



**Improved Durability and Cost-effective Components for New Generation Solid Polymer Electrolyte Direct Methanol Fuel Cells**

Collaborative Project - FCH JU GRANT AGREEMENT N° 278054

SP1-JTI-FCH.2010.4.4 Components with advanced durability for Direct Methanol Fuel Cells

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**Project Coordinator:** Antonino Salvatore Aricò – CNR-ITAE

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**DELIVERABLE REPORT**

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<b>D3.2 – SUPPLY OF OPTIMISED POLYPHOSPHONIC AND SULFONATED POLYSULFONE MEMBRANES</b>	
Due Date	1st January 2013
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Workpackage	WP3 – Innovative Membranes
Workpackage leader	CNRS
Lead Beneficiary	CNRS
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Date released by Coordinator	1st April 2013

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**NATURE OF THE DELIVERABLE**

<b>R</b>	<i>Report</i>	<b>X</b>
<b>P</b>	<i>Prototype</i>	
<b>D</b>	<i>Demonstrator</i>	
<b>O</b>	<i>Other</i>	

**SUMMARY**

<b>Keywords</b>	<i>Membrane, sulfonated polysulfone, reference membrane, polyphosphonic acid, mixed functionality membranes, acid doped polybenzimidazole</i>
<b>Abstract</b>	<p><i>This report describes the properties of membranes developed for the different temperature targets of the project: sulfonated polysulfone in pristine form and containing silica and sulfonated silica; perfluorosulfonic acid membranes modified by molecular phosphonic acids, specifically targeted for the intermediate temperature range, and phosphoric acid doped membranes that provide an option for DMFC operation with vapour phase methanol of concentration &gt;9 mol/dm<sup>3</sup>.</i></p>

**REVISIONS**

Version	Date	Changed by	Comments
0.1	18th December 2012	D. J. Jones	Initiated
0.2	11th February 2013	D. J. Jones	Input from CNR-ITAE on sulfonated polysulfone membranes
0.3	25th February 2013	D. J. Jones	Input from FUMA on PFSA-phosphonic acid membranes
0.4	31st March 2013	D. J. Jones	Input from CNRS on acid doped PBI membranes

## D3.2– OPTIMISED PHOSPHONIC ACID (MEDIUM HIGH TEMPERATURE) AND SULFONATED POLYSULFONE (LOW TEMPERATURE) MEMBRANES

This work package aims at developing innovative direct methanol fuel cell membranes for two specific applications i.e. portable and APU uses and corresponding targeted temperatures (up to 60 °C, 120°-150 °C). Stable polyphosphonic and sulfonated polysulfone hydrocarbon membranes as well as composite polymer electrolytes will be developed for high temperature APU and low temperature portable applications and tested in combination with enhanced durability electrocatalysts.

This deliverable report describes the further optimisation of membranes targeted for the low and intermediate (80-120 °C) temperature range, and high temperature ranges in work performed at CNR-ITAE, CNRS and FuMA-Tech over the first twelve months of the project.

### 1. Sulfonated polysulfone

In the deliverable 3.1 the preparation process of sulfonated polysulfone was discussed. The preparation procedure allowed preparation of membranes with satisfactory physico-chemical properties. In the present deliverable, the sulfonated polysulfone membranes down-selected from the previous activity were supplied for electrochemical characterisation. Thus the main efforts in this deliverable for the SPSf are addressed to evaluate in-situ some relevant properties, including cross-over, in a membrane-electrode assembly in order to get a feed-back regarding the perspective of using such membranes in DMFCs.

The main physical-chemical characteristics of the specific polysulfone membranes down-selected from the previous Deliverable 3.1 i.e. sulfonated polysulfone (SPSf), composite silica-SPSf (SPSf-SiO<sub>2</sub>) and composite acidic silica-SPSf (SPSf-SiO<sub>2</sub>-S) membranes are summarised in Table 1.

**Table 1.** Characteristics of different membranes

Samples	Membrane Thickness (μm)	IEC 25°C (mmol g <sup>-1</sup> )	Water uptake @ 25°C (%)	1M CH <sub>3</sub> OH uptake @ 25°C (%)	Proton conductivity 30°C (mS cm <sup>-1</sup> )	Proton conductivity 60°C (mS cm <sup>-1</sup> )
SPSf	90	1.37	32.2	31	36	50
SPSf-SiO <sub>2</sub>	100	1.32	32.5	31.2	20	25
SPSf-SiO <sub>2</sub> -S	100	1.34	31.4	31	27	37

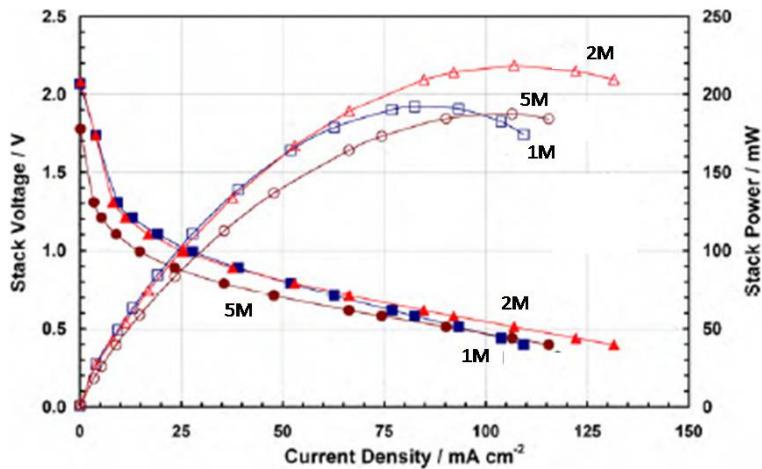
The activity herewith reported deals with the electrochemical characterisation of the supplied materials.

The bare SPSf membrane was studied in an active-mode DMFC single cell and in a passive-mode three-cell monopolar mini-stack; whereas the composite membrane based on SPSf and bare silica was investigated only in an active-mode single cell and compared to the bare SPSf membrane.

The monopolar three-cell stack consisted of two 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. 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 geometrical area of each electrode was  $4 \text{ cm}^2$  and the total area of the stack was  $12 \text{ cm}^2$ . 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 and release the  $\text{CO}_2$  produced, was attached to the anode side. The MEAs for this stack design (three cells) were manufactured by simultaneously assembling three sets of anode and cathode pairs on each side of the membrane ( $90^\circ\text{C}$  for 5 min and  $30 \text{ kg cm}^{-2}$ ), then sandwiching them between the two PCBs. Series connections between the cells were made externally through the electric circuit.

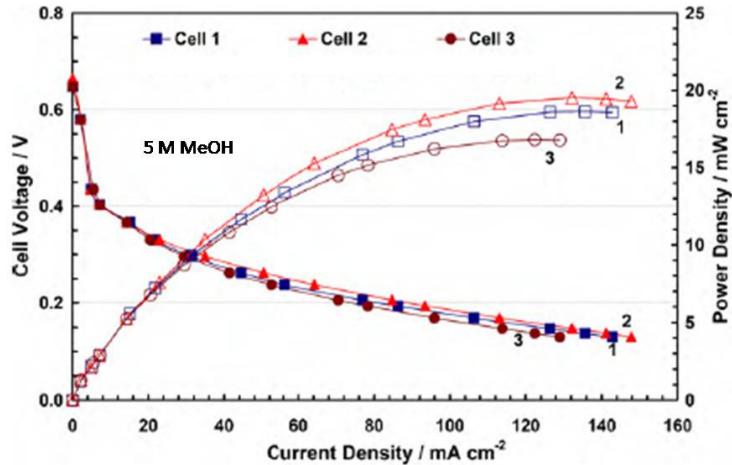
The electrodes for the mini-stack were composed of commercial gas-diffusion layer-coated carbon cloth for high temperature (HT-ELAT, E-TEK) and low temperature operation (LT-ELAT, ETEK) at the anode and cathode, respectively. Unsupported baseline Pt–Ru (Johnson-Matthey) and Pt (Johnson-Matthey) catalysts were mixed under ultrasound with 15 wt.% Nafion ionomer (Ion Power, 5 wt.% solution) and deposited by doctor blade technique onto the diffusion media for the anode and cathode, respectively. A Pt loading of  $4 \text{ mg cm}^{-2}$  was used for all MEAs, both at the anode and cathode. The stack was operating in passive mode at room temperature ( $22 \pm 3^\circ\text{C}$ ) and with different methanol concentrations (from 1 to 5M). 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.

Fig. 1 shows the polarization and power density curves for the three-cell mini-stack equipped with the SPSf membrane. 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 V) 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. A maximum stack performance of 220 mW was obtained at a current density of  $110 \text{ mA cm}^{-2}$  with 2M 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  $19 \text{ mW cm}^{-2}$  for each cell in the mini-stack. It was also 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. 2 shows voltage and power density as a function of the current density of three single cells equipped with the SPSf membrane in air breathing mode and 5M methanol concentration (passive).



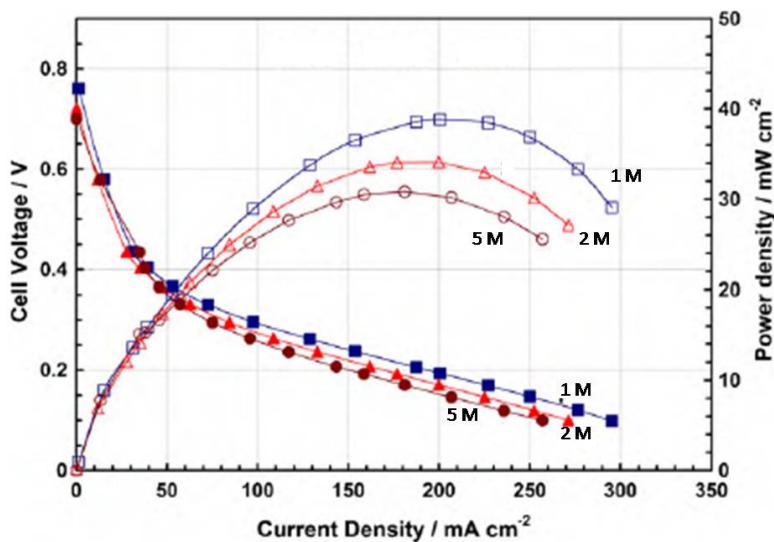
**Figure 1.** Polarization and stack power curves for MEA based on SPSf membrane at MeOH concentrations (1, 2 and 5 M).

The behaviour of the three cells is practically the same within experimental error, taking into consideration both electrochemical measurements and electrode fabrication ( $4 \pm 0.2 \text{ mg cm}^{-2}$  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.



**Figure 2.** Polarization and power density curves for each cell of the mini-stack.

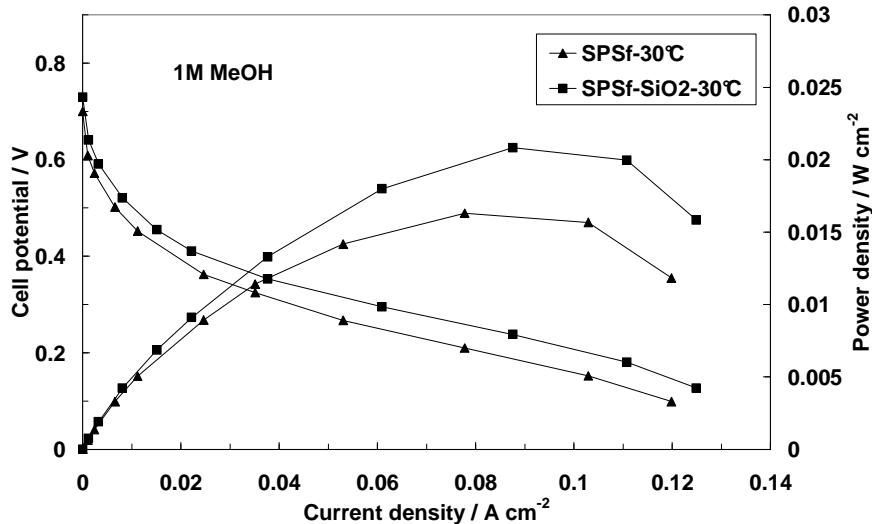
For comparative purposes, an MEA with an active area of 5 cm<sup>2</sup> (with the same MEA characteristics, i.e. SPSf membrane and 4 mg cm<sup>-2</sup> Pt loading, both at the anode and cathode) was prepared and tested in a conventional active-mode graphite single cell (serpentine flow field) using different methanol concentrations (1, 2, and 5 M). Results are reported in Fig. 3 and show a higher level of performance in active mode than in passive mode, as expected. This is also due to lower cell resistance ( $0.25 \text{ ohm cm}^2$  vs.  $0.8 \text{ ohm cm}^2$ ) when using conventional graphite plates as current collectors.



**Figure 3.** Polarization and power density curves recorded for active-mode DMFC single cell (graphite plate – serpentine flow field;  $5 \text{ cm}^2$  geometrical area;  $3 \text{ ml min}^{-1}$  MeOH;  $100 \text{ cm}^3 \text{ min}^{-1}$  air) on the SPSf membrane at different methanol concentrations.

Feeding 5 M methanol solution at the anode, the power density was  $30 \text{ mWcm}^{-2}$  in active mode compared to about  $19 \text{ mWcm}^{-2}$  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.

For the SPSf-SiO<sub>2</sub> composite membrane, the electrochemical evaluation was carried out in single cell only with the same Pt loading used for the bare SPSf membrane reported in the deliverable D3.1 ( $2.5 \text{ mg cm}^{-2}$ , see previous report).

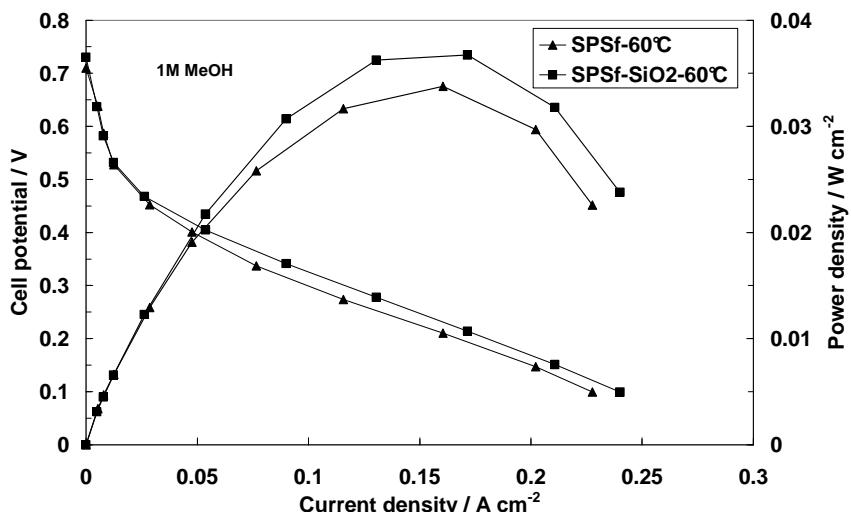


**Figure 4.** Polarization and power density curves for the cells equipped with bare SPSf and SPSf-SiO<sub>2</sub> membranes at  $30^\circ\text{C}$  (1M MeOH, dry air, atmospheric pressure).

Fig. 4 shows a comparison of the polarization curves for the different polysulfone-based membranes in a single cell experiment at  $30^\circ\text{C}$ , using 1 M MeOH at the anode and dry air at the cathode under atmospheric pressure. A higher

performance is obtained with the composite membrane based on silica ( $\text{SPSf-SiO}_2$ ) compared to pure SPSf membranes. The open circuit voltage (OCV) for the MEA equipped with the composite membrane ( $\text{SPSf-SiO}_2$ ) was about 0.73 V, whereas the SPSf-based MEA showed an OCV value of 0.7 V. The highest OCV achieved with the silica based membrane is indicating a lower MeOH crossover of the composite membrane than the bare one; this favours the achievement of high power density even if the  $\text{SPSf-SiO}_2$  membrane has a lower conductivity (see Table 1) compared to the bare SPSf membrane (which is another important requirement to reach high current densities). The  $\text{SPSf-SiO}_2$  membrane gave a maximum power density of  $21 \text{ mW cm}^{-2}$  at  $30^\circ\text{C}$ , whereas the pure SPSf membrane reached  $16 \text{ mW cm}^{-2}$ .

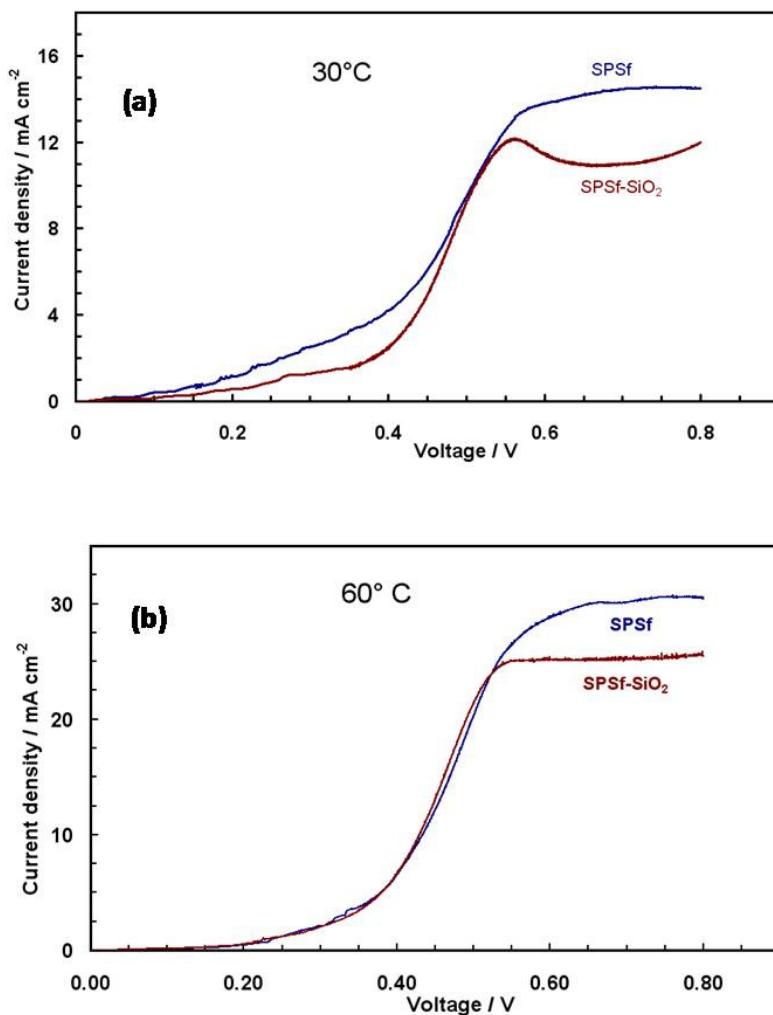
At higher temperature ( $60^\circ\text{C}$ ), an increase in performance was observed for both cells based on bare and composite membranes (Fig. 5). Also in this case, higher performance and OCV were recorded for the composite membrane-based MEA, probably due to a reduction of methanol cross-over.



**Figure 5.** Polarisation and power density curves for the cells equipped with bare SPSf and  $\text{SPSf-SiO}_2$  membranes at  $60^\circ\text{C}$  (1M MeOH, dry air, atmospheric pressure).

In order to quantify the methanol cross-over through the two membranes, measurements were carried out electrochemically using 1 M MeOH ( $3 \text{ ml min}^{-1}$ ) at anode side and He ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) at cathode. The methanol permeating the MEA is oxidized at cathode (Pt catalyst) generating a positive current, which reaches a plateau when all methanol is converted in  $\text{CO}_2$  in the steady state condition. The crossover experiments were carried out by linear sweep voltammetry (LSV) mode with a voltage scan rate of  $2 \text{ mVs}^{-1}$  and in the voltage range from 0 to 0.8 V.

Fig. 6 shows the MeOH crossover behaviour of pure SPSf and composite  $\text{SPSf-SiO}_2$  membranes at  $30^\circ\text{C}$  (a) and  $60^\circ\text{C}$  (b). The limiting current densities for these studied MEAs varied from  $11$  to  $14 \text{ mA cm}^{-2}$  at  $30^\circ\text{C}$  and  $25$  and  $30 \text{ mA cm}^{-2}$  at  $60^\circ\text{C}$ , which is a clear indication of the very low MeOH crossover of this type of polymer and its composite membranes even compared with thicker Nafion type-membranes (Nafion 115,  $\sim 100 \text{ mA cm}^{-2}$  at  $65^\circ\text{C}$ ). The composite  $\text{SPSf-SiO}_2$  membrane has the lowest crossover current compared to the bare membrane (SPSf). These differences are ascribed to the increasing diffusion path length of MeOH/ $\text{H}_2\text{O}$  clusters in the composite membranes, generally known as the tortuosity factor.



**Figure 6.** Comparison of methanol crossover current density for the SPSf and the composite SPSf-SiO<sub>2</sub> membrane obtained at 30 °C (a) and 60 °C (b) in a single cell.

## 2. Mixed functionality membranes based on PFSA polymer (sulfonic acid polymer-bound) and molecular bound phosphonic acids

Mixed functionality membranes containing sulfonic acid and phosphonic acid functional groups were supposed to be used for vapour-fed DMFC application at intermediate temperatures. FUMATECH has developed and characterised mixed functionality membranes based on PFSA polymer (sulfonic acid polymer-bound) and molecular bound phosphonic acid R-PO<sub>3</sub>H<sub>2</sub>. Samples of optimised membranes have been supplied to CNR-ITAE and CNRS for further ex-situ and in-situ characterisation.

During the first 12-month period of the DURAMET project, many modifications of mixed functionality membranes based on PFSA polymer (sulfonic acid polymer-bound) and molecular bound phosphonic acids R-PO<sub>3</sub>H<sub>2</sub> have been carried out. Main modifications are related to: