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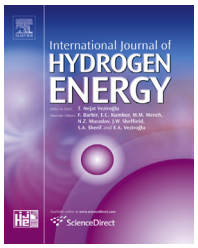

Conductivity of Nafion® 117 membrane used in polymer electrolyte fuel cells

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ABSTRACT

The membrane electric transport (MC) directly influences the performance of the polymer electrolyte fuel cells (PEMFC). The membrane conductivity is determined by a number of parameters such as: hydration technique, graphite cell geometry and pressure applied when the membrane electrode assembly (MEA) is joined. In addition, the membrane conductivity might be influenced by the electrode position due to the possibility of anisotropic electric conductivity.

This paper describes the technique used to measure the normal conductivity of Nafion® 117 applying direct current (DC). The membrane was previously hydrated with two different acid techniques. These two conditioning protocols have identical thermal treatments, the only difference is the acid utilized in each technique. The first treatment involved Nitric Acid while the second one was developed using Sulfuric Acid. The results obtained with the different treatments allowed us to identify the difference in the conductivity, issue that could not be appreciated when we studied only the degree of hydration of the membrane because the quantity of water molecules per sulfonic group was the same using both acids.

The conductivity was measured using directly carbon paper/membrane/carbon paper samples fully immersed in deionized water. Carbon papers were previously painted with different graphite inks that allowed us to analyze the results and select the best one.

The cell used for measuring conductivity was built with two graphite plates, copper connectors and conductive silver epoxy glue that allowed us to form a device similar to the one proposed in the literature. The results are reproducible and consistent with the published data.

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1. Introduction

The main purpose of any investigation related to the composition and operation of a fuel cell is to find the way to achieve high proton conductivity, low electronic conductivity, low permeability to fuel, low electro osmotic drag coefficient, good chemical/thermal stability, good mechanical properties and low cost. When it comes to membranes used for solid polymer electrolyte fuel cells, many studies have been developed

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around perfluorinated, partially perfluorinated and non-perfluorinated ones in order to enhance fuel cell performance and decrease membrane cost [1–3].

The conditioning technique applied to perfluorinated polymeric membranes has a major importance to get the maximum hydration. Their physicochemical properties influence directly the hydration method. As known, the perfluorinated homogeneous membranes refer to uncrosslinked polymers with cluster structure. The samples used in this study were conditioned by a thermal acid treatment that allowed us to reach up to 20 molecules of water per sulfonic acid group. This technique was developed in a previous paper where different acids were tested [4]. In this study, only Nitric and Sulfuric Acids were used.

In agreement with other studies [5], irreversible alteration of the cluster's size occurs due to the thermal treatment. This effect can be proved by rehydrating the membrane with deionized water; it also depends on the drying temperature [6].

In particular, the hydration technique employed, the graphite cell geometry and the pressure applied when the membrane electrode assembly (MEA) is joined are important properties that must be controlled when measuring the conductivity. Also, an unfavorable cell temperature and humidification can affect the transport processes within the cell. The conductivity of the membrane in a PEMFC is directly related to its water content but, on the other hand, any liquid water produced by the cell reaction has to be removed from the cathode in order to improve oxygen transport to the catalyst [7]. Despite the hydration is crucial, the presence of a layer of water on the pore wall can reduce the effectiveness of the pore size leading to a dissolution and diffusion of the gas.

Conductivity measurements are influenced by the water content of the membrane, particularly when the membrane is in its acid form [8]. This situation happens when the membrane dries out at low humidity condition, collapsing the structure channels and difficulting the proton transport [9]. Many theories explain the proton transport within the membrane; the most common approach [6] considers the membrane as a homogeneous phase in which water is dissolved. Reasonably, when a concentration gradient is present a diffusion transport is expected. An alternative point of view is to consider the membrane permeable, as a capillary network medium [10]. A diffuse transport is developed when the membrane is made of amorphous polymers but a convective transport is expected when the pore diameter is over 5 nm. Generally, when an interaction between the polymer and outer species happens, the transport occurs both ways. According to other papers [6,10], this is expected for Nafion membranes. The way to explain the transport is considering that at high water content the channels and clusters get connected, allowing the proton to pass through them. The pore consists of eight CF_3–CF_3 and four CF_3–SO_3H entities which are arranged on a single helix [11]. It has been experimentally established that the transport through this narrow channels requires an activation energy that increases when the content of water gets lower [5]. Other authors [12–15] studied the interactions between two side chains and the dissociation of the sulfonic acid group. It was discovered that the proton dissociates when the membrane is hydrated with 3 molecules of water per sulfonic acid group.

In order to get an optimum cell performance, the membrane must be hydrated assuring high proton conductivity. The study was developed using a fully hydrated Nafion® 117 membrane with maximum number of water molecules per sulfonic group of 20. Despite using a different hydration procedure, the conductivity results are comparable with other works.

The conductivity was calculated at all times with the electrode area resistance of Nafion® 117 and the hydrated membrane thickness, 0.195 mm, which was measured by SCHWYZ caliber.

The method applied to measure the normal direction conductivity consists of pressing the Nafion® 117 membrane directly between two electrodes. This technique seems to be similar of a real fuel cell system.

According to other publication [16], the tangential and normal conductivity should be in the same range when the water content is similar. In this study, only the normal conductivity was investigated.

2. Material and methods

2.1. *Membrane hydration treatment*

This procedure is as simple as possible and allows us to reach maximum hydration following just three steps. First of all, the membranes were boiled in 3% H_2O_2 for 1 h to eliminate organic residues. To ensure the complete acid form of the membrane, the samples were boiled in Nitric Acid and in a second study they were boiled in Sulfuric Acid for 3 h using three different concentrations, 0.05 M, 0.5 M and 1 M. In the last step, the membranes were boiled in deionized water for 3 h. After each step the samples were placed in deionized water at room temperature for 15 min.

2.2. *Proton conductivity measurement*

The conductivity measurements were performed in a cell made with two graphite electrodes based on the model developed in this paper [5]. The cell was built with two rectangular pieces of graphite (3.5 cm width × 5.5 cm height × 0.5 cm thickness) where two copper connectors were fixed with conductive silver epoxy glue at the top of the graphite electrodes.

The conductivity was measured using directly carbon paper/membrane/carbon paper samples, brought in contact between two graphite electrodes using a press which was adjusted manually. The active area of the electrodes was the group CP/Membrane/CP with a dimension of 1.5 cm × 2 cm, with the membrane exceeding this area. The system was immersed in a container filled with deionized water, keeping the connections outside (Fig. 1). This consideration allowed us to ensure the hydration of the membrane. The conductivity was measured at room temperature and two samples per each acid concentration were studied to ensure reproducibility. Also, three measurements per sample were performed.

Carbon papers were previously painted with different graphite inks that allowed us to analyze the results and select the best one. The first ink tested contained Carbon Black

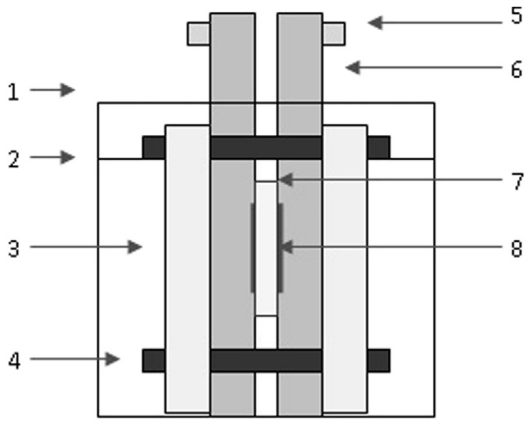

Fig. 1 – Components of the conductivity cell for Nafion 117 membrane: (1) acrylic container, (2) water level, (3) press, (4) set screws, (5) copper electric connections, (6) graphite current collectors, (7) membrane and (8) carbon paper electrodes.

Vulcan XC-72. An unexpected electrolysis occurred at the beginning of the experience when the cell was immersed in water and connected. Due to this effect, this ink was discarded. A second ink was tested; in this case the mix contained 10% Platinum. The result was very satisfactory, the conductivity could be measured and the system found the expected equilibrium. In both cases, we worked with direct current, 0.39 Amper and 4 V. The circuit was built like the image described in Fig. 2.

3. Theory/calculation

The conductivity of the membrane (σ) was calculated according to the Equation (1).

$$\sigma = k/R_m \quad (1)$$

Where k is the cell constant which was calculated according to the Equation (2).

$$k = \text{membrane thickness/electrode active area} \quad (2)$$

The membrane thickness was measured with the SCHWYZ caliber when it was hydrated.

The membrane resistance (Equation (3)), R_m, was calculated considering the difference between the cell resistance obtained with the Equation (4) and the resistance of the empty conductivity cell, R_i: 0.07 Ω.

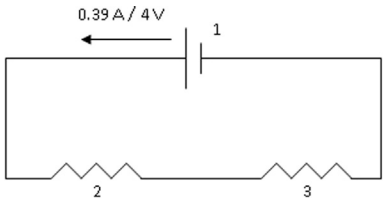

Fig. 2 – (1) Source, Agilent Technologies NS 743 A, (2) conductivity cell and (3) external resistance of 9.85 Ω.

$$R_m = R_c - R_i \quad (3)$$

$$R_c = V_c/V_r \times R_r \quad (4)$$

Where R_c is the cell resistance, V_c is the cell potential, V_r is the potential in the external resistance and R_r is the resistance of the external one.

Two measurements were made with FLUKE 189 Multimeter. The first potential measured was the complete system and then the second potential measured was the external resistance. The difference is the potential in the cell, V_c.

4. Results and discussion

4.1. Membrane hydration treatment

The following tables contain the quantity of water molecules obtained with different concentrations of the proposed acids considering the average (λ_a) value of two samples per acid concentration and the standard deviation (s) of each measure.

Each table details the quantity of water molecules per sulfonic acid group obtained in the relevant steps of the procedure. These main steps are:

1. H_2O_2 3% + deionized H_2O
2. Studied acid in different concentrations + deionized H_2O
3. Boiled H_2O + deionized H_2O

4.1.1. Nitric acid

Any difference between the three concentrations was not noticed in Table 1. The results showed that the method is appropriate considering that 19 molecules per sulfonic acid group were obtained.

4.1.2. Sulfuric acid

The study did not show a difference after comparing these results with the ones obtained from the Nitric Acid test. As it can be seen in Table 2, a maximum hydration membrane was also reached.

Table 1 – Results obtained in the Nitric Acid treatment with different concentrations.

Steps	HNO_3 0,05 M		HNO_3 0,5 M		HNO_3 1 M	
	λ_a	s	λ_a	s	λ_a	s
1	14.7081	0.15	15.2998	0.47	15.6527	0.4
2	18.2201	0.57	15.489	0.45	15.9843	0.11
3	18.5657	0.24	17.7482	0.01	19.1307	0.11

Table 2 – Results obtained in the Sulfuric Acid treatment with different concentrations.

Steps	H_2SO_4 0,05 M		H_2SO_4 0,5 M		H_2SO_4 1 M	
	λ_a	s	λ_a	s	λ_a	s
1	15.9599	0.89	15.157	0.36	15.4258	0.57
2	19.0842	0.41	15.0447	0.51	15.251	0.28
3	19.7837	1.19	18.1267	0.78	18.5164	0.04

Table 3 – Conductivity results when the membrane is hydrated with Nitric Acid.

	HNO_3 0,05 M				HNO_3 0,5 M				HNO_3 1 M			
	Membrane 1		Membrane 2		Membrane 1		Membrane 2		Membrane 1		Membrane 2	
	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}
1	0.032	0.203	0.0214	0.3031	0.0323	0.2014	0.0297	0.2185	0.0222	0.2929	0.0282	0.2302
2	0.0318	0.2046	0.0212	0.3067	0.0421	0.1543	0.0262	0.2479	0.0229	0.2832	0.0272	0.2387
3	0.0302	0.2149	0.0197	0.3302	0.0232	0.2801	0.0267	0.2433	0.0232	0.2802	0.0257	0.2527
Average	0.0313	**0.2075**	0.0208	**0.3134**	0.0325	**0.2119**	0.0276	**0.2366**	0.0228	**0.2854**	0.0271	**0.2406**
s	0.001	0.0064	0.001	0.0147	0.0095	0.0635	0.0019	0.0158	0.0005	0.0066	0.0013	0.0114

Table 4 – Conductivity results when the membrane is hydrated with Sulfuric Acid.

	H_2SO_4 0,05 M				H_2SO_4 0,5 M				H_2SO_4 1 M			
	Membrane 1		Membrane 2		Membrane 1		Membrane 2		Membrane 1		Membrane 2	
	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}	$R_{m\ ohm}$	σ S cm^{-1}
1	0.0681	0.0955	0.0354	0.1836	0.0373	0.1743	0.1663	0.0391	0.1035	0.0628	0.1166	0.0557
2	0.0706	0.0921	0.0359	0.1811	0.0375	0.1732	0.1678	0.0387	0.0987	0.0659	0.1148	0.0566
3	0.0686	0.0948	0.0341	0.1904	0.0358	0.1817	0.1647	0.0395	0.0992	0.0655	0.1146	0.0567
Average	0.0691	**0.0941**	0.0351	**0.185**	0.0369	**0.1764**	0.1663	**0.0391**	0.1005	**0.0647**	0.1153	**0.0564**
s	0.0013	0.0018	0.0009	0.0048	0.001	0.0046	0.0016	0.0004	0.0027	0.0017	0.0011	0.0005

4.2. *Proton conductivity measurement*

4.2.1. *Nitric acid*

Conductivity results when the membrane is hydrated with Nitric Acid are shown in Table 3. Considering all the individual results that are in the same range of analysis, its standard deviation is 0.04 S cm^{-1}. The average conductivity result when the membrane is treated with Nitric Acid is 0.2492 S cm^{-1} ($\bar{\sigma}$).

4.2.2. *Sulfuric acid*

Conductivity results when the membrane is hydrated with Sulfuric Acid are shown in Table 4. Considering all the individual results that are in the same range of analysis, its standard deviation is 0.06 S cm^{-1}. The average conductivity result when the membrane is treated with Sulfuric Acid is 0.1026 S cm^{-1} ($\bar{\sigma}$).

Comparing both results, the study performed with Nitric Acid showed better membrane conductivity. This difference could not be appreciated when the membrane hydration was only studied.

5. Conclusions

Membrane conductivity values obtained from both acid hydration treatments were higher than the expected results using the cell built as it was described above.

Therefore, it can be stated that the treatment applied is efficient to achieve enhanced membrane hydration and a high conductivity value, whether Nitric or Sulfuric Acid is being used.

Besides this observation, the treatment with Nitric Acid seems to be a better option to hydrate the membrane, achieving a 0.2492 S cm^{-1} conductivity value.

More acids will be tested using the same hydration and conductivity technique in order to find better results.

Abbreviations

σ	conductivity of the membrane.
k	cell constant.
R_m	membrane resistance.
R_i	resistance of the empty conductivity cell.
R_c	cell resistance.
V_c	cell potential.
V_r	potential in the external resistance.
R_r	resistance of the external resistance.
λ_a	average value of water molecules per sulfonic acid group.
s	standard deviation.
$\bar{\sigma}$	average conductivity of each acid.

REFERENCES

[1] Peighambardoust SJ, Rowshanzamir S, Amja M. Review of the proton exchange membranes for fuel cell applications. Int J Hydrogen Energy 2010;35:9349–84.

[2] Steck AE. In: Savadogo O, Roberge PR, Veziroglu TN, editors. Proceedings of the first International Symposium on new materials for fuel-cell systems 1995. p. 74. Montréal, Canada.

[3] Steck AE. In: Savadogo O, Roberge PR, editors. Proceedings of the second International Symposium on new materials for fuel-cell and modern battery systems 1997. p. 792. Montréal, Canada.

[4] Napoli L, Lavorante MJ, Franco J, Sanguinetti A, Fasoli H. Effects on Nafion® 117 membrane using different types of strong acids in various concentrations. J New Mater Electrochem Syst 2013;16:151–6.

[5] Berenzina NP, Timofeev SV, Kononenko NA. Effect of conditioning techniques of perfluorinated sulphocationic membranes on their hydrophylic and electrotransport properties. J Membr Sci 2002;209:509–18.

[6] Cappadonia M, Erning JW, Saberi Niaki SM, Stimming U. Conductance of Nafion 117 membranes as a function of temperature and water content. Solid State Ionics 1995;77:65–9.
[7] Freire TJP, González ER. Effect of membrane characteristics and humidification conditions on the impedance response of polymer electrolyte fuel cells. J Electroanal Chem 2001;503:57–68.
[8] Stenina IA, Sistat Ph, Rebrov AI, Pourelly G, Yaroslavtsev AB. Ion mobility in Nafion 117 membranes. Desalination 2004;170:49–57.
[9] Sumner JJ, Creager SE, Ma JJ, DesMarteau DD. Proton conductivity in Nafion® 117 and in a novel bis [(perfluoroalky) sulfonyl] imide ionomer membrane. J Electrochem Soc 1998;145:107–10.
[10] Eikerling M, Kharkats YI, Kornishev AA, Volfkovich YM. Phenomenological theory of electro-osmotic effect and water management in polymer electrolyte proton-conducting membranes. J Electrochem Soc 1998;145:2684–99.
[11] Ilhan MA, Spohr E. Hydrogen bonding in narrow protonated polymer electrolyte pores. J Electroanal Chem 2011;660:347–51.
[12] Paddison SJ, Elliott JA. Molecular modeling of the short-side-chain perfluorosulfonic acid membrane. J Phys Chem 2005;A 109:7583–93.
[13] Paddison SJ, Elliott JA. The consequences of side chain flexibility and backbone conformation on hydration and proton transfer in perfluorosulphonic acid membranes. J Phys Chem 2006;8:2193–203.
[14] Paddison SJ, Elliott JA. The effects of backbone conformation on hydration and proton transfer in the 'short-side-chain' perfluorosulfonic acid membrane. Solid State Ionics 2006;177:2385–90.
[15] Paddison SJ, Elliott JA. Selective hydration of the 'short-side-chain' perfluorosulfonic acid membrane. An ONIOM study. Solid State Ionics 2007;178:561–7.
[16] Silva RF, De Francesco M, Pozio A. Tangential and normal conductivities of Nafion membranes used in polymer electrolyte fuel cells. J Power Sources 2004;134:18–26.