Finally, the sulfonated polysulfone powders in sodium form (SPSfNa) were dried at 70 °C.

2.2. Preparation of membranes

The SPSfNa polymer powders obtained (0.5–1 g) were dissolved in 5–15 ml of *N,N*-dimethylacetamide (DMAc) at room temperature to form a homogeneous solution. The membrane was then prepared by casting the SPSfNa solution on a glass plate and slowly evaporating the solvent at 50 °C for at least 15 h. Subsequently, each membrane was peeled off the glass in distilled water, then dried in an oven at 80 °C under vacuum for at least 24 h. Membranes with different thicknesses (70, 120 and 150 μm) were prepared. For several specific purposes, membranes up to 180 μm were also prepared. Finally, all the membranes were converted into acid form through treatment with 1 M H_2SO_4 solution at 50–60 °C for 15 h; they were subsequently rinsed with distilled water for several times.

Synthesis conditions and some physico-chemical characteristics of the sulfonated polysulfone samples are listed in Table 1.

2.3. Physico-chemical characterization of PSf and sPSf samples

The prepared membranes were characterized using different techniques.

Ion-exchange capacities (IECs) were determined by titration. A known amount of dry polymer (0.4–1.0 g) in acid form (after exchange in 1 M H_2SO_4 at 70 °C for at least 6 h) was suspended in 100 ml of 0.5 M NaCl solution that was stirred continuously for ~18 h at 50–60 °C (see Table 1). The amount of H⁺ released was then determined by titration with a 0.1 M NaOH solution using phenolphthalein as an indicator.

The water and 2 M MeOH uptake on membranes was obtained by measuring the weight change under dry and wet conditions. Membranes of about 4 cm × 4 cm (about 0.3–0.5 g) with a thickness of about 180 μm were used for these measurements. Before uptake measurements, the SPSf membranes were dried at 70 °C under vacuum for at least 18 h. They were then immersed in water or 2 M MeOH at 25 °C for 24 h, wiped dry and quickly weighed/measured again. The amount of uptake (wt%) was obtained using the equation $\mathrm{wt\%} = (\mathrm{wt_{wet}} - \mathrm{wt_{dry}})/\mathrm{wt_{dry}} \times 100$, where $\mathrm{wt_{wet}}$ and $\mathrm{wt_{dry}}$ are the weights of wet and dry membranes, respectively.

2.4. Passive DMFC performance in mini-stack

The monopolar three-cell stack consisted of two plastic plates (printed circuit boards – PCBs) without any specific flow field for liquid/gas diffusion; the current collectors consisted of a thin gold film deposited on the external borders of the fuel and oxidant compartment apertures where electrodes were placed in contact [41,42]. Designed as such, the central part of the electrode was exposed directly to ambient air (for the cathodes) and methanol solution (for the anodes). The two plates were assembled as shown in Fig. 1. The resistance of current collectors and external circuit was measured without MEA (membrane and electrodes assembly), inserting for each of the three cells two pieces of highly conductive carbon paper. The electronic resistance thus measured was 8 mΩ for three-cell stack hardware without a membrane-separator.

The geometrical area of each electrode was 4 cm² and the total area of the stack was 12 cm². A methanol reservoir (containing a total of 21 ml of methanol solution divided into three compartments) with three small holes in the upper part to fill the containers (see Fig. 1(a)) and release the CO_2 produced, was attached to the anode side. The MEAs (Fig. 1(b)) for this stack design (three cells) were manufactured by simultaneously assembling three sets of anode and cathode pairs on each side of the membrane (90 °C for 5 min and 30 kg cm⁻²), then sandwiching them between the two PCBs. Series connections between the cells were made externally through the electric circuit. The MEA design in this monopolar stack is not significantly different from that of a single cell. Thus, our approach is also useful for fundamental investigations under conditions appropriate for application in portable electronic devices. The electrodes used in this investigation were prepared as those

Table 1
Characteristics of sulfonated polymer samples.

Samples	X^a	Sulfonation time (h), 50 °C	Sulfonation level (%)	IEC by titration (mequiv. g^{-1})	Water uptake (%), 25 °C	2 M CH$_3$OH uptake (%), 25 °C	Proton conductivity (S cm^{-1})
SPSf1	2.5	5	57	1.16	24.3	25.7	0.0083
SPSf2	2.5	6	66	1.34	27.2	28.9	0.028

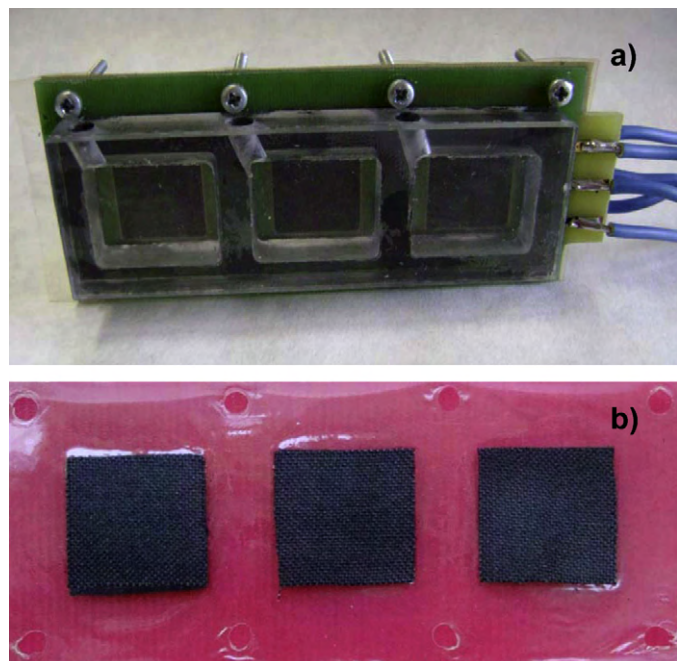[a] X = molar ratio of sulfonating agent to polymer repeating unit.

Fig. 1. Pictures of the (a) passive DMFC three-cell stack and (b) complete SPSf-based MEA.

used in our previous work [41,42], consisting of composite catalytic layers with 15 wt% Nafion ionomer (Ion Power, 5 wt% solution) and 85 wt% catalyst, and commercial backing layers HT-type (E-TEK) at the anode and LT-type (E-TEK) at the cathode.

An unsupported Pt–Ru (1:1 atomic ratio, Johnson-Matthey) was used as the anode catalyst and a Pt black (Johnson-Matthey) catalyst was utilized at the cathode for all MEAs. A Pt loading of 4 mg cm^{-2} was used for all MEAs, both at the anode and cathode (Table 2). Membranes of sulfonated polysulfone at different degrees of sulfonation and thicknesses were used as polymer electrolytes. The stack was operating in passive mode at room temperature (22 ± 3 °C) and with different methanol concentrations (from 1 to 5 M).

Performance was investigated by steady-state galvanostatic polarizations using an AUTOLAB PGSTAT 302 Potentiostat/Galvanostat (Metrohm) equipped with an FRA module of impedance. Polarization curves were recorded just after filling the reservoir with the methanol solution, in this way limiting an increase in temperature due to methanol crossover [12,15,43–45]. Impedance measurements were taken in a frequency range from

Table 2
Composition of MEA.

MEA	Pt loading (mg cm^{-2})	Catalyst	Nafion loading in electrodes (wt%)
Anode	4.0	Pt–Ru black Johnson-Matthey	15
Cathode	4.0	Platinum black Johnson-Matthey	15

to 0.01 to 100 kHz by frequency sweeping in the single sine mode. In this case, also, the experiments were carried out so that similar temperatures could be maintained for all measurements. This was achieved by cooling down the stack and changing the methanol solution after each measurement.

2.5. Single cell DMFC performance and cell resistance measurements

Electrodes for single cell measurements were prepared by the same method described above, using the same catalyst, ionomer amount and GDL used for testing the mini-stack. Membrane and electrodes assemblies (MEAs) were prepared by hot pressing the electrodes (anode and cathode) onto the sulfonated polysulfone membranes at 90 °C and 30 kg cm^{-2} for 5 min. The MEAs were tested in a 5 cm^2 single cell (GlobeTech Inc.) connected with an Autolab PGSTAT 302 Potentiostat/Galvanostat (Metrohm). The methanol solution was fed at the anode with a flow rate of 3 ml min^{-1}, whereas dry air was fed without pressure at the cathode at a flow rate of 100 ml min^{-1}. The performance of each MEA was measured under steady-state conditions. Cell resistance measurements (proton conductivity) were determined for the 5 cm^2 single cell during start-up and fuel cell operation by electrochemical impedance spectroscopy (EIS).

3. Results and discussion

3.1. Physico-chemical characteristics of membranes

Two samples of sulfonated polysulfone membranes, SPSf1 and SPSf2, were prepared. The sulfonation levels, ion-exchange capacity (IEC), and water and methanol uptake/swelling, measured at 25 °C, are reported in Table 1. The degrees of sulfonation in the samples studied were 57 and 66 wt%, and calculated by the titration method. The water uptake for SPSf1 and SPSf2 membranes ranged from 24 to 27 wt% at 25 °C, whereas a 2 M MeOH uptake of 26–29 wt% was recorded. These values indicate a low water/MeOH uptake and moderate swelling as required for DMFC applications.

3.2. Electrochemical characterization

As is well known, lower methanol crossover is one advantage that a sulfonated aromatic polymer as the SPSf membrane has over Nafion. Although we did not carry out specific methanol permeability measurements, we know from the current literature that SPSf materials have a significantly lower methanol permeability than Nafion membranes (see Table 3) [27,46–48]. It has also been pointed out that polysulfone membranes with similar or slightly higher ion-exchange capacity of Nafion-based membranes show lower proton conductivity, but this negative aspect can be compensated by a decrease in membrane thickness without a corresponding significant increase in methanol crossover. In this regard, Manea and Mulder [48] asserted that the methanol permeability coefficients of polysulfone (SPSf) and polyethersulfone/SPSf blends were approximately 1–2 orders of magnitude lower than Nafion. Whereas, Fu and Manthiram [27] found that the values of methanol crossover current density for SPSf were one-third

Table 3
Methanol permeability of the sulfonated polysulfone membranes at different sulfonation levels from literature data.

Sample	IEC (mequiv. g^{-1})	Methanol concentration	Permeability (cm^2 s^{-1})	Permeability [cm^3(STP) cm (cm^2 s cmHg)$^{-1}$]	Crossover current density (mA cm^{-2})	Reference
Nafion 115	0.91	2 M	1.17×10^{-6}	–	–	[46]
SPSf-48%	1.0	2 M	5.93×10^{-8}	–	–	[46]
SPf-69%	1.39	2 M (60 °C)	1.67×10^{-7}	–	–	[46]
Nafion 117	0.844	2 M (60 °C)	2.38×10^{-6}	–	–	[47]
SPSf5	0.85	2 M (60 °C)	1.4×10^{-7}	–	–	[47]
SPSf7	1.45	2 M (60 °C)	4.7×10^{-7}	–	–	[47]
Nafion 117	0.91	≈6 M		1.3×10^{-6}	–	[48]
SPSf	1.32	≈6 M		4.9×10^{-7}	–	[48]
Nafion 115	0.91	2 M (65 °C)	–	–	186	[27]
SPSf-57	1.17	2 M (65 °C)	–	–	58	[27]
SPSf-65	1.32	2 M (65 °C)	–	–	63	[27]

than Nafion 115. The differences of methanol permeabilities of swelled ionomer membranes can be explained on the basis of their dependence on various parameters such as degree of sulfonation, membrane swelling and methanol/water concentration. However, the data in Table 3 show that all samples of polysulfone membranes exhibit permeabilities from 2 to 20 times lower than the methanol permeability in Nafion membranes.

Fig. 2 shows the polarization curves and power densities recorded for an MEA containing the SPSf1 membrane (IEC = 1.16 mequiv. g^{-1}) at different methanol concentrations in a passive-mode direct methanol fuel cell mini-stack operating at room temperature. The open circuit voltage (OCV) for the stack decreased as methanol concentration increased; this clearly indicates that the methanol crossover rate increases with an increase in methanol concentration. This was noticeable in the performance recorded with 1 M methanol solution, which is better than that obtained with higher concentrations, particularly at low current densities, whereas at higher currents, performance suffers from mass transfer limitations. At increased methanol concentrations (2 and 5 M), lower mass transfer constraints were observed. Maximum stack performance was 50 mW at a current density of 25 mA cm^{-2}, significantly lower than that of the Nafion 117 membrane [42].

The low performance obtained with a SPSf1 membrane could be explained by taking into account the low conductivity (8.3×10^{-3} S cm^{-1}) of this membrane, which can negatively influence both the OCV and power density of the mini-stack. For this reason, membranes with higher sulfonation levels were studied. Fig. 3 shows the polarization and power density curves for the three-cell mini-stack equipped with the SPSf2 membrane (IEC = 1.34 mequiv. g^{-1}; thickness 70 μm). The influence of different methanol concentrations (1, 2, and 5 M) on the electrochemical

behaviour of the stack was investigated. An open circuit voltage (OCV) higher than 2 V (2.07) was recorded with 1 and 2 M methanol solutions, whereas it was 1.8 V with a concentrated solution of 5 M due to higher methanol crossover under this condition. Nevertheless, this OCV value is similar to or slightly higher than that recorded with the same device equipped with the Nafion 117 membrane [41,42], indicating lower methanol crossover with the 70 μm SPSf2 membrane than with the thicker 175 μm Nafion 117 membrane. A maximum stack performance of 220 mW was obtained at a current density of 110 mA cm^{-2} with 2 M methanol, whereas slightly lower values of 192 and 188 mW were achieved with 1 and 5 M solutions, respectively. The 220 mW power corresponds to an average power density of 19 mW cm^{-2} for each cell in the mini-stack. These results are similar to those obtained from electrodes with the same Pt loading and equipped with the Nafion 117 membrane [41,42]. This result is quite promising if one considers that we are not aware of any previous application of these polysulfone membranes in a DMFC mini-stack. Moreover, there is only limited knowledge about the influence of the degree of sulfonation on the properties of SPSf membranes such as proton conductivity, methanol crossover, and DMFC performance, which, to some extent, was investigated in this study.

In current literature, the thickness of Nafion membranes is one of the most critical factors in DMFC performance because it determines the methanol crossover. Unfortunately, thick membranes reduce power density due to their high ionic resistance [41–45,49,50]. Therefore, in selecting the appropriate thickness of a membrane, a compromise must be made between higher power density and a more stable, durable performance. Most investigations into passive DMFC stacks have been concerned with thick Nafion membranes (usually Nafion 117 or 115).

Liu et al. [50] investigated the effect of membrane thickness on the performance of a passive micro-DMFC using various Nafion
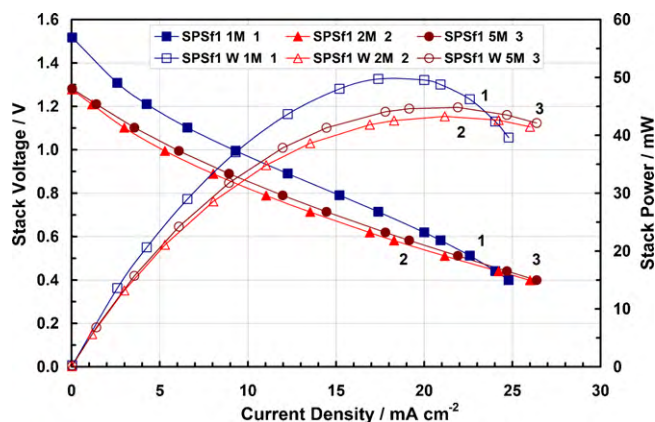

Fig. 2. Polarization and stack power curves for MEA based on SPSf1 (57% sulfonation) membrane (70 μm) at different methanol concentrations (1, 2 and 5 M).
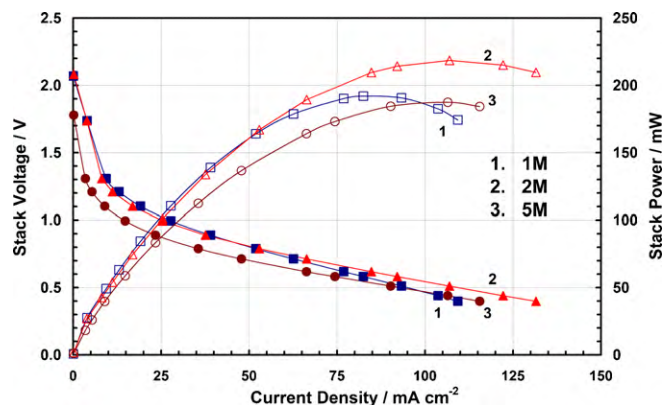

Fig. 3. Polarization and stack power curves for MEA based on SPSf2 (66% sulfonation) membrane (70 μm) at different methanol concentrations (1, 2 and 5 M).
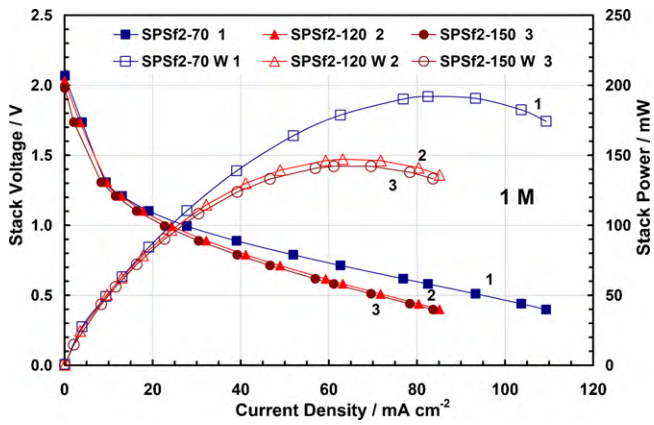
Fig. 4. Influence of the membrane thickness (70, 120 and 150 μm) on the performance of the stack based on SPSf2 membrane at 1 M methanol concentration.

Fig. 5. Influence of the membrane thickness (70, 120 and 150 μm) on the performance of the stack based on SPSf2 membrane at 2 M methanol concentration.

membranes, namely 117, 115, and 112, with thicknesses of 175, 125 and 50 μm, respectively [50]. The findings showed that when the cell was fed with a low methanol concentration (2 M), a thicker membrane performed better at low current densities; whereas at higher current densities, the cell with a thinner membrane yielded a better performance. At higher methanol concentration, the three membranes exhibited similar cell voltages over a wide range of current densities. From these results, the researchers recommended thicker membranes for passive micro-DMFCs with high methanol concentration because, even though the cell performed more or less the same with thinner membranes, higher fuel efficiency was achieved.

For this reason, as well as the fact that there are only limited studies on sulfonated polysulfone membranes in passive DMFCs, a series of membranes (SPSf2, 66% sulfonation) with different thicknesses were prepared and investigated in a passive DMFC mini-stack. Comparisons were made between membranes with thicknesses of 70, 120, and 150 μm as a function of methanol concentrations of 1, 2, and 5 M at room temperature.

Fig. 4 shows the polarization and power curves for the stack in 1 M methanol solution with SPSf2 membranes of different thicknesses. The curves show that the SPSf2-70 membrane (70 μm) has both high OCV (2.07 V) and stack power (192 mW) compared to thick SPSf2-120 (120 μm) and SPSf2-150 (150 μm) membranes. These latter membranes reached power performances of 147 and 142 mW, respectively. The results show that performance is influenced mainly by ohmic resistance (see the slope of the I–V curves) for thick membranes; therefore, the mini-stack's efficiency was controlled primarily by the ohmic drop, not methanol crossover. This observation was also confirmed by similar OCVs for the stack equipped with different membranes (from 70 to 150 μm) in 1 M methanol solution. These findings indicate that methanol crossover has less influence on the performance of these aromatic sulfonated polymer materials in a monopolar DMFC mini-stack than in passive DMFC cells or stacks operating with Nafion membranes, in which methanol crossover is the main issue [41–45,49,50].

Fig. 5 shows a comparison of mini-stack's performance using 2 M methanol solution. With this concentration, a better performance was also obtained with the thin SPSf2 membrane (SPSf2-70) with a peak power for the mini-stack of 220 mW (average power density of about 19 mW cm^{-2} for each cell). This value is similar to that obtained for the same mini-stack's configuration with the Nafion 117 membrane (225 mW at ≈110 mA cm^{-2}) [42]. Polarization curves show that the OCV was practically independent of the thickness of membranes, while voltage losses in the activation zone (low current density) appeared the same for the different membranes. Differences, however, were more significant in the ohmic
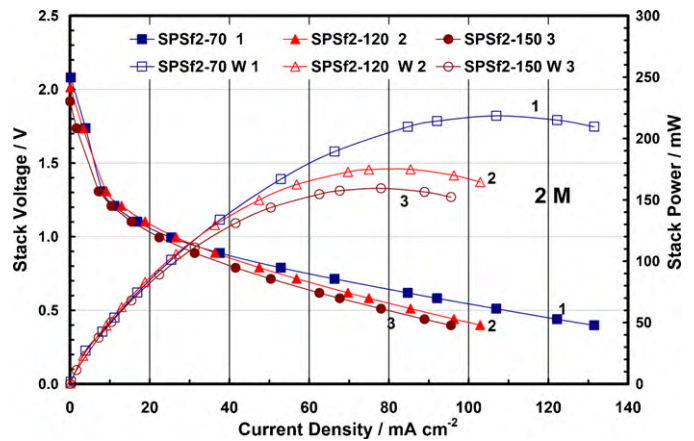
region where the thinnest membrane (minor thickness) allowed a higher limiting current (and consequently higher power density). The maximum power density for the thick membranes was 175 mW at 85 mA cm^{-2} and 160 mW at 78 mA cm^{-2} for SPSf2-120 and SPSf2-150 membranes, respectively. The SPSf2-70 membrane (70 μm) allowed an increase in the stack's power of 26% and 38% compared to SPSf2-120 and SPSf2-150 membranes, respectively.

Fig. 6 illustrates a comparison of the DMFC mini-stack's performance with three membranes of different thicknesses at 5 M methanol concentration. At high concentration, the OCV was highest for the SPSf2-150 membrane, followed by the SPSf2-120 and, successively, the SPSf2-70. This indicates that when using high methanol concentration, methanol permeation through the membranes becomes relevant for the thin membrane (as expected); accordingly, in this case, the OCV is found to be influenced by the thickness of the membrane. However, with the other methanol concentrations (1 and 2 M), maximum DMFC performance is obtained with the thin SPSf2-70 membrane, confirming that the main parameter influencing the behaviour of the stack equipped with SPSf membranes is ionic conductivity.

An investigation of the ohmic characteristics of membranes with different thicknesses was carried out by an impedance analysis of the complete stack at a fixed potential of 0.9 V. Under this stack potential, DMFC performance was governed by a number of interdependent physical and chemical processes proceeding at different rates, which were investigated by electrochemical impedance spectroscopy. Fig. 7 shows the Nyquist plots recorded at 0.9 V for
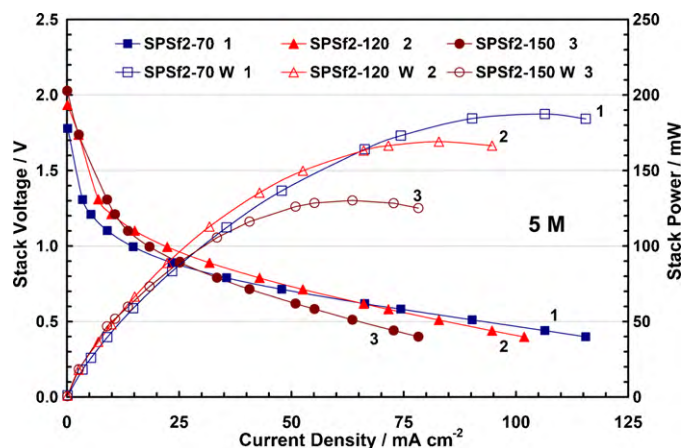

Fig. 6. Influence of the membrane thickness (70, 120 and 150 μm) on the performance of the stack based on SPSf2 membrane at 5 M methanol concentration.
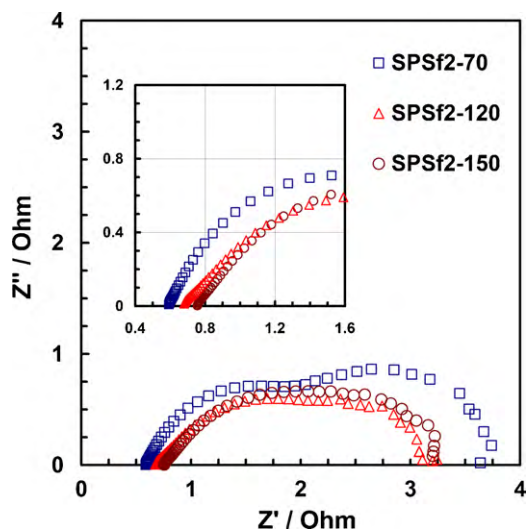
Fig. 7. Impedance spectra for the three-cell DMFC stack at 0.9 V, 2 M methanol for MEA based on SPSf2 membranes of different thickness.

Fig. 9. Polarization and power density curves recorded for active-mode DMFC single cell (graphite plate – serpentine flow field; 5 cm² geometrical area; 3 ml min MeOH; 100 cm³ min air) on the SPSf2 (66% sulfonation) membrane (70 μm) at different methanol concentrations.

mini-stacks equipped with the SPSf2 membranes of different thicknesses. The plots consist of two overlapping semicircles, one at high and medium frequencies, the other at low frequency, and are related to anodic (methanol electro-oxidation) and cathodic (oxygen reduction) processes, respectively [49]. The impedance spectra show that stack resistance increases with an increase in membrane thickness, as seen in the inset of Fig. 7.

As described in the experimental section, the mini-stack consists of three cells with series connection made throughout the external electrical circuit. Accordingly, it was possible to study the behaviour of each cell by changing the external connections, which was useful in order to understand the behaviour of a single cell's performance in terms of efficiency. Fig. 8 shows voltage and power density as a function of the current density of three single cells equipped with the SPSf2-70 membrane (70 μm) in air breathing mode and 5 M methanol concentration (passive). The behaviour of the three cells is practically the same and within experimental error taking into consideration both electrochemical measurements and electrode fabrication (4 ± 0.2 mg cm⁻² Pt loading in each electrode). The OCV is about 0.65 V for each cell, which is appropriate taking into account the 5 M methanol concentration, passive mode, and low temperature. For comparative purposes, an MEA with an active area of 5 cm² (with the same MEA characteristics, i.e. SPSf2-70 membrane and 4 mg cm⁻² Pt loading, both at
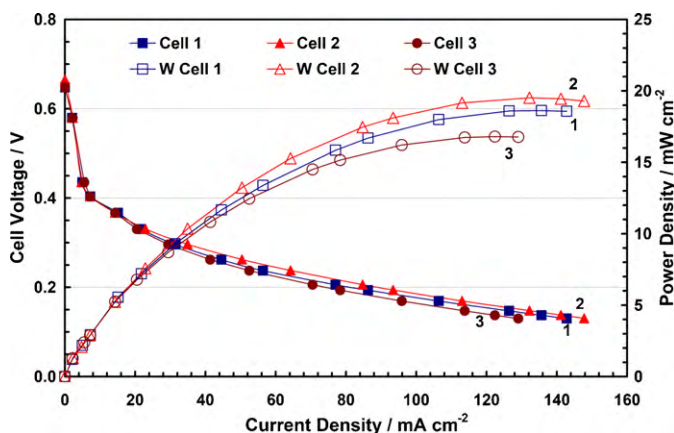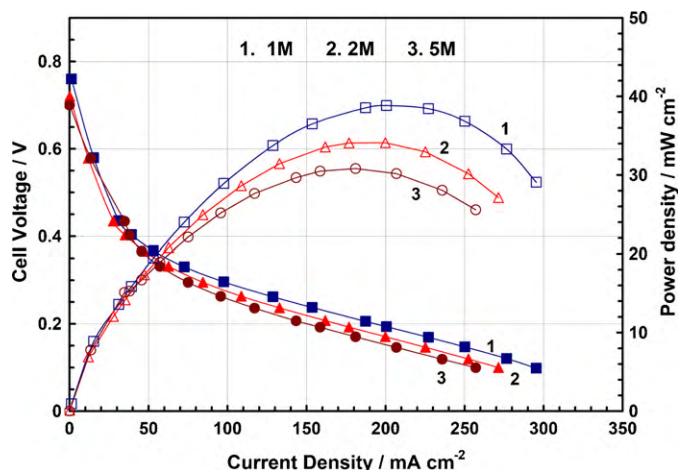
the anode and cathode) was prepared and tested in a conventional active-mode graphite single cell (serpentine flow field) using different methanol concentrations (1, 2, and 5 M). Results are reported in Fig. 9 and show a higher level of performance in active mode than in passive mode, as expected. This is also due to lower cell resistance (0.25 Ω cm² vs. 0.8 Ω cm²) when using conventional graphite plates as current collectors. The SPSf2 membrane conductivity measured by electrochemical impedance measurements at OCV and 0.3 V was 2.8 × 10⁻² S cm⁻¹ at room temperature. This value is similar to those reported in literature [27,31,40] at room temperature for polysulfone membranes of similar sulfonation degree. In this type of cell setup, a decrease in OCV resulted from increasing the level of methanol concentration in active mode and, in contrast to passive mode, the best performance was observed with the lowest level of concentration (1 M) as also usually reported in the literature [14,17,51]. Feeding 1 M methanol solution at the anode, the power density was 38 mW cm⁻² in active mode compared to about 19 mW cm⁻² in passive mode. This suggests that further improvement in performance under passive-mode operation could be achieved, in particular by modifying the electrodes or the mini-stack's structure. To validate the suitability of SPSf membranes for DMFC applications, a short time-stability test of about 200 min of continuous operation was carried out on the three-cell stack equipped with the SPSf2-120 membrane (120 μm) at a current density of 50 mA cm⁻² using 5 M methanol solution (Fig. 10). In
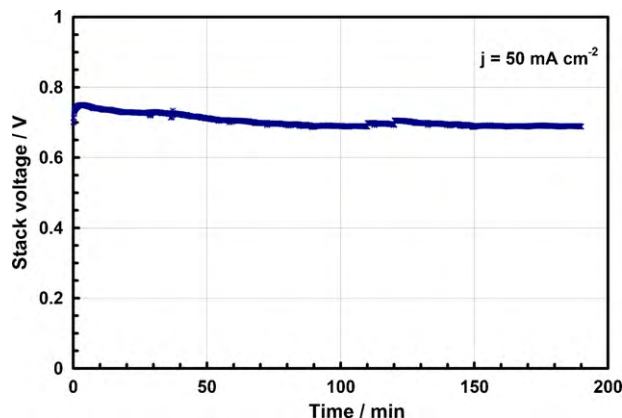

Fig. 8. Polarization and single cell power density curves for passive DMFC stack on the SPSf2 (66% sulfonation) membrane (70 μm) at 5 M methanol concentration.

Fig. 10. Chrono-amperometry behaviour of the mini-stack based on the SPSf2 membrane (120 μm) in passive-mode operation at 50 mA cm² and 2 M methanol.

this case, intermediate thickness was selected for the membrane in order to guarantee low methanol crossover, thus, a more stable performance. A slight decrease in current was observed during the first 50 min with a concentrated solution of methanol (5 M), which was probably due to either methanol crossover or a flooding effect at the cathode. Subsequently, more stable behaviour was observed. This might be explained by taking into account methanol consumption during operation (dilution effect) or the slight increase in temperature that limits the flooding of the cathode (even if methanol crossover increases with an increase in temperature). A more in-depth analysis of these phenomena is currently underway.

However, even if this short-time test is insufficient to validate the durability of sulfonated polysulfone, the moderate water/methanol uptake of these membranes at room temperatures indicates interesting properties for applications in DMFC systems because of fewer problems with interfacial delamination between the electrode layer and the membrane, which has been isolated as a critical factor in terms of durability [52–55]. This is particularly important in DMFC systems operating (as in our situation) with membranes that are alternative to Nafion (i.e. non-fluorinated sulfonated aromatic polymers). What mainly increases the probability of an interfacial failure in such systems is poor compatibility between the non-Nafion polymer in the membrane and the Nafion-bonded electrodes. However, more successful long-term performance (>3000 h) has been reported for similar families of non-fluorinated sulfonated aromatic polymers than those used in this study, such as partially fluorinated derivatives of poly(arylene ether sulfone) copolymers (SPAES) [53–55], blends based on polyetheretherketones (PEEK)s [56,57] and sulfonated polyimide membranes [39]. These results are a good starting point for advancing the development of a complete MEA based on alternative polymers to Nafion with comparable performance and desirable long-term stability.

4. Conclusion

The sulfonated polysulfone was synthesized and used as a polymer electrolyte in a direct methanol fuel cell mini-stack (three cells). The stack was operated at room temperature in a passive-mode using membranes with different degrees of sulfonation (57 and 66%) and thicknesses (70, 120, and 150 μm). The best performance was obtained with the SPSf2 membrane (66% sulfonation; IEC = 1.34 mequiv. g^{-1}) with a thickness of 70 μm. A maximum power density of 220 mW (average cell power density of about 19 mW cm^{-2}) was achieved. The conductivity of this SPSf2 membrane was 2.8×10^{-2} S cm^{-1} at room temperature. A short time-stability test (200 min) showed good stability during chrono-amperometric measurements. A comparison between cells operating in passive (mini-stack) and active (single cell) mode showed that sulfonated SPSf2 membranes reached power densities of 19 and 38 mW cm^{-2}, respectively. This result indicates that further improvements in passive-mode (DMFC mini-stack) could be obtained by modifying electrodes and the mini-stack's structure.

References

[1] L. Carrette, K.A. Friedrich, U. Stimming, ChemPhysChem 1 (2000) 162–192.
[2] R. Dillon, S. Srinivasan, A.S. Aricò, V. Antonucci, J. Power Sources 127 (2004) 112.
[3] J.-H. Wee, J. Power Sources 161 (2006) 1–10.
[4] B.K. Kho, B. Bae, M.A. Scibioh, J. Lee, H.Y. Ha, J. Power Sources 142 (2005) 50.
[5] A. Kundu, J.H. Jang, J.H. Gil, C.R. Jung, H.R. Lee, S.-H. Kim, B. Ku, Y.S. Oh, J. Power Sources 170 (2007) 67–78.
[6] G. Jewett, Z. Guo, A. Faghri, J. Power Sources 168 (2007) 434.
[7] B. Bae, B.K. Kho, T.-H. Lim, I.-H. Oh, S.-A. Hong, H.Y. Ha, J. Power Sources 158 (2006) 1256.
[8] C.Y. Chen, P. Yang, Y.S. Lee, K.F. Lin, J. Power Sources 141 (2005) 24.
[9] R. Chen, T.S. Zhao, J. Power Sources 167 (2007) 455–460.
[10] Y. Zhang, J. Lu, S. Shimano, H. Zhou, R. Maeda, Electrochem. Commun. 9 (2007) 1365–1368.
[11] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, J. Power Sources 117 (2003) 22–25.
[12] J.J. Martin, W. Qian, H. Wang, V. Neburchilov, J. Zhang, D.P. Wilkinson, Z. Chang, J. Power Sources 164 (2007) 287–292.
[13] G.Q. Lu, C.Y. Wang, T.J. Yen, X. Zhang, Electrochim. Acta 49 (2004) 821.
[14] Y.S. Kim, M. Sumner, W. Harrison, J.E. McGrath, B.S. Pivovar, J. Electrochem. Soc. 151 (2004) A2150–A2156.
[15] V.S. Silva, S. Weisshaar, R. Reissner, B. Ruffmann, S. Vetter, A. Mendes, L.M. Madeira, S. Nunes, J. Power Sources 145 (2005) 485–494.
[16] X. Li, C. Liu, D. Xu, C. Zhao, Z. Wang, G. Zhang, H. Na, W. Xing, J. Power Sources 162 (2006) 1–8.
[17] L. Jorissen, V. Gogel, J. Kerres, J. Garche, J. Power Sources 105 (2002) 267–273.
[18] M.A. Navarra, C. Abbati, B. Scrosati, J. Power Sources 183 (2008) 109–113.
[19] V. Gogel, L. Jorissen, A. Chromik, F. Schonberger, J. Lee, M. Schafer, K. Krajinovic, J. Kerres, Sep. Sci. Technol. 43 (2008) 3955.
[20] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Membr. Sci. 185 (2001) 73–81.
[21] O. Savadogo, J. Power Sources 127 (2004) 135–161.
[22] V. Baglio, A.S. Aricò, A. Di Blasi, V. Antonucci, P.L. Antonucci, S. Licoccia, E. Traversa, F.S. Fiory, Electrochim. Acta 50 (2005) 1241–1246.
[23] W.L. Harrison, M.A. Hickner, Y.S. Kim, J.E. McGrath, Fuel Cells 5 (2005) 201–212.
[24] K. Miyatake, Y. Chikashige, M. Watanabe, Macromolecules 36 (2003) 9691–9693.
[25] B. Liu, Y.S. Kim, W. Hu, G.P. Robertson, B.S. Pivovar, M.D. Guiver, J. Power Sources 185 (2008) 899–903.
[26] P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poinsignon, J.Y. Sanchez, J. Membr. Sci. 185 (2001) 59–71.
[27] Y.-Z. Fu, A. Manthiram, J. Power Sources 157 (2006) 222–225.
[28] S.-L. Chen, A.B. Bocarsly, J. Benziger, J. Power Sources 152 (2005) 27–33.
[29] Y.-Z. Fu, W. Li, A. Manthiram, J. Membr. Sci. 310 (2008) 262–267.
[30] Y. Yang, Z. Shi, S. Holdcroft, Macromolecules 37 (2004) 1678–1681.
[31] F. Lufrano, V. Baglio, P. Staiti, A.S. Aricò, V. Antonucci, J. Power Sources 179 (2008) 34–41.
[32] F. Lufrano, V. Baglio, P. Staiti, A.S. Aricò, V. Antonucci, Desalination 199 (2006) 283–285.
[33] M. Gil, X. Ji, X. Li, H. Na, J.E. Hampsey, Y. Lu, J. Membr. Sci. 234 (2004) 75–81.
[34] M.L. Di Vona, D. Marani, A. D'Epifanio, E. Traversa, M. Trombetta, S. Licoccia, Polymer 46 (2005) 1754.
[35] L. Li, J. Zhang, Y. Wang, J. Membr. Sci. 226 (2003) 159–167.
[36] B. Liu, D.-S. Kim, J. Murphy, G.P. Robertson, M.D. Guiver, S. Mikhailenko, S. Kaliaguine, Y.-M. Sun, Y.-L. Liu, J.-Y. Lai, J. Membr. Sci. 280 (2006) 54–64.
[37] Y. Woo, S.Y. Oh, Y.S. Kang, B. Jung, J. Membr. Sci. 220 (2003) 31–45.
[38] J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K.-I. Okamoto, Macromolecules 35 (2002) 9022–9028.
[39] A. Kabasawa, J. Saito, H. Yano, K. Miyatake, M. Uchida, M. Watanabe, Electrochim. Acta 54 (2009) 1076–1082.
[40] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, Solid State Ionics 145 (2001) 47–51.
[41] V. Baglio, A. Stassi, F.V. Matera, A. Di Blasi, V. Antonucci, A.S. Aricò, J. Power Sources 180 (2008) 797.
[42] V. Baglio, A. Stassi, F.V. Matera, V. Antonucci, A.S. Aricò, Electrochim. Acta 54 (2009) 2000–2009.
[43] J.Y. Cao, Z.Q. Zou, Q.H. Huang, T. Yuan, Z. Li, B. Xia, H. Yang, J. Power Sources 185 (2008) 433.
[44] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, J. Power Sources 163 (2007) 743.
[45] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, Electrochem. Commun. 7 (2005) 288–294.
[46] H.B. Park, H.-S. Shin, Y.M. Lee, J.-W. Rhim, J. Membr. Sci. 247 (2005) 103–110.
[47] R. Pedicini, A. Carbone, A. Saccà, I. Gatto, G. Di Marco, E. Passalacqua, Polym. Test. 27 (2008) 248–259.
[48] C. Manea, M. Mulder, J. Membr. Sci. 206 (2002) 443–453.
[49] N. Nakagawa, Y. Xiu, J. Power Sources 118 (2003) 248–255.
[50] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, J. Power Sources 153 (2006) 61–67.
[51] S. Ren, C. Li, X. Zhao, Z. Wu, S. Wang, G. Sun, Q. Xin, X. Yang, J. Membr. Sci. 247 (2005) 59–63.
[52] Y. Tian, G. Sun, Q. Mao, S. Wang, H. Liu, Q. Xin, J. Power Sources 185 (2008) 1015–1021.
[53] M. Sankir, Y.S. Kim, B.S. Pivovar, J.E. McGrath, J. Membr. Sci. 299 (2007) 8–18.
[54] Y.S. Kim, B.S. Pivovar, ECS Trans. 1 (2005) 457–467.
[55] Y.S. Kim, B. Pivovar, in: 208th Meeting of the Electrochemical Society, 2005 (Abstract 1215).
[56] B. Lakshmanan, W. Huang, D. Olmeijer, J.W. Weidner, Electrochem. Solid-State Lett. 6 (2003) A282–A285.
[57] V. Neburchilov, J. Martin, H. Wang, J. Zhang, J. Power Sources 169 (2007) 221–238.