

## Aging studies of nanostructured inorganic membrane for fuel cell applications

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**Abstract**—This paper presents structural and electrochemical characterizations of nanoporous alumina membranes used as template for ionic conductor membrane allowing to fabricate different assemblies to be used in different types of fuel cell. The alumina membrane produced via a double anodising process. This typical procedure of membrane preparation is based on a two-step self-organized anodising of aluminium carried out at the temperature of about 5 °C. In this study, alumina membranes were fabricated in 0.3 M oxalic acid under the anodising potential range of 45 V. Ageing behaviour has been investigated in potassium sulphate solution, using electrochemical impedance spectroscopy (EIS). It was found that the lifetime of the membrane depends on its time of immersion which drives the formation of hydration products. The analysis was completed with the aid of the SEM and X-ray diffraction analysis. The SEM image of alumina membrane shows the array of circular pores is randomly distributed on the surface. The resulting array of nanopores have a pore diameter strongly depends on duration of anodising. The XRD shown that non-crystalline phase was obtained (amorphous alumina).

**Keywords**-Alumina membrane; Double anodising; fuel cells.

### I. INTRODUCTION

Due to the high cost of polymeric membranes and poisoning effects of catalyst in presence of hydrocarbon fuel there is a large research effort aimed to exploit fuel cell assembly based on lower cost membranes and electrocatalytic materials [1]. In this frame different strategies have been suggested based on the fabrication of membranes, which could operate at higher temperatures where poisoning effects of catalysts are minimized. This choice would exclude the actual polymeric membranes employed in PEMFC which lose their stability and good performance as proton conductor owing to dehydration effects.

In this frame we have suggested [2] the use of porous anodized alumina membranes as template for the fabrication, by filling the pores of alumina membranes with a proton conductor, of inorganic membranes to use in fuel cell at temperatures higher than usual PEMFC. Porous alumina membranes can be electrochemically grown in a rather wide range of thickness (from few micron to hundreds micron) and porosity (from 10% to 30%) with pores diameter ranging from 20 to 200 nm depending on anodising parameters [3], [4].

By taking into account the good thermal stability of alumina membranes in a rather wide range of temperatures our approach will make possible to prepare different MEA for different temperatures provided that a suitable electrolyte and pore filling procedure is devised.

The application of procedure the two anodising steps gives a self-organized porous structure on anodised aluminium, this technique become promising for preparing such ordered porous structures due to its low cost and relative easy use. The procedure involves two separate anodising processes. The first anodising process consists of a short period of anodising forming the disordered porous structure. After the removal of the oxide, an array of highly ordered dimples is formed on aluminium. These dimples act as initiation sites for growing highly ordered porous structure [5].

In this work we present the preliminary results of a more systematic research aimed to exploit the possible use of porous alumina membranes as support for preparation of membrane electrode assembly (MEA) to be used in hydrogen –oxygen fuel cell, operating in a range of temperature between 423 and 443 K.

### II. EXPERIMENTAL METHODE

#### A. Materials

Rectangular coupons (50 × 30 × 3 mm) of a cast Al–Mg alloy were used as the substrate for elaboration of alumina membrane. The composition of this alloy (wt %) was 2.75 % Mg, 0.1 % Mn, 0.4 % Si, 0.1% Cu, 0.4% Fe, 0.25% Zn, 0.25% Cr other, and Al balance.

#### B. Anodising procedure

Prior to anodising, aluminium sheet was degreased in acetone, and electropolished at a constant current of 0.5 A cm<sup>-2</sup> during 1 min at 10 °C in an electrolyte containing perchloric acid and ethanol in a ratio of 1:4 by volume and anodised at 5 °C in oxalic acid solution 0.3 M at a constant potential of 45 V during 4 h and 2 h for the first and the second samples respectively. Then the anodic oxide layer, part of which was disordered, was removed in a phosphoric acid. Next, the plate was anodised again during 8h for the first sample and 4 h for the second sample in the same conditions of the first anodising step. After the second anodising step, the remaining aluminium was removed in a

saturated solution of  $\text{CuCl}_2$ . Subsequently, the transparent AAO was etched by a 0.3 mol/L phosphoric acid solution. Finally the resulting AAO films were cleaned thoroughly with deionised water and dried at  $50^\circ\text{C}$ .

Samples treated were then subjected to analyse by the X-Ray diffractometer, D 8-ADVANCE model of BRUKER-AXS (University of Jijel), followed the observations by the scanning electron microscope (SEM of LACM-DTI Laboratory in Reims University, French).

The ageing behaviour of alumina membrane was studied under the potentiostatic control of a Radiometer Analytical type Voltalab 40 PGZ301 potentiostat / galvanostat controlled by a computer using a software Voltmaster 4 for treatment and data acquisition (Laboratory LIME University of Jijel), using the conventional three-electrode configuration. Electrochemical impedance measurement was carried out at room temperature by applying AC amplitude of 10 mV on open-circuit potential over the frequency range 100 kHz to 1 MHz, with five points per decade. The ageing behaviour of alumina membrane was studied by immersing of the samples in an unstirred and aerated 0.2 M potassium sulphate solution at different periods of immersion: 30 min, 2, 4 and 24 h, respectively. A three-electrode cell setup with a saturated calomel electrode (SCE) as reference electrode and platinum plate as counter electrode was used. The exposed surface area of samples was  $1\text{ cm}^2$ . Impedance diagrams were recorded for the anodised specimens, immediately after anodising and after different ageing.

### III. RESULTS AND DISCUSSION

#### A. Structure of alumina membrane

The XRD patterns for the alumina membrane generated by a double anodising for the two specimens are shown in Fig. 1. It exhibits multiple intense peaks that are clearly distinguishable. All of the diffraction peaks can be perfectly indexed to the face-centred cubic Al, and the peak positions are in good agreement with the known data (JCPDS 85-1327). It appears that the structure of the alumina membrane is composed of non-crystalline, amorphous alumina was obtained, as it can be seen in Figure 1(a-b) in the  $2\theta$  angle ranging from  $22^\circ$  to  $82^\circ$ ; and by both samples there is a preferential aluminium orientation in the planes [111], [200], [220], [311], [222], [101]; which indicates that the phase transformation from Al to  $\text{Al}_2\text{O}_3$  occurs more easily, which is similar to the structure of the films obtained from other acidic electrolytes [6], [7].

Comparing the XRD spectra of the two specimens is found that: in the case of the first specimen, there are two peaks which locate in positions of ( $2\theta = 16.652^\circ, 25.478^\circ$  respectively) corresponding to Mg particles, where it considered as impurities on the surface of the alumina membrane, and the peak positions are in good agreement with the known data (JCPDS 01-1141).

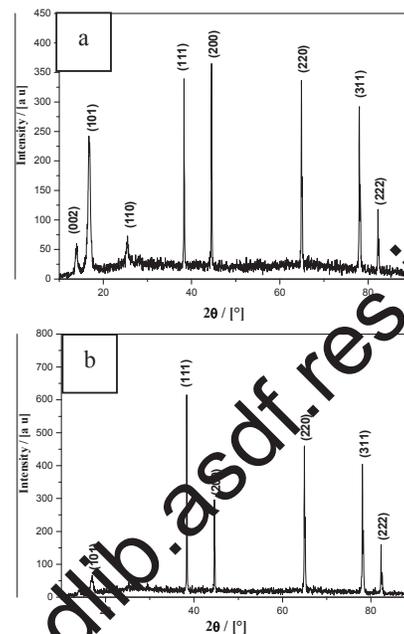


Figure 1. XRD pattern of alumina membrane obtained by a double anodising process. Anodising is carried out in a 0.3 M oxalic acid, under voltage 15 V at temperature  $5^\circ\text{C}$  during 4 h, 2 h for the first anodising step and 8 h, 4 h for the second anodising step for specimens a and b, respectively.

#### B. Scanning electron microscopy

The surface texture of the membranes was examined by SEM. Figure 2 shows the surface morphology of the alumina membranes formed at  $5^\circ\text{C}$  in oxalic acid 0.3 M solution. It can be seen that circular pores are randomly distributed on the surface. However, because of the different growth velocity, the depth of some pores is different. Some has imbedded into the bottom of aluminium, while, some has just formed, such as those darkish pores in Figure 2. Remarkable defects (fissures and cavities) are observed on the microphotographs obtained that is due to the roughness of the surface prior to anodising process. It may indicate a heterogeneous distribution of the pore.

Comparing the two membranes obtained by the different anodising time it is remarkable that the sample anodised during 4 hours and 8 hours for the first and the second anodising step, respectively has a porosity greater than that obtained during 2h, 4h the first and second anodised, respectively this may be explained by the first sample has enough time to the magnification of the membrane cell and consequences the wall of the pore, pore diameter and the distance interpore.

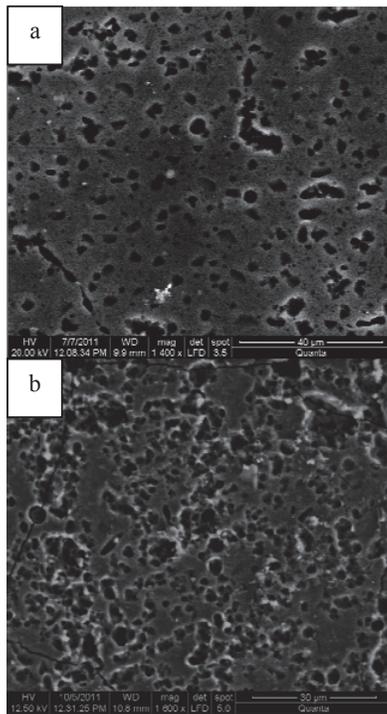


Figure 2. SEM surface morphology of alumina membrane obtained by a double anodising process. Anodising is carried out in a 0.3 M oxalic acid under voltage 45 V at temperature 5 ° C during 4 h, 2 h for the first step of anodising and 8h, 4 h for the second step of anodising for sample a and b, respectively.

C. Impedance characteristics of alumina membrane

Figure 3(a - b) shows the impedance plots obtained by impedance spectroscopy measurements with membranes in contact with K<sub>2</sub>SO<sub>4</sub> (0.2M) solution at different time of immersion. Similar curves were obtained in the different time of immersion. The analysis of impedance data was carried out by complex plane method, which involves plotting the impedance imaginary part (-Z<sub>im</sub>) versus the real part (Z<sub>real</sub>) as in Figure 3(a,b).

Figure 3 reports the evolution of impedance diagrams vs. immersion time in a K<sub>2</sub>SO<sub>4</sub> solution; in general, the existence of two capacitive arcs located one at the high frequency and another at the low frequency, who attribute the first capacitive arc (high -frequency) to the electrolyte solution and the second capacitive arc ( low- frequency) to the alumina membrane . The electrolyte solution could not be detected due to a high conductivity of the electrolytic solution.

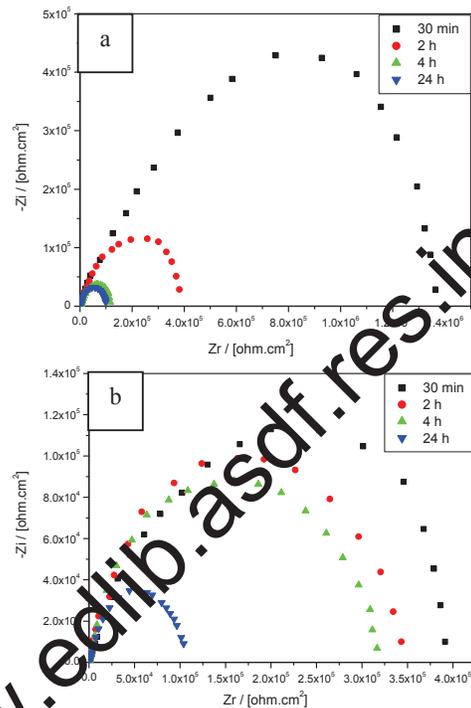


Figure 3. EIS analysis of alumina membrane at different immersion times (black) 30 min; (red) 2 h; (green) 4 h; (blue) 24 h in 0.2 M K<sub>2</sub>SO<sub>4</sub> solution at 25 ° C. Anodising is carried out in a 0.3 M oxalic acid under voltage 45 V at temperature 5 ° C during 4 h, 2 h for the first anodising step and 8h, 4 h for the second anodising step for specimens a and b, respectively.

Complex systems may present different relaxation times and the resulting plot is a depressed semi-circle, such as shown in Figure 4. In these cases, a non-ideal capacitor, known as a constant phase element (CPE) is considered; the CPE admittance is expressed by [8]

$$Q(\omega) = Y_0 (j\omega)^n \tag{1}$$

Where Y<sub>0</sub> and n are two empirical parameters (0 ≤ n ≤ 1).

The electrochemical behaviour of alumina membrane inside the electrolyte solution can be represented by the equivalent circuit shown in Figure 4. The experimental data for the whole range of frequency were fitted to a circuit which consists of two elements in series, namely the membrane and the electrolyte solution as shown in Figure 4: the membrane contribution is represented by a parallel (R<sub>m</sub> Q<sub>m</sub>) circuit, while the electrolyte part is a parallel (R<sub>e</sub>C<sub>e</sub>) one. These results allow us to determine the resistance and capacitance values of the electrolyte and the membrane by means of a non-linear program [9].

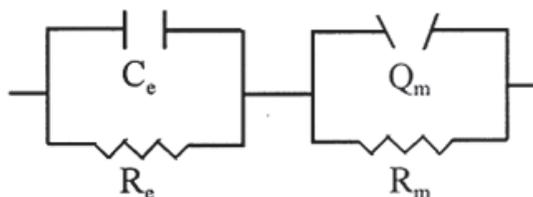


Figure 4. Circuit equivalent of alumina membrane.

We are particularly interested in low-frequency resistance corresponding to the intersection with the real axis at low-frequency. Comparison of low-frequency resistance can be estimated qualitatively which system is more resistant over time. The variations of resistance ( $R_m$ ) deduced from the Nyquist diagrams for the two specimens are gathered in the Figure 5:

The values of resistance ( $R_m$ ) have a primary interest in this comparative study because more the value of ( $R_m$ ), better the alumina membrane is, more resistant to hydration ( $Al(OH)_3$ ), (ageing). However, the membrane resistance values are strongly dependent on the insertion and penetration of  $K_2SO_4$  solution inside the pores, which is mainly attributed to the effect of the electrolyte taken up by the membrane [10].

From Figure 5, it can be seen that the resistance of alumina membrane ( $R_m$ ) obviously decreases with immersion time. In initial stage, then  $R_m$  value strongly decreases with immersion time. This behaviour indicates that the alumina membrane become more resistant in initial stage and better in the case of specimen a.

The interpretation of the  $R_m$  resistance variation according to time can be explained by: At the beginning of immersion, the  $K_2SO_4$  solution has not yet reached all area of wall of the pore; it is still constituted of alumina, more or less contaminated by the electrolyte anodizing anions. Of this fact the progress of the  $K_2SO_4$  solution through the pores up to the all of the well pore has the effect of decreasing rapidly  $R_m$  by hydration of this membrane. The progressive formation of hydration products ( $Al(OH)_3$ ) in the shape of the gel leads a slow decreasing of  $R_m$  then stabilization of this last one to a minimal value. According to Pourbaix [11], the hydroxide-like gel will evaluate to a final state which is hydrogylite  $Al_2O_3 \cdot 3H_2O$ , crystallizing in the monoclinic system. This evolution of the aluminium hydroxide is known as ageing.

#### IV. CONCLUSIONS

Thin film alumina membranes can be used as template for ionic conductor membrane allowing fabricating different assemblies to be used in different types of fuel cell. The easy preparation of alumina membranes also in large area, their low production cost and wide range of thermal stability could make them attractive for more economically viable

fuel cell by allowing increasing the working temperature of the fuel cell and the use of less expensive catalyst.

In this study, we have addressed the preparation of alumina membranes by a double anodising approach. The alumina membranes are obtained with a random distribution of pores. The duration of anodising has an effect on the porosity and cell dimensions of alumina membrane, more duration of anodising is along more the cell membrane grows and takes large dimensions as diameter pore and inter pore distance.

Characterization by XRD allowed us to achieve results on the composition of the films prepared by both techniques is to provide information on their structures; alumina membranes are composed of amorphous alumina.

Ageing behaviour of alumina membrane is observed in  $K_2SO_4$  solutions. The membrane resistance decrease with immersion time because the hydration of the alumina membrane. This behaviour indicates that the alumina membrane become more resistant in initial stage and better. Then as the immersion time further increases,  $R_m$  values slightly decrease.

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