

Nanoscale membrane electrode assemblies based on porous anodic alumina for hydrogen–oxygen fuel cell

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Abstract In this paper, we demonstrate that nanoscale membrane electrode assemblies, functioning in a H₂/O₂ fuel cell, can be fabricated by impregnation of anodic alumina porous membranes with Nafion[®] and phosphotungstic acid. Porous anodic alumina is potentially a promising material for thin-film micro power sources because of its ability to be manipulated in micro-machining operations. Alumina membranes (Whatman, 50 μm thick, and pore diameters of 200 nm) impregnated with the proton conductor were characterized by means of scanning electron microscopy, X-ray diffraction, and thermal analysis. The electrochemical characterization of the membrane electrode assemblies was carried out by recording the polarization curves of a hydrogen–oxygen 5 cm² fuel cell working at low temperatures (25±80 °C) in humid atmosphere. Our assemblies realized with alumina membranes filled with phosphotungstic acid and Nafion[®] reach respectively the peak powers of 20 and 4 mW/cm² at room temperature using hydrogen and oxygen as fuel and oxidizer.

Keywords Porous anodic alumina · Hydrogen–oxygen fuel cell · Composite proton conductors

Abbreviations

MEA membrane electrode assembly
AAM anodic alumina membranes
PWA phosphotungstic acid

Introduction

In the literature, very few works are dedicated to the study of electrolytes that can find possible applications in micro-fuel cell [1]. At present, the membranes commonly used in practical fuel cells systems [2, 3] and micro-fuel cells [4–6] are based on perfluorosulfonic ionomer like Nafion[®] because of high proton conductivity, and good chemical and mechanical stability. However, they present real disadvantage in terms of costs, CO tolerance, and temperature of functioning [7] and, moreover, are not easily integrated with standard micro-fabrication techniques used in making micro fuel cell, owing to the possible volumetric changes with hydration level. Anodic alumina membranes (AAM) with highly ordered porous structure typically serve as ideal templates for the formation of nanostructured materials [8, 9], can be fabricated in a rather wide range of thickness (from a few microns to hundreds of microns) and porosity (from 10 to 30%) with a pore diameter ranging from 20 to 200 nm depending on the anodizing parameters [10, 11, and references therein], and exhibit good compatibility with conventional micro-fabrication techniques, having moreover, a good thermal and chemical resistance.

The advantages related to the use of porous alumina are: (1) building less expensive and thinner proton-conducting membranes to be used in thin-film fuel cell. For example, Nafion[®] membranes below 30 μm are unpractical because of mechanical instability and possible high crossover of the reagent gases [12]. Also, some solid proton conductors (like salts or solid acids) loose mechanical stability at low thickness; (2) the possibility to exploit the ability of AAMs to be manipulated in *micromachining* operations [13] proposing these membranes as novel candidate electrolytes for miniaturized fuel cell.

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In this work, we want to enrich the conviction expressed by testing the results shown in our previous paper [14] that AAM can find a novel application as an electrolyte supporting solid proton conductors in the field of fuel cell. The potential employ of AAMs in the field of fuel cell has been developed studying the behaviour of the membranes after filling with Nafion[®] and 12-phosphotungstic acid, which give high proton conductivity at low temperatures ($T_{\text{cell}}=25\div 80$ °C). The composite AAMs obtained were used to build thin-film fuel cell fed with humidified hydrogen/oxygen and the polarization characteristics studied at different cell temperatures.

Materials and methods

Preparation of AAMs filled with proton conductors

The AAMs employed in this work were commercial (Anodisc-47, Whatman, 0.2 μm) and home-prepared electrochemically grown membranes. The electrochemical growth was performed in H_3PO_4 0.4 M at 160 V. All the anodising parameters are well described in a previous paper [15]. The membranes were characterized by pore diameters around 200 nm, porosity of about 30% [estimated by scanning electron microscopy (SEM) analysis], and thickness of 50 μm . Alumina membranes were filled with $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (Sigma–Aldrich) by impregnation for 30 min of the AAM sample in saturated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution. The membranes were subsequently dried by exposure to air for 30 min and assembled with the electrodes. The pore filling with Nafion[®] was realized by the immersion of the AAM in a commercial Nafion[®] aqueous alcoholic solution (Liquion-1100 Nafion[®], 1100 EW Solution Ion Power) at different times.

Membranes characterization

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ as received and composite AAM/phosphotungstic acid (PWA) membranes were analysed by X-ray diffractometry performed by a Philips X-ray generator (model PW 1130) and a PW (model 1050) goniometry. Copper $K\alpha$ radiation and a scanning rate of 2θ 1°/min was used. The identification was performed according to the JCCD International Centre for Diffraction data.

The SEM analysis of AAM before and after the filling procedure was performed by using a Philips XL30 ESEM scanning electron microscope. Specimen surfaces were sputter coated with gold before SEM examination. The differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were realized on powdered $\text{H}_3\text{PW}_{12}\text{O}_{40}$ by using a Netzch STA/409/2 thermal analysis equipment at a heating rate of 5 °C min^{-1} .

Membrane electrode assembly preparation and fuel cell test

The composite membranes prepared were finally sandwiched between two carbon paper electrodes (Toray 40% wet-proofed E-Tek) covered with a mixture of Pt black/C black (30% Pt on Vulcan XC-72, E-Tek), stirred in *n*-butyl acetate for at least 3 h. The catalyst loading was 0.8 mg cm^{-2} of black platinum, an average value obtained by gravimetric measurements over numerous electrodes before and after catalysis. The active area was delimited by insulating silicon rubber having a square hole of 5 cm^2 so that the reported current density are referred to this active area of the membrane electrode assembly (MEA). The composite AAM were assembled without pressing to avoid any breaking of the sample.

The MEAs were then assembled in a single fuel cell apparatus (Electrochem) and fed with humidified nitrogen (99.95% purity, 2 bars) during the initial thermal heating. After reaching the chosen temperature, the cell was fed with humidified oxygen (99.5% purity, 3 bars) and hydrogen (99.5% purity, 1 bar), preheated at the working temperature. The humidification of the anode and cathode gases was done by passing the gases through stainless steel bottles containing double-distilled water. The temperature of the bottles was kept about 5 °C above the fuel cell temperature to avoid water condensation along the gas lines. The temperature of the fuel cell, as well as that of the humidifiers, was monitored by individual temperature controllers (Electrochem). The flow rates for the two gases were measured by two flowmeters (Matheson Instruments) placed before the heating bottles. The fuel cell was tested at different temperatures, depending on the membrane used. Polarization curves were obtained by using a PAR potentiostat 273A. An XY chart recorder (HP) was used to record the polarization curves.

After each test performed at the fuel cell, the MEAs were disassembled to verify the integrity of the composite membrane.

Results and discussion

AAMs filled with PWA

Considering that the proton conductivity of PWA depends on its hydration level, it is important to perform X-ray and DTA analysis. X-ray diffraction (XRD) patterns obtained on phosphotungstic acid as received and AAMs after impregnation with the saturated PWA solution and subsequent drying show that the PWA is in the hydrated form with 21 molecules of water at room temperature. The endothermic peaks from the DTA measurements reveal that the melting/decomposition temperature of the acid as

received is 89 °C, slightly lower than 95 °C, the value reported in the data sheet given by the producer. To avoid any decomposition, the experiments in the fuel cell were carried out at a temperature not higher than 60 °C.

The SEM studies performed on the surfaces and cross sections of the membranes after functionalization have given important information about the distribution of the acid inside the porous structure. In Fig. 1a, the micrographs of the surfaces of the composite PWA/AAM are reported, showing the presence of a uniform layer of PWA above the alumina support. Below this structure, the alumina pores and their filling level comes out, as shown in Fig. 1b. As better evidenced in Fig. 1c at higher magnification, the acid seems to cover about 40–50% of the total porosity.

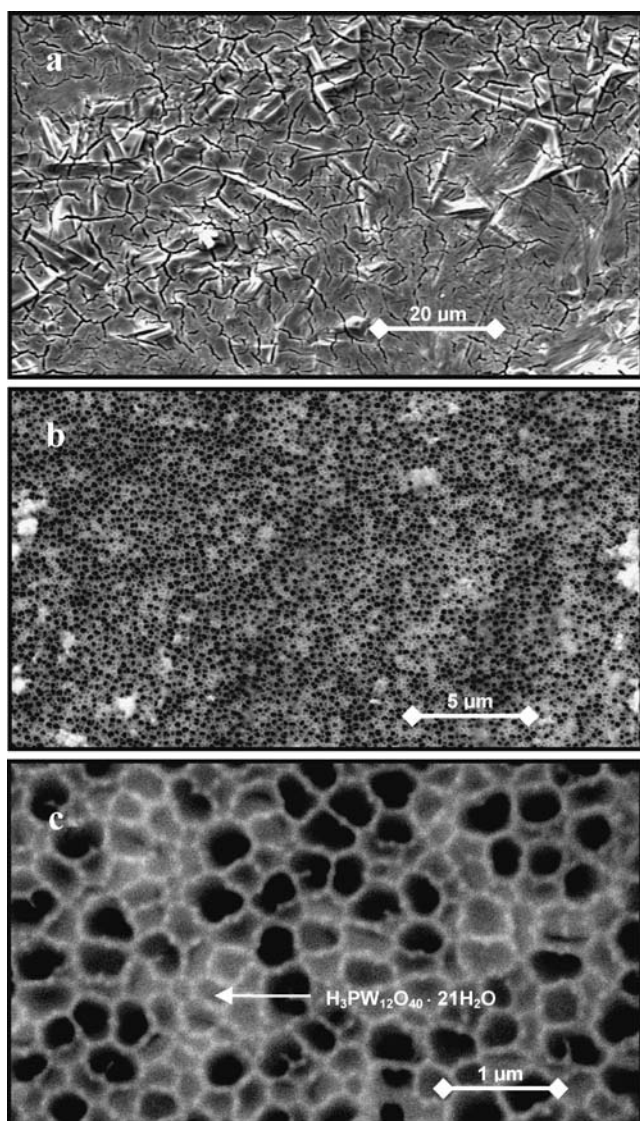


Fig. 1 a SEM morphology of the PWA layer on the surface of anodic alumina membranes after filling with PWA. b Filling grade of alumina pores under the PWA layer of a. c Detail at higher magnification evidencing the filling of the pores of b. Energy dispersive X-ray inside the filled pores confirm the presence of elements P, W, O

The cross-sections of the composite membranes show a partial filling of the pores (Fig. 2). The PWA inside the pores has a compact and not granular morphology, at variance of AAM/CsHSO₄ membranes that displayed a granular structure inside the pores, as shown in a previous work [14]. Compact morphologies with perfectly sealed pores are preferred because they favour the proton mobility and decrease the crossover of the gases.

In Fig. 2a, it is possible to see a discontinuity of the proton conductor along the pores. It is not clear at the moment if a detachment of the acid occurred during the section preparation performed by cutting the membranes into liquid nitrogen. However, we want to stress that an interesting

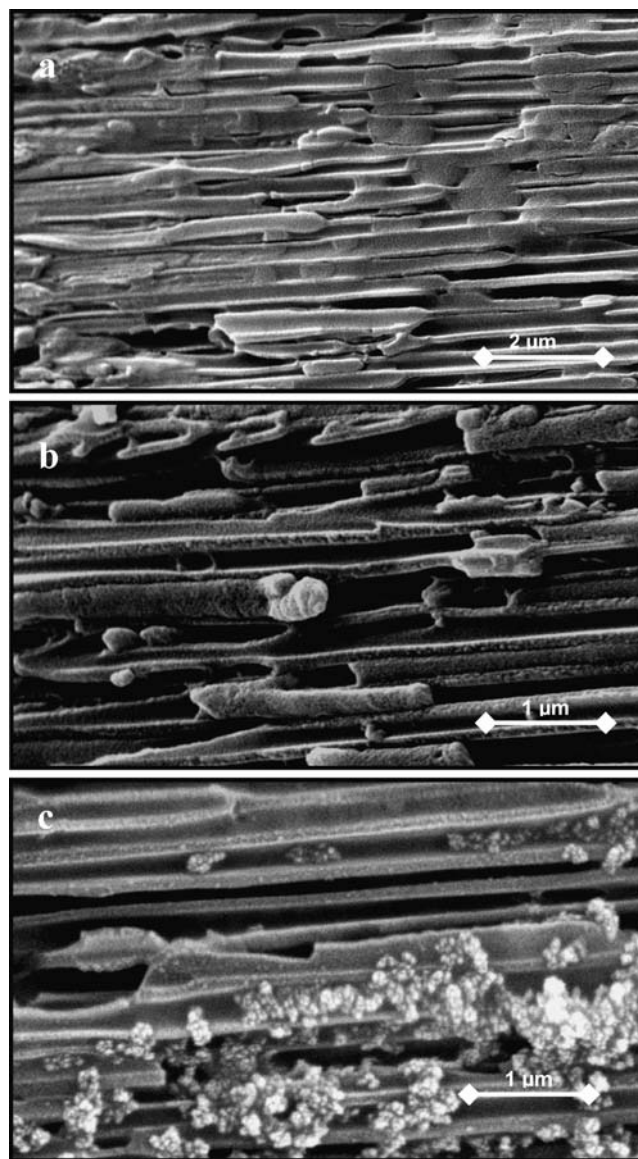


Fig. 2 a SEM morphology of the pore structure of the broken membranes for the anodic alumina membranes after filling with PWA. b Detail at higher magnification evidencing nanorods of PWA inside the pores. c Granular structures of PWA inside the pores

characteristic of the acid morphology is its ability to reproduce the cylindrical form of the pore, evidenced in Fig. 2b. Only in very few areas did the acid form granular-like structures (Fig. 2c). This property offers the possibility to use such a filling technique to also prepare PWA nanowires from an anodic alumina template.

Considering that the pore filling does not exceed the 40–50% of the total porosity, the cross-over of H_2/O_2 in the fuel cell is expected with the consequent decreasing of the open circuit voltage (OCV) value with respect to the thermodynamic one.

The OCV was monitored vs time after opening the reagent gases. Before recording the polarization curves of the fuel cell, we kept the cell in the open circuit condition until a quasi-steady state condition (15 min) was reached.

The fuel cell behaviour was studied at different temperatures (25, 40, 60 °C) using different samples of membranes.

In Fig. 3, we report the initial polarization and output power density curves for the single fuel cell representative of the temperature of 25 °C. These graphs represent our best results obtained with composite membrane AAM/PWA. As reported in the figure, a value of short circuit current density around 60 mA cm^{-2} was measured for different assemblies with a peak power density of about 20 mW cm^{-2} at 25 °C.

The influence of temperature on the behaviour of AAM/PWA composite membranes is reported in Fig. 4. By increasing the cell temperature, we assist to a rapid reduction of the short circuit current density and open circuit potential. It seems that, at higher temperature, the increased solubility of PWA in the water produced at the cathodic side, as well as acid decomposition due to local

increasing of the temperature, counterbalance the positive effect of an increased proton conductivity of the PWA with the humidity.

The stability of the cell was studied for each cell temperature by performing different cycles of polarization curves. In Fig. 5, it is possible to observe a large hysteresis by cycling the cell from OCV to the short circuit potential. By continuously cycling the cell, a fast degradation process of cell performance occurs (see Fig. 5, at 25 °C). This degradation process affected very much the short circuit current density value, which, for this cell, changes from the initial 60 mA cm^{-2} to 20 mA cm^{-2} after the third cycle and to 10 mA cm^{-2} after the ninth cycle. It was often observed in literature [16 and references therein] that this behaviour is related to the solubility of the acid in the cathodic region. In Fig. 6, the effect of cycling at the different cell temperature is shown. It can be observed that at the temperature of 60 °C, the cycling effect is less evident, probably because, at the first polarization curve, the short current density is lower, and lower is the water produced at the cathode. The OCV was much less affected by cycling, ranging from 0.984 to 0.86 V after the sixth cycle for a cell temperature of 25 °C.

AAMs filled with Nafion®

Different techniques were adopted to functionalize the AAMs with Nafion®, but the immersion of the specimens into the solution for long times (50 h) at room temperature gives better results at the fuel cell station. Filling the pores with the commercial Nafion® aqueous alcoholic solution is rather difficult because, during the evaporation of the solvent, the solution become more and more viscous.

Fig. 3 Polarization curves (E = cell voltage) and power density under linear potential scan (5 mV s^{-1}) for a 5 cm^2 humidified H_2/O_2 fuel cell at the cell and gas temperature of 25 °C working with AAM/PWA membranes

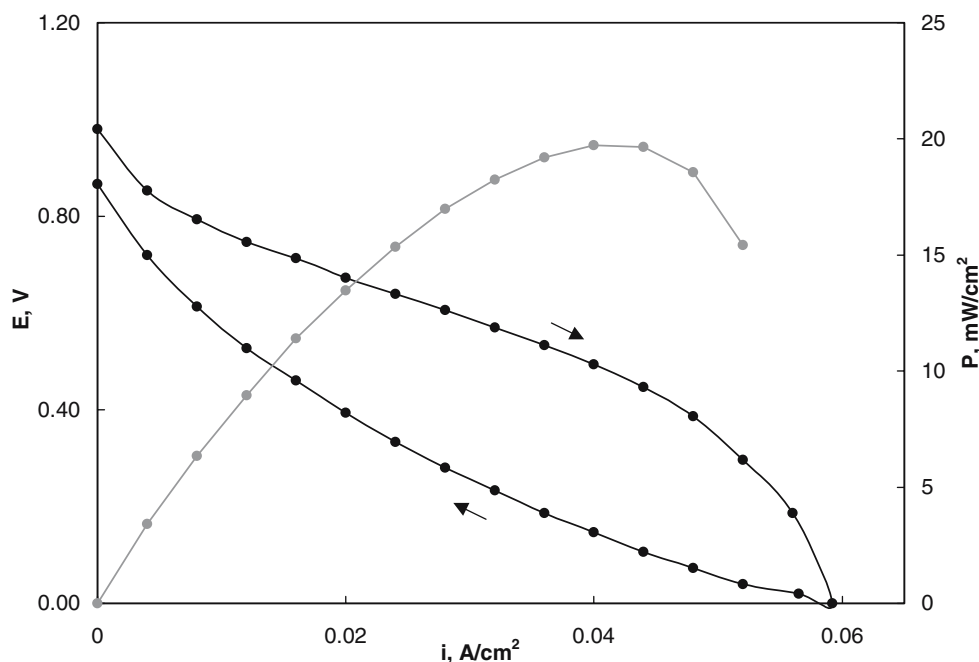
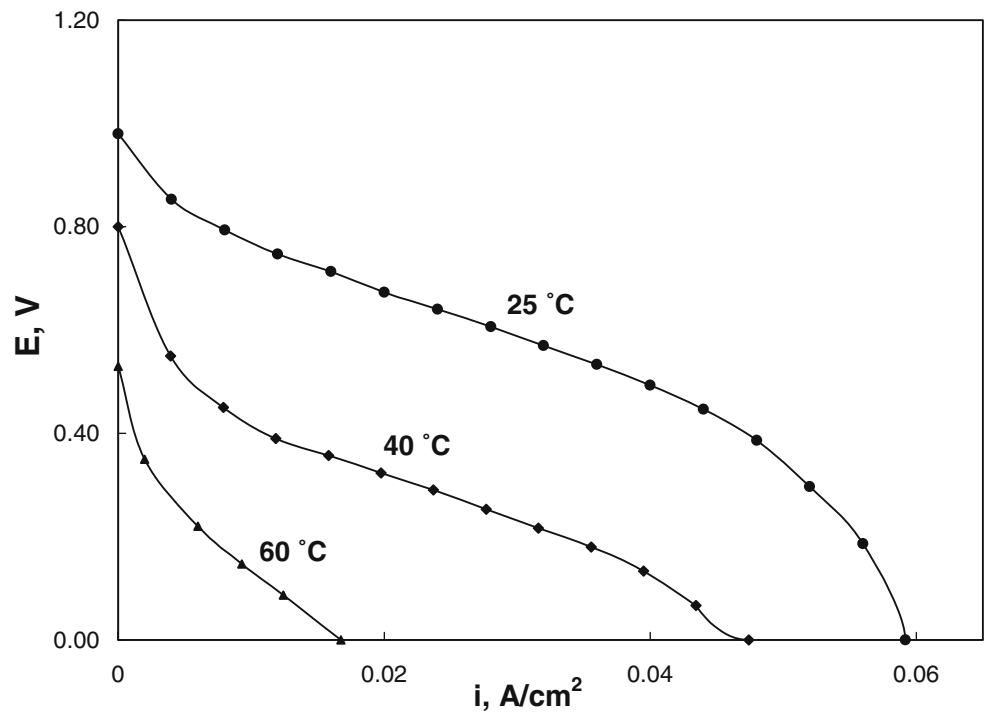


Fig. 4 Influence of cell temperature on the polarization curves (E = cell voltage) recorded under linear potential scan (5 mV s^{-1}) for a 5 cm^2 humidified H_2/O_2 fuel cell working with AAM/PWA membranes



The SEM analysis shows that the polymer does not cover all the surface of the alumina membranes (Fig. 7a and b). Anyway, the cross-section of the membranes after functionalization for 50 h shows that the pore filling is good in proximity of the surfaces and poor in the centre of the samples (Fig. 8a and b).

The SEM micrographs of the cross-sections of the AAMs immersed for different times show that the porous structure is completely empty at 15 min, and the pores start to fill for the immersion time in the order of hours. The

SEM analysis of the pore-filling grade is in agreement with the results obtained at the fuel cell station for a different time of immersion. As reported in Fig. 9, the short circuit current density increases with the immersion time of the membranes. In Fig. 10, we report the best polarization curves relative to AAM filled with Nafion[®] by immersion in a commercial Nafion[®] solution for 50 h and cell temperature of 25 °C with humid atmosphere. Such assemblies give an OCV of 0.85 V and short current density of about 16 mA cm^{-2} with a peak power of 4 mW cm^{-2} .

Fig. 5 Polarization cycles (E = cell voltage) relative to a 5 cm^2 humidified H_2/O_2 fuel cell working with AAM/PWA membranes at a cell temperature of 25 °C

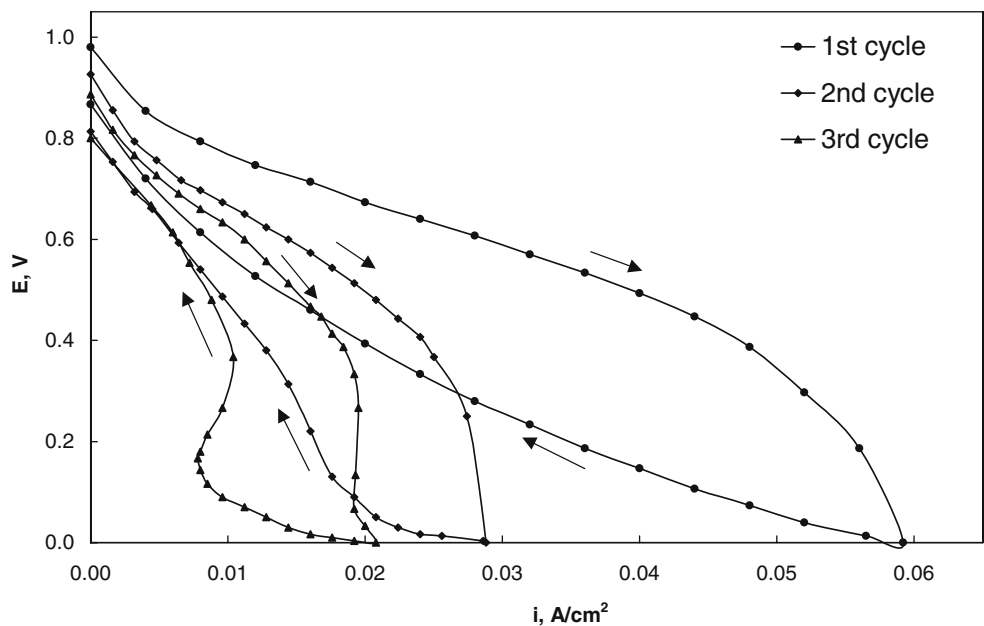
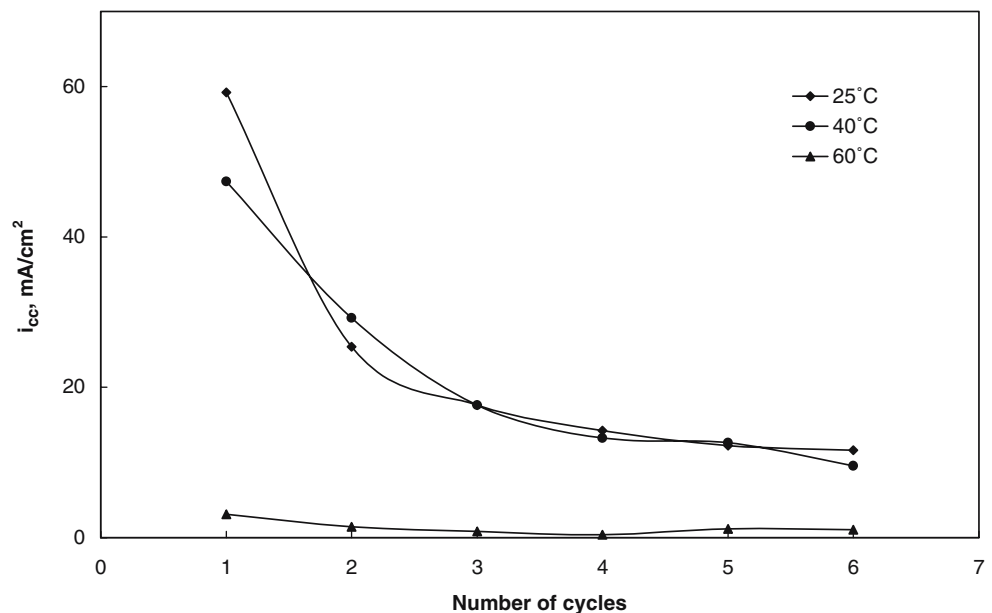


Fig. 6 Short circuit current density (i_{cc}) reported as function of the number of polarization cycles for a 5 cm^2 humidified H_2/O_2 fuel cell at different cell and gas temperatures working with AAM/PWA membranes



The cell seems to be rather stable in terms of power generated at voltage efficiency higher than 50%, as shown in the polarization cycles of Fig. 11. The short circuit current density decreases from 16 to 12 mA cm^{-2} , probably because of the irregular distribution of the polymer into the porous matrix revealed by SEM, which can slow down the

water transport through the membrane and cause a decrease of the proton conductivity of the electrolyte during the functioning of the cell. The negative effect of the non-uniform pore filling on the fuel cell performance emerges also by increasing the cell and the gas temperature. These

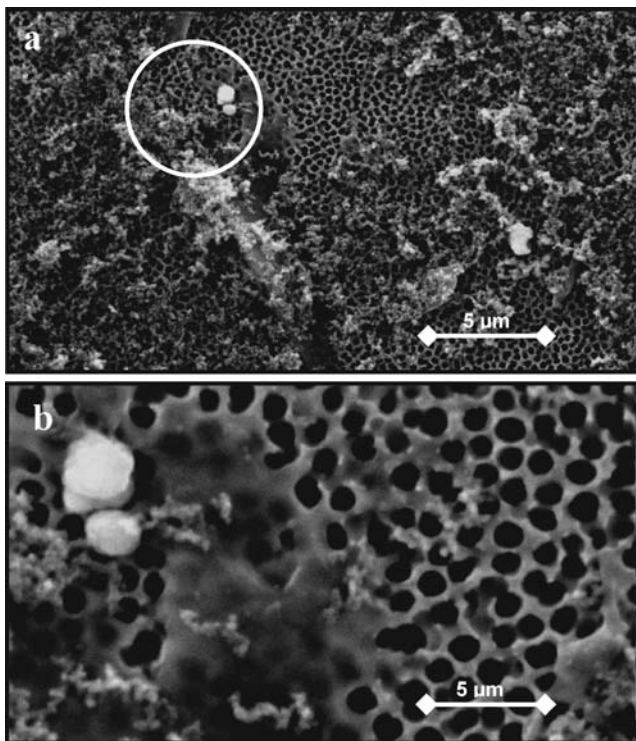


Fig. 7 **a** SEM morphology of the surface of anodic alumina membranes after filling with Nafion® for 50 h. **b** Detail at higher magnification evidencing the distribution of Nafion® on the alumina surface

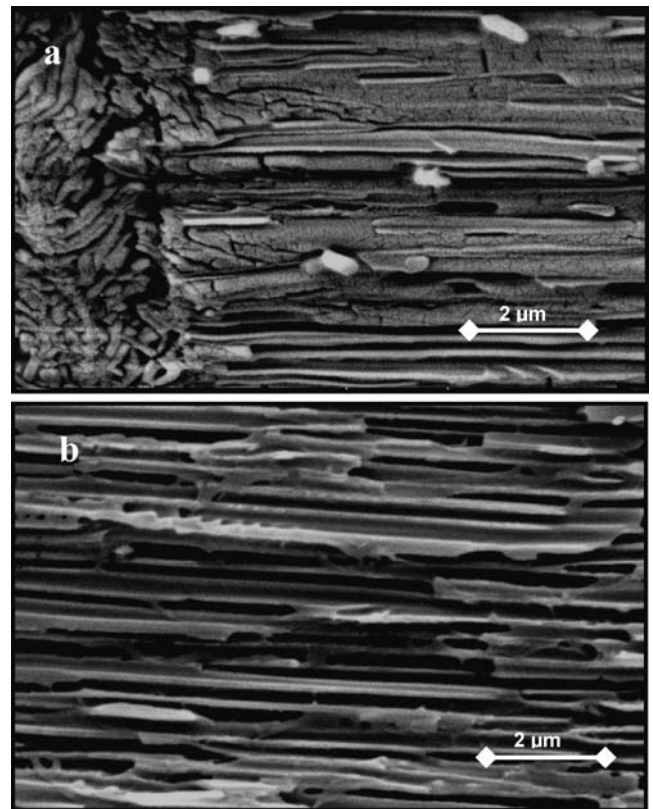
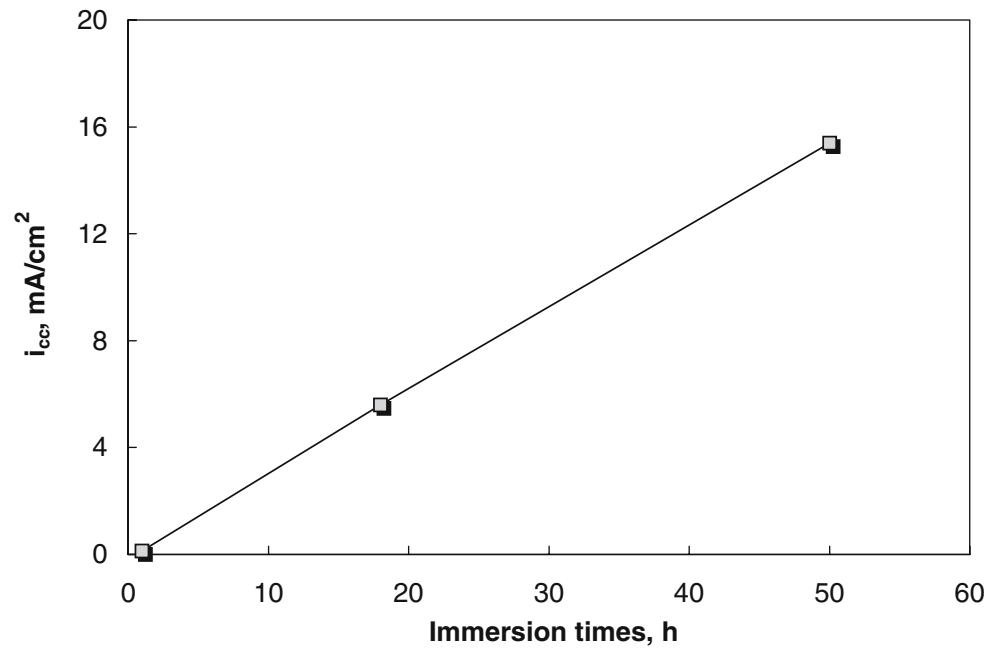


Fig. 8 SEM morphology of the pore structure of the broken membranes for the anodic alumina membranes after filling with Nafion® for 50 h. **a** Border area, **b** central area

Fig. 9 Short circuit current density (i_{cc}) reported as function of the immersion times for a 5 cm² humidified H₂/O₂ fuel cell at the cell and gas temperature of 25 °C working with AAM/Nafion[®] membranes



experiments were performed on different specimens of the composite membrane AAM/Nafion[®]. The short circuit current densities relative to this kind of assemblies at different temperatures and polarization cycles are illustrated in Fig. 12. A drastic worsening of the cell performance occurs from 25 to 40 °C, whereas a slow further decrease of the cell performance is observed going from 60 to 80 °C.

This finding can be attributed to the prevalence of dehydration phenomena of Nafion[®] rods with increasing cell and gas temperature. A dehydration of Nafion[®] with a corresponding falling down of the proton conductivity can arise from a slow diffusion of the water molecules inside

the Nafion[®] rods restricted into the pores of AAM. Moreover, decreasing the gas and cell temperature, the fuel cell performance does not recover its initial value. This indicates that the AAM/Nafion[®] properties change irreversibly with the increasing temperature. At the moment, we cannot exclude that other phenomena due to the irregularity of the pore filling and local increase of temperature are responsible of such behavior.

The preliminary results of this work seem to indicate that the swelling phenomena of Nafion[®] rods are negligible.

The results obtained in our experimental conditions (short times of functioning of about 10³ s) suggest a good

Fig. 10 Polarization curves (E = cell voltage) and power density under linear potential scan (5 mV s⁻¹) for a 5 cm² humidified H₂/O₂ fuel cell at the cell and gas temperature of 25 °C working with AAM/Nafion[®] membranes

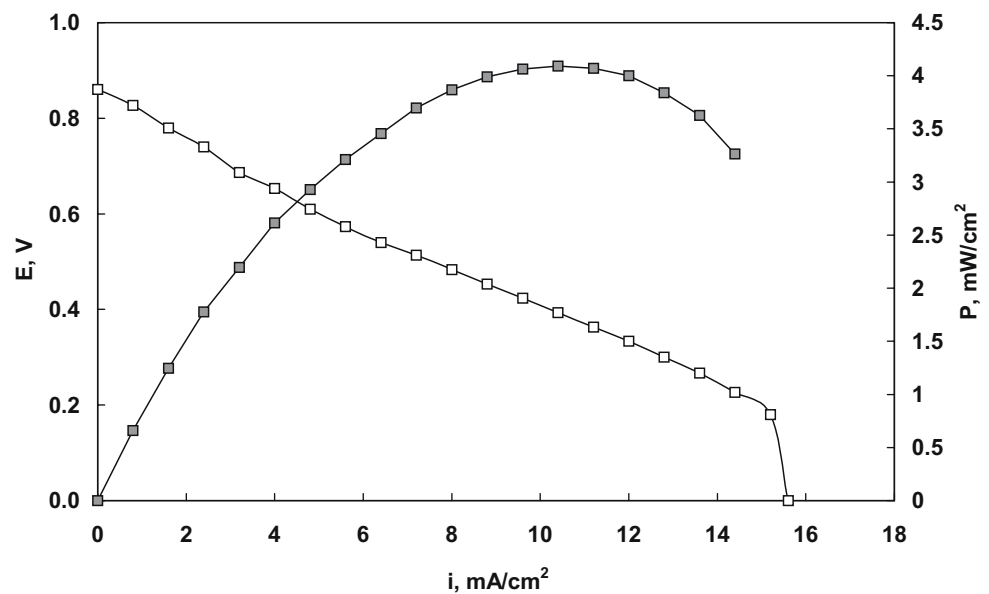
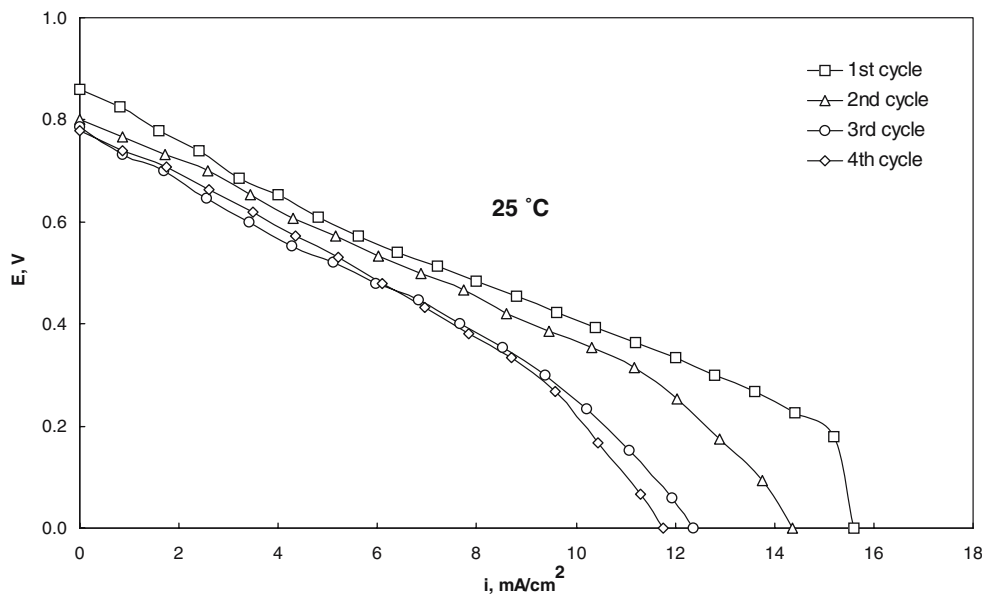


Fig. 11 Polarization cycles ($E =$ cell voltage) obtained under linear potential scan (5 mV s^{-1}) for a 5 cm^2 humidified H_2/O_2 fuel cell at the cell and gas temperature of 25°C working with AAM/Nafion[®] membranes



chemical stability of alumina membranes in the presence of the acidic species PWA and Nafion[®]. Further investigations are necessary to reach final conclusions on both important issues related to the long-term stability of a micro-fuel cell.

On the basis of such results, new filling techniques are under study to improve the behaviour of investigated systems.

Conclusions

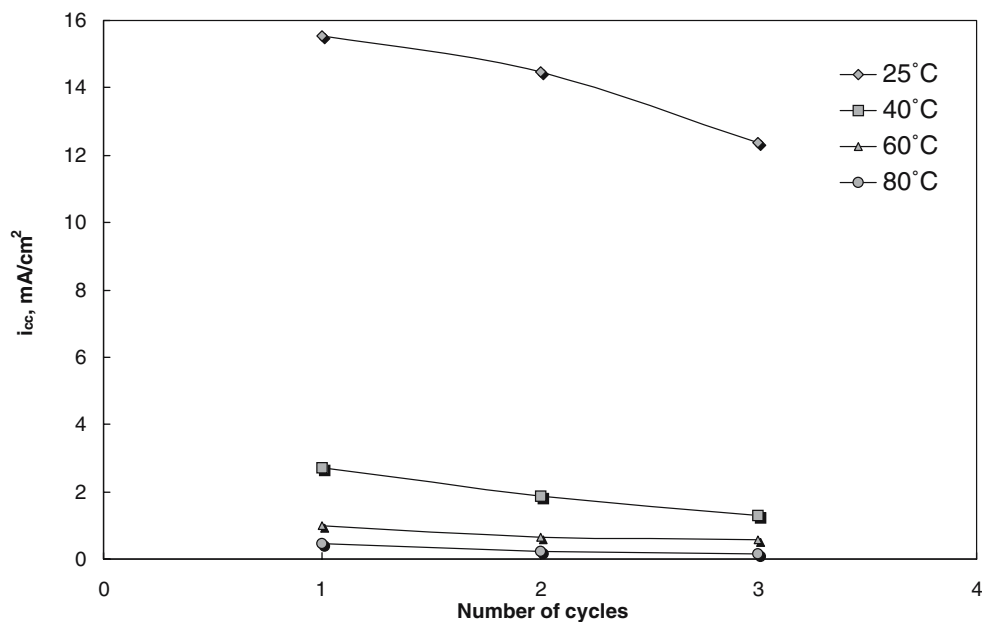
In a previous paper [14], we have shown for the first time that thin-film alumina membranes can be used as templates for high-temperature ionic conductor membranes (CsHSO_4). In this work, we succeeded to build MEAs based on thin

porous anodic alumina filled with phosphotungstic acid and Nafion[®] proton conductors able to produce peak powers of 20 and 4 mW/cm^2 , respectively, at room temperature in a hydrogen/oxygen fuel cell.

Further work is now in progress to have a better understanding of the poor stability of the membranes, for example, by performing in situ impedance measurements of the MEAs and to improve the pore filling of the AAMs by using different techniques.

However, we expect that the results obtained in this paper with different fillers of AAMs will encourage future studies of these composite membranes in fuel cell devices, in particular, miniaturized systems where materials compatible with standard micro-fabrication techniques are required.

Fig. 12 Short circuit current density (i_{cc}) reported as function of the number of polarization cycles for a 5 cm^2 humidified H_2/O_2 fuel cell at different cell and gas temperatures working with AAM/Nafion[®] membranes



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