Development of a Dynamic Hydrogen Electrode coupled to Proton Exchange Membrane Fuel Cell

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This work reports the results of using a Dynamic Hydrogen Electrode (DHE) as a reference electrode for performance measurements in an Proton Exchange Membrane Fuel Cell (PEMFC) operated at high temperature conditions and low relative humidity (T = 120 ºC y HR = 23 %). The performance of PEMFC was measured by using a composite membrane (SBA−16) and the results compared to those obtained with a commercial Nafion-115 membrane. The reference electrode was made using a platinum black deposit on the platinum wire surface. The DHE was introduced in the PEMFC close to the cathode electrode and it was stable under fuel cell operation. The kinetic parameters of anode and cathode reactions were estimated in a separated way.

1. INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFC's) are well known as an environmentally friendly and sustainable technology to generate electrical power [1-5]. Recent efforts on this technology have been pursed to elevate the performance efficiency and operation time life [6] of these systems. The principal objectives are mainly focused on the incorporation of new materials to bipolar plates, the use of new geometric cell designs [7-11], the creation and use of new membranes [12-15]

and the reduction of platinum loading on the electrodes [16-21]. Despite all the efforts behind of this technology, fuel cells will only reach consumers after their performance and the understanding of all the phenomena mechanisms inside of the fuel cell [22].

Several techniques has been applied in order to obtain that knowledge, these techniques includes the visualization across of transparent fuel cells [23-26], coupling neutron imaging , X- ray [27-29] and magnetic resonance imaging [30-33]. The disadvantage of use these techniques is the need for cell modifications [34]. A less invasive method correspond the sensing electrodes use; this kind of technology can provide more information about the electrochemical reactions inside of the fuel cell. The inconvenient of sensors using is the major modifications made in the cell for sensing electrode coupling [35, 36]. In order to minimize this cell alteration, is necessary to build small electrodes like the DHE, these kind of electrode has a smaller size than the conventional electrodes, and has excellent voltage stability under controlled temperature and pressure conditions [3, 34, 37, 38].

Another issue is the field of fuel cells turns around of the water management. Poor water quantity in the system decreases the proton conductivity and increases the cell resistance and the cell voltage decreases. Unnecessary water amounts in the cathode causes flooding; the water blocks the supply gases in the porous media resulting in mass – transport limitations, increasing the cathode overvoltage, and in considerable power losses in the PEMFC [39-41]. One alternative is the operation of PEMFC's at high temperatures (above 100 °C). At this condition the water management can be simplified when a single phase of water is considered and the reaction gases can be introduced with lows amounts of water [42-44]. More advantages of work at high temperature and low relative humidity are (i) the improvement on the kinetics of the oxygen reduction reaction [44]; (ii) higher tolerance to CO [45, 46]; (iii) the omission of cooling systems [44]; and (iv) waste heat can be recovered [40]. In order to work at high temperature, Nafion membrane must be modified. One effective procedure consist in the incorporation of inorganic materials as Al_2O_3 [47], SiO_2 [48], ZrO_2 [49] and TiO_2 [50]. These compounds can improve the water retention as well as the mechanical properties of the membrane [47, 50, 51]; inhibits the permeation of the reactant gases [50], and water molecules are strongly coordinated to the dipoles or ions in the inorganic material, enhancing the membrane hydration [52].

The aim of the present work is the incorporation of a Dynamic Hydrogen Electrode (DHE) on a Nafion – 115 and SBA –16 membranes into a PEM fuel cell and to evaluate the stability of the electrode under high temperature (140 ºC) and low relative humidity (22.9 %) conditions.

2. EXPERIMENTAL

2.1 Construction of Dynamic Hydrogen Electrode (DHE)

The DHE (Figure 1) consists of a platinum wire with 1 mm of diameter; the expose area was $3.14 \times 10^{-7} m^2$, the wire was cleaned and then platinized following the procedure previously described [1, 2, 3, 34]. In order to obtain a platinum black deposit on the platinum wire surface the platinum wire was pressed between two membranes (Nafion – 115 or SBA -16) at 30 bars and 120 °C during 10 s.

On each membrane was deposited a square of $1.6 \times 10^{-5} m^2$ or area with 1 mg of Pt – Vulcan (ETEK 10% w/w). Then the electrode was placed on a chamber inside of the Fuel Cell hardware. Hydrogen was fed inside the chamber at 100 cm^3 min^{-1} and 25 °C, the hydrogen and the voltage was monitored using the MTS – 150 Electrochem System.
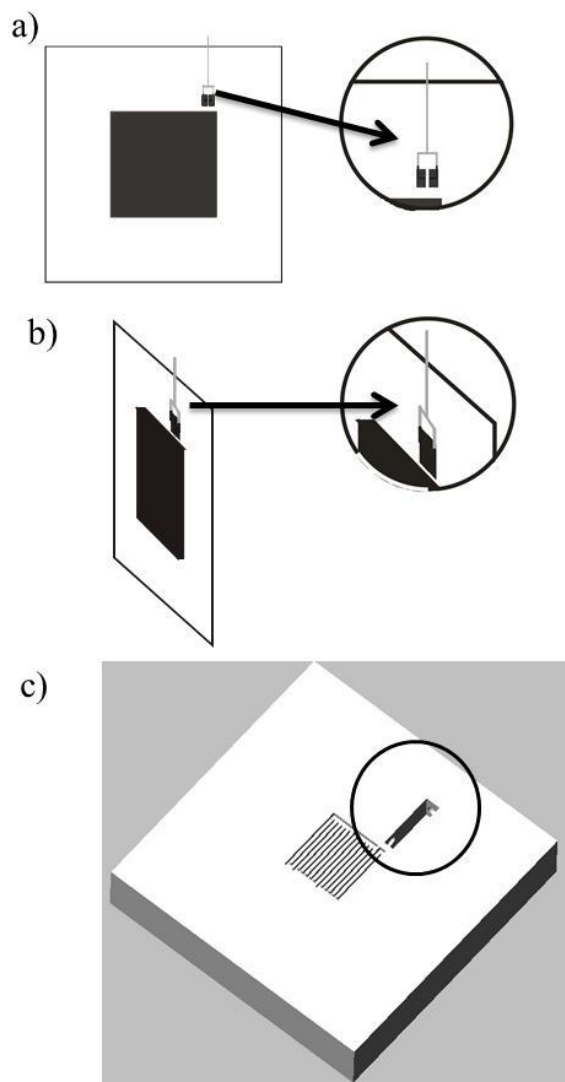
Figure 1.Schematic view of the DHE on the membrane (a and b) and placement on the bipolar plate (c).

2.2 Membrane Electrodes Fuel Cell Operation

The electrocatalytic deposit was made through a spray method by Ion Power Inc. with a platinum loading of 0.3 mg Pt/C 30% (ETek) on the composite membranes. A high-temperature carbon cloth with Teflon was used as gas diffusion layers (Ion Power Inc.). The performance test was carried out on a single 5 cm^2 cell (Electrochem) connected to an Autolab 302 coupled to Booster

Autolab 20 A. Electrochem Compucell Power Station was employed to manipulate the flow, humidity and temperature of gases. The experimental conditions are shown in Table 1.

**Table 1**. Experimental conditions of the fuel cell system.

Cell Temperature (°C)	Back Pressure (psi)	Relative Humidity (% RH)	Gases Stoichiometry	
			H_2	O_2
80	30	100	1.5	2
	30	22.9	1.5	2
100	30	22.9	1.5	2
120	30	22.9	1.5	2
140	30	22.9	1.5	2

3. RESULTS AND DISSCUSION

Figure 2 shows the operation and stability of the DHE with a Nafion membrane. The DHE has good stability with respect of the time. The cathode and anode voltages are stable with the period measured and with the current density applied. Same behavior is observed with the use of SBA – 16 membrane.

Polarization curves show anode and cathode potentials at temperature and humidity controlled (80 °C and RH = 100%). Cathode voltage is similar to the global cell polarization curve and the anode voltage increases with the current density. In order to verify the global voltages obtained, the anode voltage was subtracted from the cathode voltage.
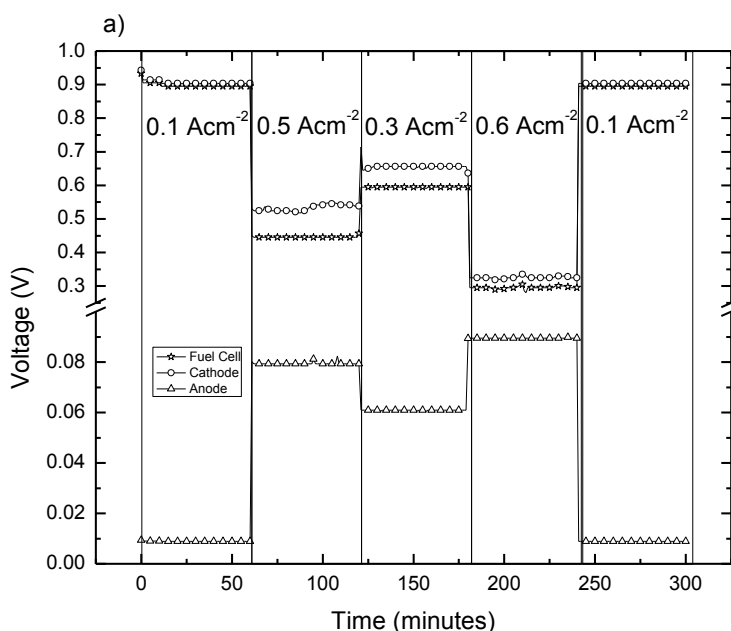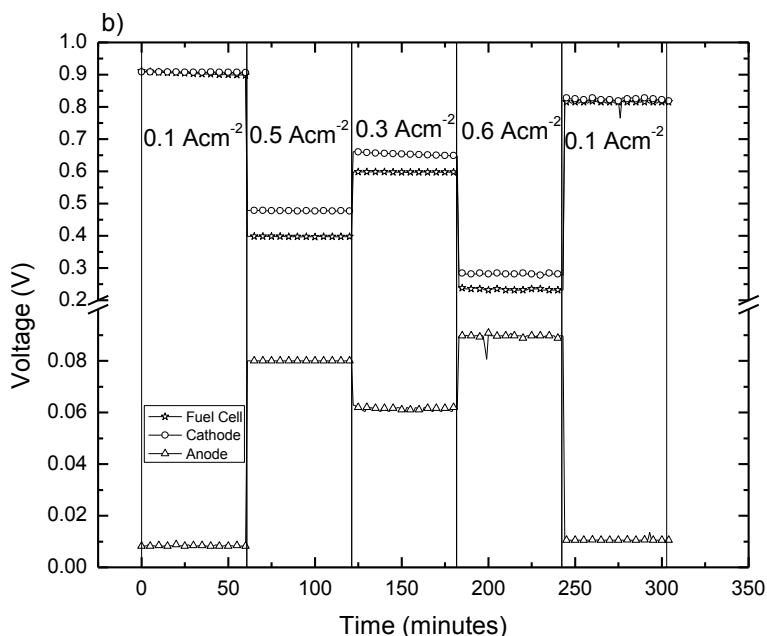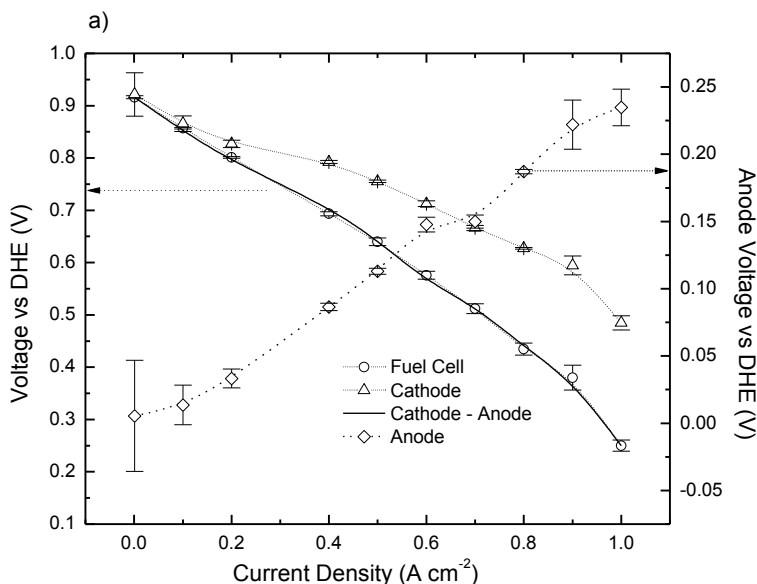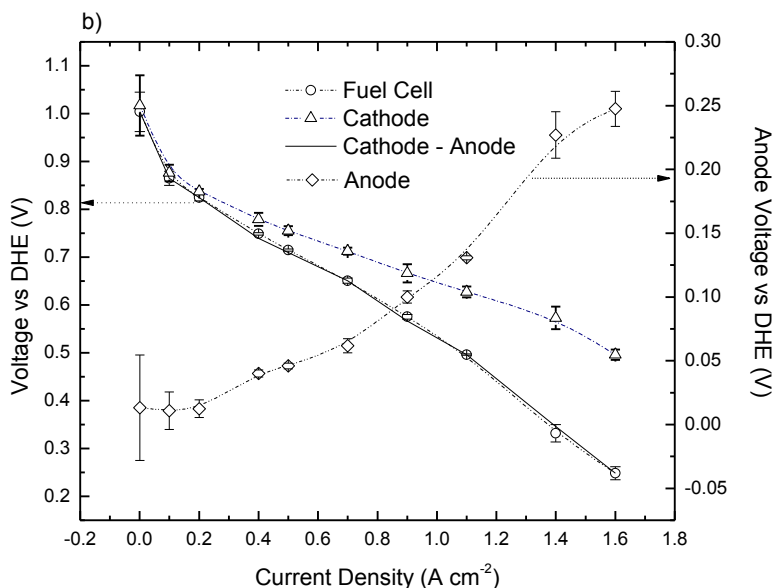
Figure 2. DHE stability with controlled temperature and humidity (T = 80° and RH = 100%) for a) Nafion and b) SBA − 16.

On the Nafion membrane (Figure 3a) at optimal conditions the voltages obtained have an acceptable dispersion, the only difference was on the anode voltages, the dispersion in each data point is bigger than the cathode voltage, this behavior is attributed to the location of the DHE electrode that was placed near from the cathode electrode. It means that when the anode voltages were obtained, the reference electrode was far from this electrode. Same trend was observed with the SBA − 16 membrane (Figure 3b).

At high temperature and low relative humidity (120 °C and RH = 23 %), the voltages obtained with the reference electrode were stables (Figure 3). Due to that the DHE chamber, we maintained constant the temperature at 40 °C and 100 % of relative humidity.
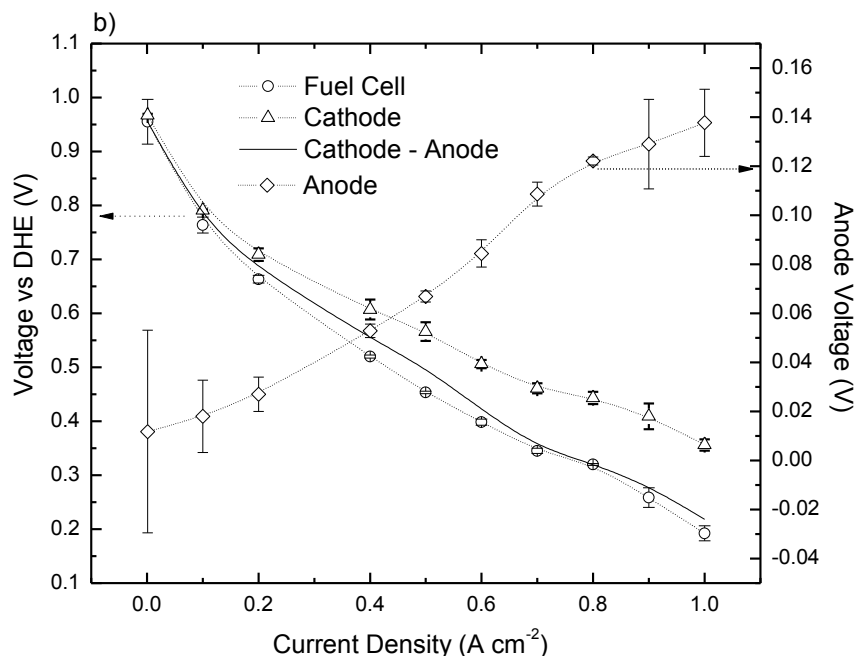
Figure 3. Polarization Curve with controlled temperature and humidity (T = 80° and RH = 100%) for a) Nafion and b) SBA – 16.

On the Nafion membrane (Figure 4a), the corresponding voltages values obtained show a bigger dispersion than those obtained at 80 °C. This voltage data deviation is observed mainly on the ohmic region, this behavior is attributed to the membrane dehydration. On the composite membrane (Figure 4b) the behavior is similar, but the ohmic drop is less than those when Nafion membrane is used. This result could be related with the interactions of the inorganic filler and the water molecules into the Nafion matrix.
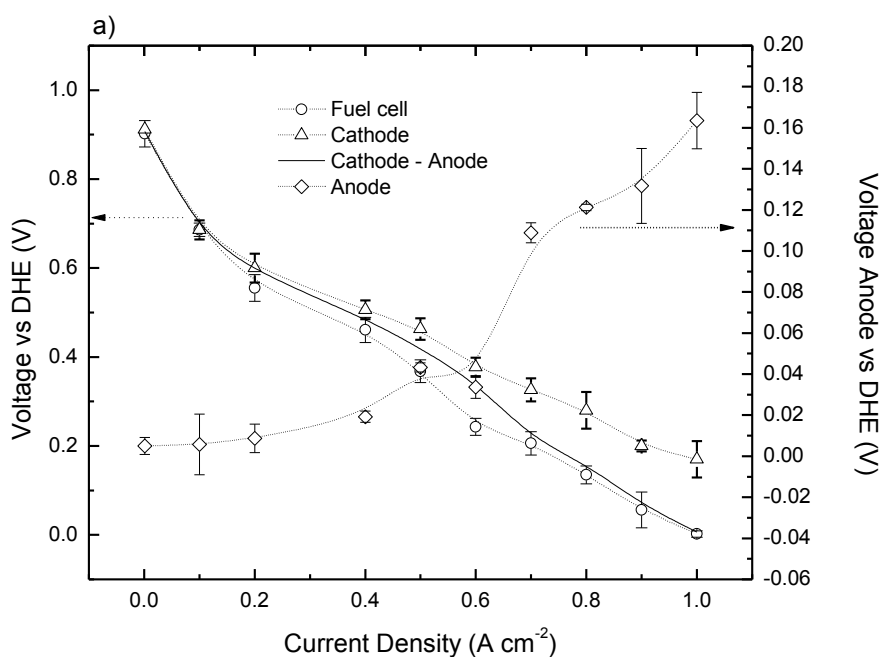
Figure 4. Polarization Curve with controlled temperature and humidity (T = 120° and RH = 23.3 %) for a) Nafion and b) SBA − 16.

The values obtained from the cathode were adjusted with the following equation (1) in order to obtain the electrokinetic parameters:

$$V = E_r - b \log \frac{i}{i_0} - Ri \qquad (1)$$

Where:

E_r = Open Circuit Voltage vs the DHE; R = Fuel Cell Resistance; V = Cathode Voltage; i = current density; i_0 = exchange current and b = Tafel slope.

The electrokinetic parameters obtained are shown in Table 2, the Tafel slope and the exchange current increase with the temperature. The composite membranes showed a better performance than the Nafion membrane. The data obtained in complete fuel cell shows a decrease on the Tafel slope, compared when the mathematical adjustment was performed only with the cathode voltage values. The cathode values it is observed an increment on the Tafel slope values, confirming the theory of the increment of electrokinetic parameter with the temperature. In the complete system, other contributions affect the electrokinetic performance as the membrane resistance, membrane degradation, ohmic drops; and with the incorporation of DHE on the fuel cell, only the cathode voltage contribution is tested.

Table 2. Electrokinetic parameters obtained with the DHE.

Membrane		Complete Fuel Cell				Cathode			
		80 ºC	100 ºC	120 ºC	140 ºC	80 ºC	100 ºC	120 ºC	140 ºC
Nafion – 115	b	45	63	45	49	41	57	65	72
	i_0	$2.32 \cdot 10^{-4}$	$2.07 \cdot 10^{-4}$	$3.69 \cdot 10^{-4}$	$3.65 \cdot 10^{-4}$	$1.63 \cdot 10^{-3}$	$1.89 \cdot 10^{-3}$	$2.07 \cdot 10^{-3}$	$2.35 \cdot 10^{-3}$
SBA – 16	b	61	70	51	45	63	73	77	80
	i_0	$2.13 \cdot 10^{-4}$	$2.97 \cdot 10^{-4}$	$3.07 \cdot 10^{-4}$	$2.68 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$	$2.47 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$
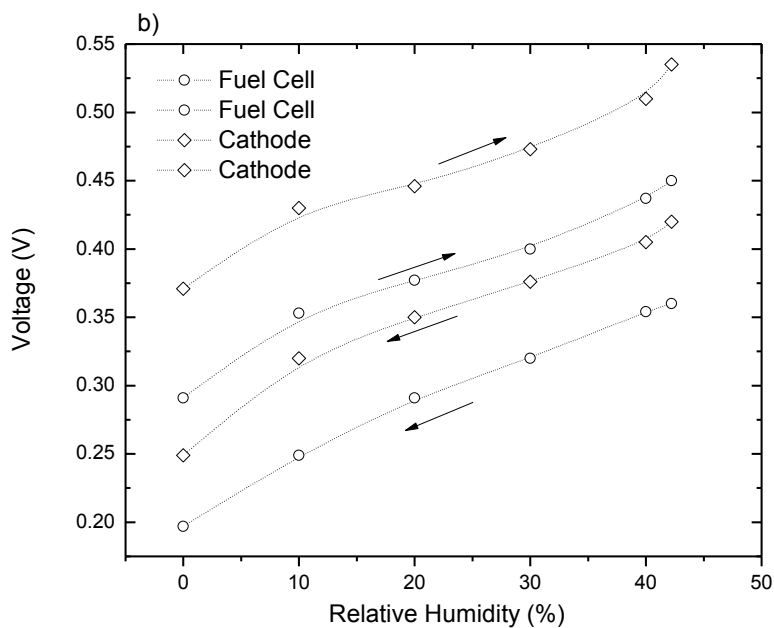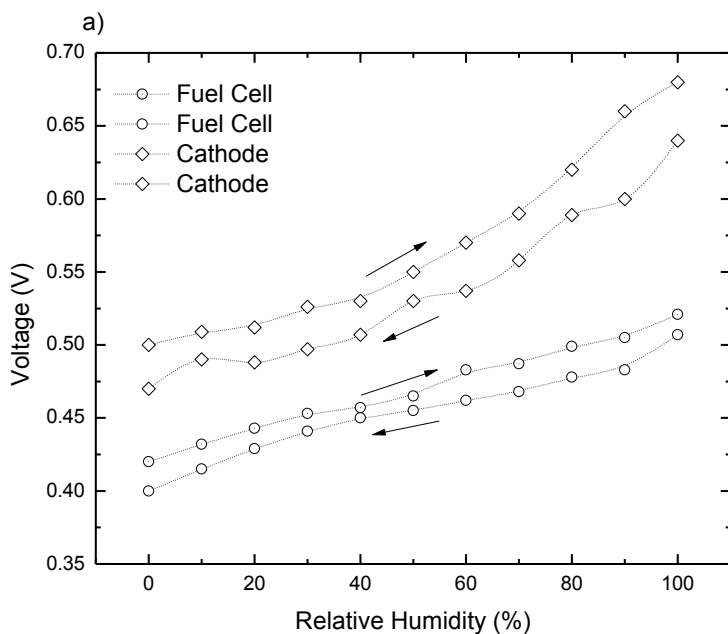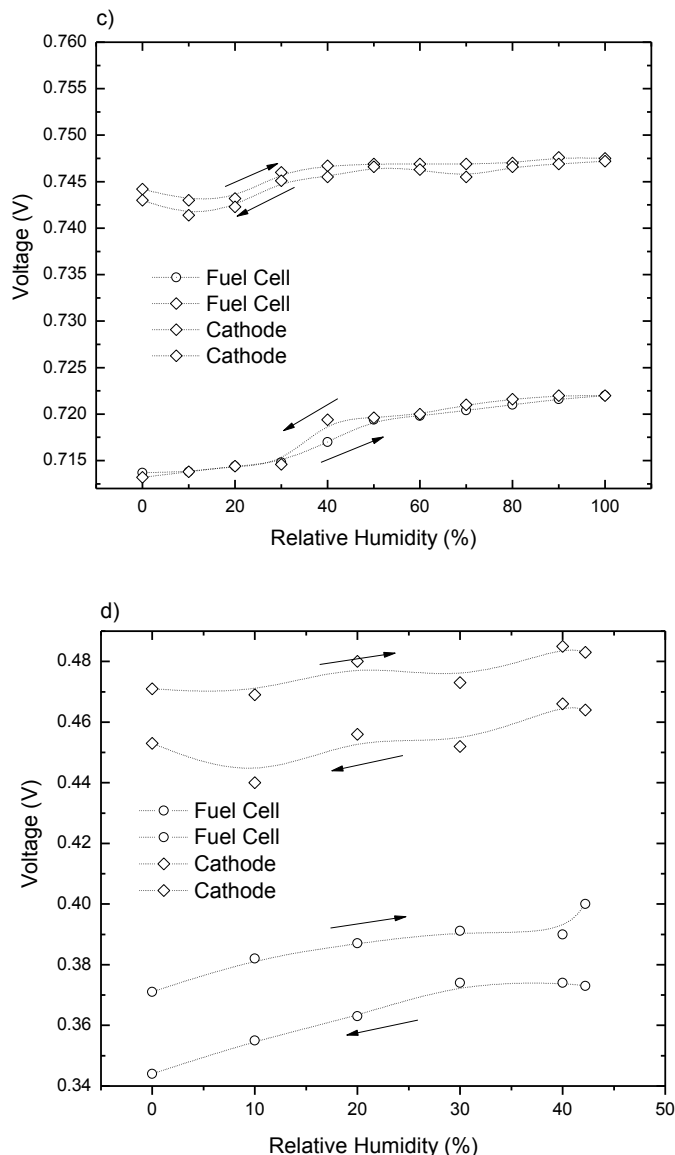
Figure 5. DHE stability with controlled temperature and humidity (T = 80° and RH = 100%) for a) Nafion and b) SBA − 16.

The incorporation of the DHE shows that the oxygen reduction reaction can be studied independently from other effects or electrode reactions.

Figure 5 presents the effect of the relative humidity on the cathode at 80 and 120 °C. Relative humidity was increased each 20 minutes followed by a stabilization period of 10 minutes and an applied current density of 0.6 Acm^{-2}. Nafion membrane (Figure 5a), increases the voltage with the increment of relative humidity; this result could be attributed to the membrane hydration due to the sulfonic acid groups and the hydrogen bonds interactions in the channel. The water molecules traveled via hopping mechanism inside the Nafion, at high humidity, water content is high ($\lambda \approx 14$), the connections between the channels are strong and high voltages are reported (100 % R.H.). When the relative humidity decreases, the voltage also diminishes in around 6 % as difference of both processes,

due to dehydration processes, losing the connections between the channels inside of the membrane. When the temperature of the system is 120 °C (Figure 5b), the voltage drops around 30.5 %. This behavior is explained because the Nafion membrane trend to be dehydrated, decreasing the water content inside the membrane ($\lambda < 14$) and the connection between channels are weak, diminish the water transport [40].

Figure 5c shows the performance of SBA − 16 membrane at 80 °C with respect to relative humidity, the voltage obtained is constant in all the relative humidity range tested. When the temperature of the fuel cell increases to 120 °C (Figure 5d), the composite membrane maintains a voltage difference (around of 8 %) better than Nafion membrane, due to the inorganic filler.

Composite membrane, at high temperatures and low RH conditions has a better performance than Nafion membrane due to the interactions between the inorganic filler and the water molecules into the Nafion matrix. Water transport through a commercial membrane (Nafion) occurs as a function of the water content inside of the membrane. In regions with a low water concentration, the water is transported via diffusion through a structure of low porosity [34]. However, with the incorporation of inorganic fillers, the porosity increases improving the water content into the Nafion matrix ($\lambda \approx 14$) due to the SiO_2 forms Si–OH interactions. OH groups facilities the water coordination acting as water molecules trapping and vehicle molecule for proton migration and consequently increasing the cell voltage.

4. CONCLUSIONS

The DHE shows high stability at high temperature and low relative humidity allowing to obtain separately the anode and cathode voltages. The membrane based on SBA − 16 fillers revealed better performance and electrokinetic parameters at temperature of 120 °C than that obtained when Nafion membrane is used.

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