

## Evaluation of a ZrO<sub>2</sub> Composite Membrane in PEM Fuel Cells Operating at High Temperature and Low Relative Humidity

C. Guzman<sup>1</sup>, A. Alvarez<sup>1</sup>, Luis A. Godinez<sup>1</sup>, O.E. Herrera<sup>2</sup>, W. Merida<sup>2</sup>, J. Ledesma-Garcia<sup>3</sup> and L.G. Arriaga<sup>1,\*</sup>

<sup>1</sup>Centro de Investigación y Desarrollo Tecnológico en Electroquímica S.C., C.P. 76703, Querétaro, México.

<sup>2</sup>Clean Energy Research Centre, University of British Columbia, Vancouver, B.C., Canada, V6T1Z4.

<sup>3</sup>División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, C.P. 76010, Querétaro, México.

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**Abstract:** A composite membrane containing ZrO<sub>2</sub> was tested under simulated and real fuel cell operations. To simulate the fuel cell environment, the composite membrane was tested on a gated cell at low relative humidity (10 %) and high temperature (100 °C). The water flux on the composite membrane was found to be higher than a commercial membrane (Nafion 115), suggesting that under these conditions water molecules are entrapped into the membrane matrix via dipole – dipole interactions. Under real operation conditions, ZrO<sub>2</sub> membranes showed better performance at high temperature (140 °C) and low relative humidity (22.9 %) than the commercial Nafion Membrane. The performance results confirmed that composite membranes retain water and help to maintain the membrane hydration. The aging cycle (1750 cycles) showed that the composite membrane under study is stable under extreme operation conditions (22.9% RH and 120 °C).

**Keywords:** High temperatures, Low relative humidity, ZrO<sub>2</sub> Composite membrane, Water flux, High Temperature Fuel cell.

### 1. INTRODUCTION

Proton Exchange Fuel Cells (PEMFC's) are known to provide an environmentally friendly and sustainable technology to generate electrical power [1]. recent improvements on this technology have been pursued to elevate the performance efficiency and operation time life [2] these efforts have mainly focused on the reduction of platinum loading on the electrodes [3-8], the incorporation of new materials to bipolar plates, new geometric designs [9-13] and the creation and use of new membranes[14-17].

Recently, High Temperature PEMFC's (HT – PEMFC's) have received particular attention due to the enhanced electrode kinetics, increased CO tolerance and simplified water management that these operation conditions imply. Unfortunately, Nafion and other perfluorosulfonic acid membranes (PFSA) are characterized by a decreased proton conductivity at high temperatures (above 100 °C) due to dehydration which, in addition, causes shrinkage and increases the contact resistance between the membrane and the electrode [18].

For these reasons, one important goal in FC research is to create new membranes capable of working at high temperatures and low

relative humidity conditions as compared to those suited for typical PEMFC's. In this context, the inclusion of inorganic materials into the Nafion matrix such as Al<sub>2</sub>O<sub>3</sub> [19], SiO<sub>2</sub> [19, 20], ZrO<sub>2</sub> [20, 21] and TiO<sub>2</sub> [21, 22], are employed to improve the mechanical properties of the membrane and confer a new arrangement that reduces the permeation of the reactant gases and the water molecules which are strongly coordinated to the dipoles of the inorganic material, thus enhancing the membrane's hydration.

In this way, the aim of the present work was to calculate the water vapor flux (J) and evaluate the fuel cell performance using a composite membrane (based on ZrO<sub>2</sub>) under different operating conditions (temperature and relative humidity). In order to properly assess the composite membrane performance effect, the results were compared with those obtained using a commercial Nafion membrane (Nafion 115).

### 2. EXPERIMENTAL

#### 2.1. Synthesis of the inorganic fillers

Zirconium Dioxide was synthesized via the sol-gel method under acidic conditions. In this way the TEOS (Tetraethyl orthosilicate) precursor and zirconium (IV) propoxide (70 wt. % solution in 1-propanol) using HNO<sub>3</sub> as catalyst, were employed. The proper

\*To whom correspondence should be addressed: Email: larriaga@cideteq.mx

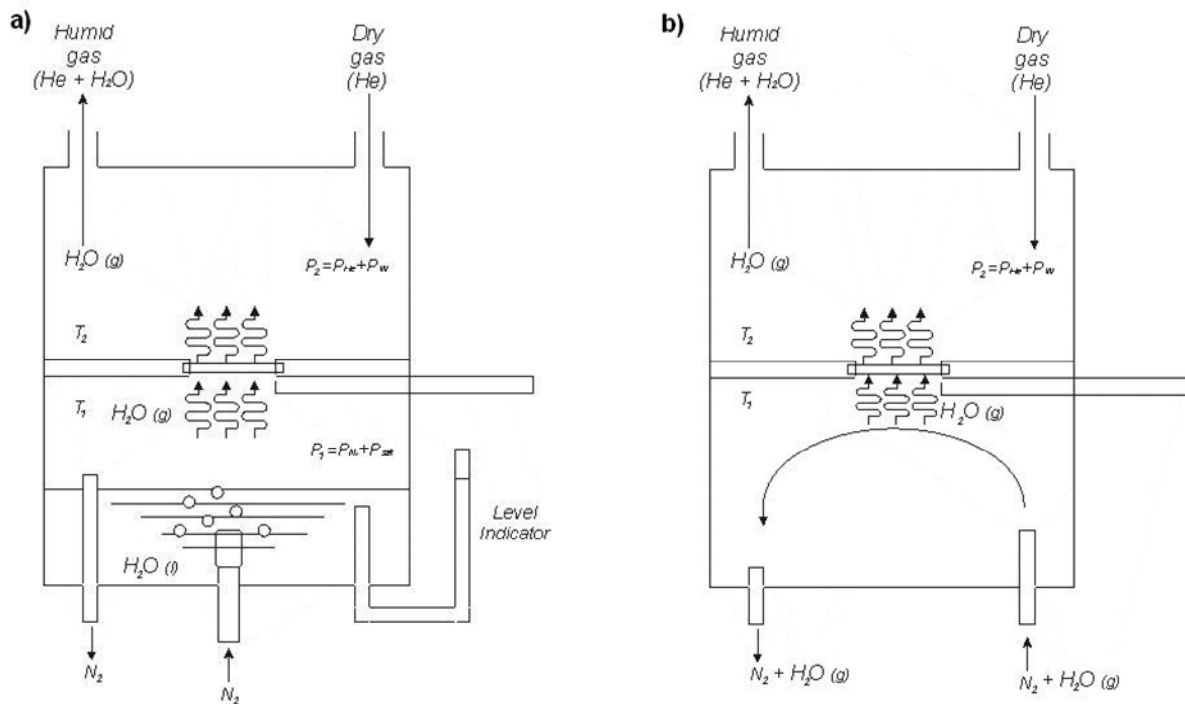


Figure 1. Complete experimental setup for water transport including the gate's activation mechanism, temperature and pressure systems for a) 100% RH and b) 10 – 50 % RH.

Alcohol/alkoxide molar ratio was kept under stirring conditions for 20 minutes. Water/acid molar ratio was stirring for 5 minutes. Finally, both solutions were mixed under stirring for 1h at 40 ° C. This colloidal solution was kept at room temperature until solid formation took place. The resulting solids were thermally treated using a tubular furnace (Barnstead Thermolyne) at 150°C for 2 h in order to remove residual alcohol and obtain the oxides of silicon and zirconium [23-25].

## 2.2. Membrane Preparation

Composite Nafion membranes containing 5% Nafion solution and 3 wt. % of ZrO<sub>2</sub> were prepared using a combination of recast and heat treatment procedures already published [26]. Subsequent chemical treatments included 3% H<sub>2</sub>O<sub>2</sub> solution followed by 0.5M H<sub>2</sub>SO<sub>4</sub> solution with intermediate boiling steps using DI water [26-29]. Finally the membranes were stored in DI water for at least 24 h prior to use. The morphology of the composite membranes was observed by Scanning Electron Microscopy (SEM) in a JEOL JSM-6060 LV microscope and the surface mapping by energy dispersive X-ray spectroscopy (EDXS).

## 2.3. Water transport experiments

The experimental set-ups shown in Figures 1a and b were used for water transport measurements. Cylindrical chambers with volumes of 125 cm<sup>3</sup> were separated by 2 cm<sup>2</sup> of the composite membrane. Dry helium gas was supplied to one chamber and worked as a carrier gas for water permeation. Dry nitrogen gas was bubbled through the other compartment in order to enhance water vaporization into the wet chamber (Figure 1a) and to maintain a constant the

relative humidity. In order to change the relative humidity (Figure 1b) nitrogen gas was introduced using a Green light Power Station (Green light power technologies FCATS – S 800). Further details of the measurement process can be found in previous reports [30, 31].

## 2.4. Fuel cell performance

Catalyst layer was deposited on our home made composite membranes by Ion Power Inc. with a platinum loading of 0.3 mg Pt/C 30% E – Tek. A carbon cloth with Teflon was used as gas diffusion layers. The FC performance tests were carried out in a single 5 cm<sup>2</sup> (Electrochem) cell connected to an Electrochem Compucell fuel cell test system. The experimental conditions are shown on Table 1.

A cyclic current aging was also performed. Each current aging cycle is illustrated in Figure 2 and it is composed by 3 current steps (high, medium and low current) which were registered by recording

Table 1. Experimental conditions of the fuel cell system.

Cell Temperature (°C)	Relative Humidity (% RH)	Gases Stoichiometry	
		H <sub>2</sub>	O <sub>2</sub>
80	100	1.5	2
	22.9	1.5	2
100	22.9	1.5	2
120	22.9	1.5	2
140	22.9	1.5	2

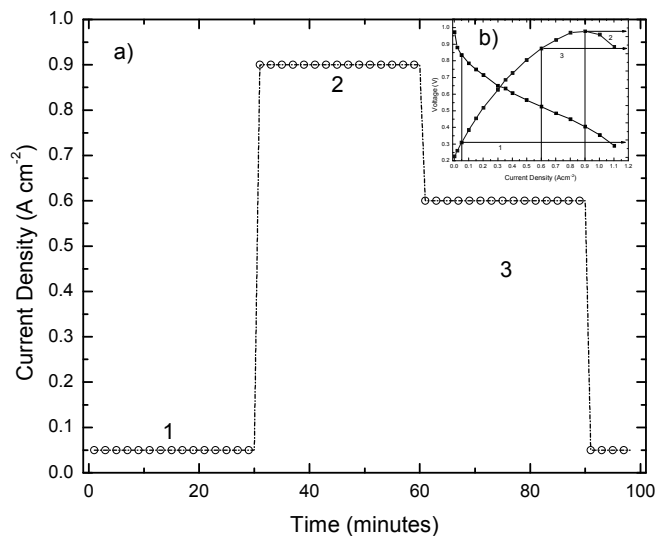


Figure 2. a) Schematic Complete Current aging cycle and b) Low, medium and High current points.

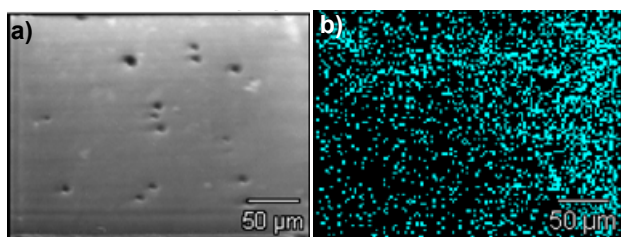


Figure 3. a) SEM image of the  $ZrO_2$  membrane and b) its corresponding zirconium mapping.

the voltage as a function of the cycle number. The degradation test was carried at  $T_{cell} = 120\text{ }^\circ\text{C}$  and 22.99 % of relative humidity.

### 3. RESULTS AND DISCUSSION

#### 3.1. Water Transport Experiments

Figure 3 shows the SEM image and their corresponding zirconium mapping. The SEM image (Figure 3 a) of the  $ZrO_2$  and its corresponding mapping image (Figure 3 b) indicates a good dispersion and homogeneity of the inorganic filler in the membrane. The figure 4 shows the water transport results. The water flux data showed good reproducibility with a maximum standard error of  $\pm 5 \cdot 10^{-4}\text{ mol m}^{-2}\text{ s}^{-1}$ . As expected, at lower helium flow rates, water flux increases reaching a maximum; above which a decreasing trend is observed. This behavior suggests that, under these conditions, the water content of the membrane on the dry side is low, resulting in a hydrophobic layer on the membrane that reduces the water flux [30-33].

Water transport experiments at 100% of RH are shown on Figure 4 a in which steady state water flux ( $J$ ) values are plotted vs helium flow rates ( $u$ ). In the whole range of temperatures surveyed (80, 90 and 100  $^\circ\text{C}$ ), the commercial Nafion – 115 membrane showed a higher water flux when compared to that corresponding to the zir-

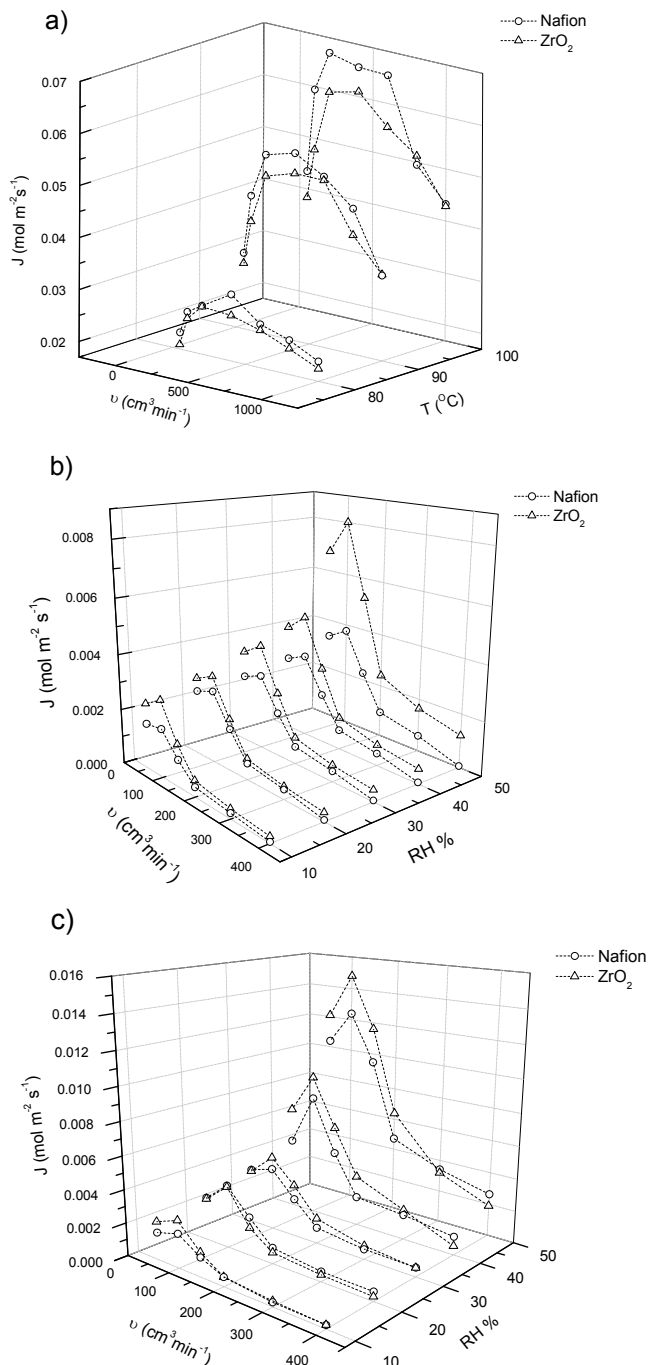


Figure 4. Steady – state Water flux at a) 100% RH, b) low RH at 80  $^\circ\text{C}$  and c) low RH at 100  $^\circ\text{C}$ .

conium composite membrane; this decrement of water flux in composite membrane is related by the water retention into the membrane matrix. When a lower relative humidity is employed (Figures 4 b and c), water transport on the composite membrane increases (at 80 and 100  $^\circ\text{C}$ ). This behavior is due to the water content into the composite membrane is higher than the Nafion membrane, improving the water transport into the composite membrane matrix.

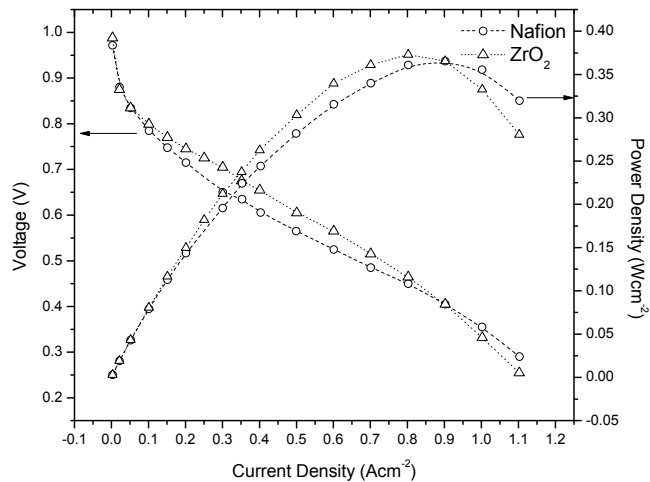


Figure 5. Polarization curves of the composite membranes at  $T_{\text{cell}} = 80\text{ }^{\circ}\text{C}$  and 100% of relative humidity.

The principal water movement into the membranes takes place via sulfonic acid groups and hydrogen bonds. At controlled relative humidity of 100 % and temperature of 80 and 100 °C, the water has free movement through the Nafion matrix as reflected by the high water flux. The composite membrane on the other hand, entraps water molecules due to dipole – dipole interactions as reflected by substantially lower values of water flux. At low relative humidity, the water amount into the Nafion matrix is low and the water transport is due to percolation, this structure is formed of spherical ionic domains connected with cylinders of water dispersed in the polymer matrix. When the composite membrane is a different situation; the inserted nanoparticle species maintains the hydration of the membrane and acts to crosslink the Nafion polymer chains, obtaining a structural inversion corresponding to a connected network of polymer aggregates, which results in the performance improved of  $\text{ZrO}_2$  membranes during high-temperature PEMFC operation [31, 34].

### 3.2. Fuel Cell Evaluation

Figure 5 shows the polarization curves of the  $\text{ZrO}_2$  composite membrane as compared to those obtained using a commercial membrane (Nafion E – Tek 0.3 mg Pt/C) at 80 °C and 100% of relative humidity. The composite membrane is characterized by a better performance than that of the commercial Nafion membrane. The same behavior is observed when the relative humidity decreases (22.9 % and cell temperature of 80 °C), suggesting that the composite membrane structure and water permeation are independent of the relative humidity (Figure 6 a). When the operating temperature of the fuel cell increases to 100 °C, and the same relative humidity is maintained, the same performance than that obtained at 80 °C was observed. This behavior was also obtained at 120 and 140 °C. On Table 2 the parameters of the  $\text{ZrO}_2$  composite membrane at different temperatures are presented. Between 80 and 100 °C on the other hand, the performance observed was similar, suggesting that Nafion as well as the composite membrane under study have an optimal working environment ( $\sigma \geq 10^{-2}\text{ Scm}^{-1}$  and fully hydrated). At 120 °C (Figure 6 c) this situation changes since

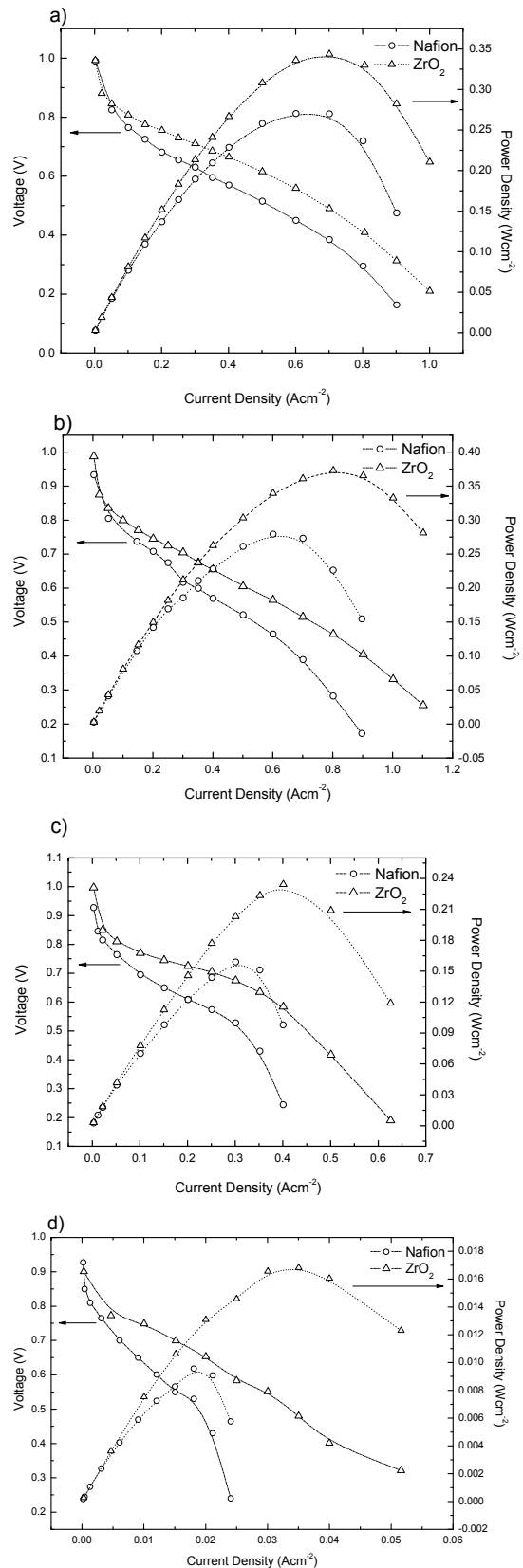


Figure 6. Polarization Curves of the composite membranes at 22.9 % of relative humidity and temperature of a) 80, b) 100, c) 120, d) 140 °C.

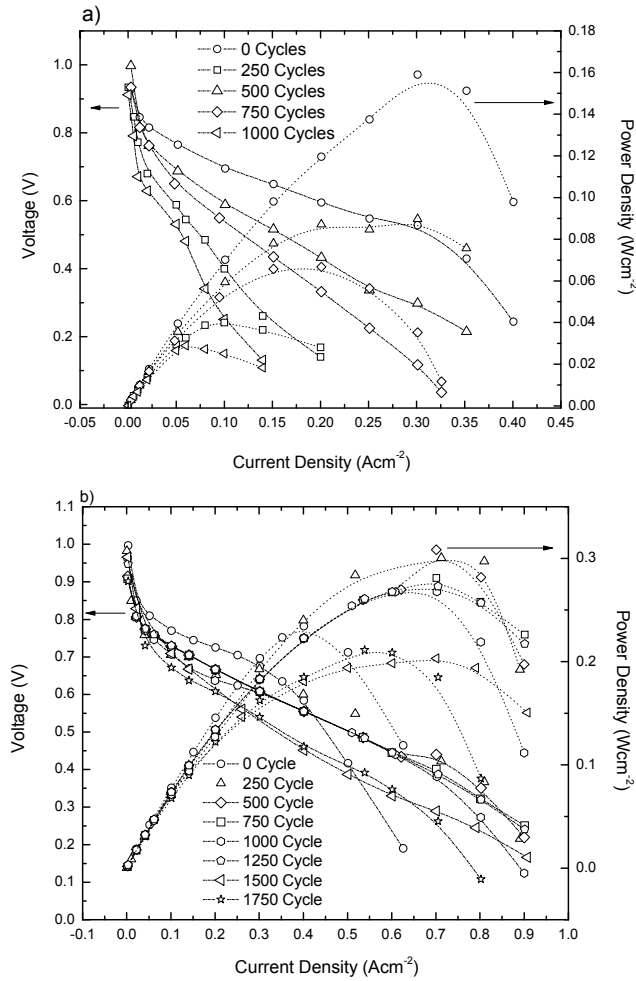


Figure 7. Polarization curves every 250 cycles at  $T_{cell} = 120\text{ }^{\circ}\text{C}$  and 22.9% of relative humidity for a) Nafion and b) ZrO<sub>2</sub>.

Nafion has a power loss of 50% as compared to that obtained at 100 °C, for the composite (ZrO<sub>2</sub>) membrane that has a power decrement of 40%. These FC performance experiments are consistent with the results of water flux and support the interpretation of modifying inorganic filler that entraps water and maintains the water content within the membrane matrix.

Although at temperatures of 140 °C the Nafion and the composite membrane's performance fell dramatically, the composite membrane maintains a better performance than that of the Nafion membrane.

Current cyclic aging experiments were performed at 120 °C and 22.9 % of relative humidity. The performance of Nafion membrane decreases with the number of cycles (Figure 7 a), resulting in a final power density of .029 W cm<sup>-2</sup>; which is about six times less than the corresponding initial value. For the ZrO<sub>2</sub> composite membrane on the other hand (Figure 7 b), the power density increases as the number of cycles increases, reaching a power density of 0.28 W cm<sup>-2</sup>, (the FC performance fell to 0.2 W cm<sup>-2</sup>). In this way, The ZrO<sub>2</sub> composite membrane maintained the power density and worked 750 cycles more than the Nafion membrane. On Table 3 the parameters obtained from the aging cycle experiments are shown.

This improvement on the fuel cell performance of the composite membrane is due to the addition of the inorganic oxide and the Nafion matrix provided better water hydration into the membrane at reduced relative humidity; ZrO<sub>2</sub> membrane were less susceptible to high temperature damage due to membrane dehydration. Dehydration of Nafion at elevated temperatures leads to the destruction of the pore structure and decreasing the proton conductivity. The ZrO<sub>2</sub> prevented these temperature structural changes maintaining the proton conductivity [2].

The experimental results described in this work showed that the composite membrane based on ZrO<sub>2</sub> modification improves its water retention into the polymeric matrix and the performance of a

Table 2. Parameters obtained from the composite membrane at different temperatures.

Membrane	R (Ω cm <sup>2</sup> )				E <sub>OCV</sub> (V)				W <sub>Max</sub> (W cm <sup>-2</sup> )			
Temperature (°C)	80	100	120	140	80	100	120	140	80	100	120	140
Nafion	0.36	0.355	0.49	1.42	0.99	0.93	0.93	0.92	0.27	0.28	0.15	0.009
ZrO <sub>2</sub>	0.31	0.36	0.41	1.32	0.99	0.98	0.99	0.9	0.34	0.37	0.21	0.016

Table 3. Parameters obtained from the composite membrane from the aging cycle.

Cycle	Membrane			Nafion			ZrO <sub>2</sub>		
	R	OCV	W <sub>Max</sub>	R	OCV	W <sub>Max</sub>	R	OCV	W <sub>Max</sub>
0	0.384	0.928	0.16	0.315	0.997	0.23			
250	0.412	0.997	0.09	0.415	0.982	0.29			
500	0.466	0.934	0.067	0.53	0.914	0.28			
750	0.626	0.934	0.04	0.53	0.917	0.28			
1000	1.241	0.912	0.029	0.52	0.966	0.28			
1250				0.49	0.947	0.27			
1500				0.55	0.964	0.27			
1750				0.91	0.901	0.21			

Cell Resistance (R) = Ω cm<sup>2</sup>; Open Circuit Voltage (OCV) = V; Power Density (W<sub>Max</sub>) = W cm<sup>-2</sup>

fuel cell at low relative humidity (22.9%) and high temperature (120 °C) operating conditions. Therefore, these kinds of membranes constitute a promising alternative for HT - PEMFC's applications.

#### 4. CONCLUSIONS

In this study the performance as well as the water flux through a ZrO<sub>2</sub> composite membrane for its potential application in High temperature Fuel cells operating under low water content was investigated. The experimental results showed that the composite membranes entrapped water into the polymeric matrix as revealed by low values of water flux (at 100 % of RH). , In this way, at low RH conditions the composite membrane shows the maximum water transport value as compared to the commercial Nafion membrane. Fuel cell performance results confirm that the composite membrane retains water as reflected by a high performance in the whole range of tested temperatures. The aging cycle also showed that the composite membrane constitute an attractive approach for FC working in environments characterized by a low relative humidity (22.99 %) and High temperature (120 °C).

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