

Development and Characterization of a Polymer Composite Electrolyte to Be Used in Proton Exchange Membranes Fuel Cells

B. A. Berns, V. Romanovicz, M. M. de Camargo Forte, D. E. O. S. Carpenter

Abstract—The Proton Exchange Membranes (PEM) are largely studied because they operate at low temperatures and they are suitable for mobile applications. However, there are some deficiencies in their operation, mainly those that use ethanol as a hydrogen source, that require a certain attention. Therefore, this research aimed to develop Nafion® composite membranes, mixing clay minerals, kaolin and halloysite to the polymer matrix in order to improve the ethanol molecule retentions and, at the same time, to keep the system's protonic conductivity. The modified Nafion/Kaolin, Nafion/Halloysite composite membranes were prepared in weight proportion of 0.5, 1.0 and 1.5. The membranes obtained were characterized as to their ethanol permeability, protonic conductivity and water absorption. The composite morphology and structure are characterized by SEM and EDX and the thermal behavior is determined by TGA and DSC. The analysis of the results shows ethanol permeability reduction from 48% to 63%. However, the protonic conductivity results are lower in relation to pure Nafion®. As to the thermal behavior, the Nafion® composite membranes were stable up to a temperature of 325°C.

Keywords—Polymer-matrix composites (PMCs), Thermal properties, Nanoclay, Differential scanning calorimetry.

I. INTRODUCTION

THE PEMFCs (Proton Exchange Membrane Fuel Cell) have been extensively studied because they operate with low temperatures ($\approx 80^\circ\text{C}$) and are used in mobile applications.

The electrolyte is a polymeric membrane and it has an important role in the cell functioning. DuPont's Nafion® membrane is considered the state-of-the-art for this application due to the fact that it remains humid and that it has high protonic conductivity [1]. The protonic conductivity in Nafion® occurs in the hydrophilic regions, by sulfonic groups. These regions are interlinked by nanometric channels, a structure that guarantees the proton conductivity, followed by water molecules, from one electrode to the other [2].

In cells that use alcohol as hydrogen source, DMFC – Direct Methanol Fuel Cell or DEFC - Direct Ethanol Fuel Cell, the Nafion® membrane presents some limitations, such as ethanol or methanol permeability through the membrane,

phenomenon known as cross-over, and it decreases the performance of the cell [3].

Clay minerals of kaolin and halloysite types were used in this work to prepare the Nafion® composite membranes, aiming to improve their physical and chemical properties and, therefore, their performance as a DEFC electrolyte.

Clays are strongly efficient as additives for the solid electrolyte composition applied to fuel cells because of their nanometric dimension, proton conductivity, and potential to reduce the fuel permeability [4]. Chavarria [5] and Jia [6] comment that very significant improvement of many nanocomposite properties occurs due to the addition of very small percentages of lamellar silicates. According to the literature [7], fuel permeation through the membrane, as well as the protonic conductivity, highly depends on the quantity and behavior of the water absorbed by the membrane, once the water influences the ionomer microstructure, the channel and the cluster.

Grotthuss mechanism is the most used model to justify the irregular proton mobility in aqueous medium, that is, the high protonic conductivity; therefore, the hydroxonium ion formation is vital for the proton transfer in the membranes [8]. With the addition of mineral load, a decrease of fuel permeability may occur due to a possible hydrophilicity, thus reducing the ethanol molecule dissolution or the obstruction of the membrane surface channels [9].

The Nafion® composite membranes obtained in this study have been chemically, morphologically and structurally characterized. The efficiency in the ethanol molecules retention was verified and the influence of the kaolin and halloysite particle size in the cross-over phenomenon was determined. Finally but not less important the influence in the protonic transportation of the Nafion® composite membrane prepared was investigated.

II. PROCEDURE

A. The Nanoclay

Halloysite was used in two ways during the composite membrane preparation, as acquired, (Aldrich) Halloysite Nanoclay 685445, in nanotubes of 30 nm x 0.25 – 4 μm , and modified. The modified halloysite was chemically treated according to procedure described by the literature [10] and [11], by using 3-(Trimethoxysilyl) propyl methacrylate 440159 (Aldrich) with the purpose to obtain an exfoliated nanocomposite.

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In this case, the composite membranes obtained were characterized by DRX, model X'Pert MPD (Philips) with Cu tube ($\lambda = 1.54 \text{ \AA}$), applying an angular range of 1.5 to 50° , with increments of 0.05° , and power of 14 kW , aiming to confirm the halloysite modification.

The procedure adopted for the preparation of the Nafion® composite membrane was based on published papers [8], [12], and [13] that used casting and solvent evaporation.

All samples were prepared in duplicates. Firstly, 5 volumes of the 5 wt. % Nafion® (DuPontDE520) solution (Clean Full Cell Energy) was mixed with 5 volumes of the methanol (Dinâmica) solution at 15% and ethanol (Vetec) and 3 volumes of N,N - Dimethylformamide – DMF (Merck). Kaolin and halloysite, as acquired, were dispersed on the prepared solution, in the proportion of 0.5, 1.0 and 1.5%, being the volume of the Nafion® composite solution 15mL. The Kaolin K7375 (Aldrich) used presented particles around $0.1 - 4 \mu\text{m}$, with more than 90% of them smaller than $2 \mu\text{m}$. The suspension was sonicated for one hour. Afterwards, the membrane was cast by placing the suspension on a Petri dish that was taken to a vacuum oven at 80°C for 20 hours until the solvent evaporated.

After that, the membranes were heated at 150 to 160° for four hours, to remove the residual DMF. The Petri dishes with the membranes were then removed from the oven and quickly cooled down in an ice bath. After cooling, the membranes were carefully separated from the recipient and were then placed into another recipient with deionized water. All the membranes obtained were activated before the characterization tests were carried out. The membranes were placed in a 5% H_2O_2 (Synth) solution and heated up to 80°C for 30 minutes and then were washed twice with deionized water. Afterwards, the membranes were placed in an H_2SO_4 (Vetec) 1 mol.L-1 solution and heated until they boiled for 30 minutes, being washed with deionized water three times and kept immersed in water for 10 minutes each time. After these procedures, the membranes were kept in a recipient with deionized water.

B. Characterization

The composite membranes obtained were characterized by DRX, model X'Pert MPD (Philips) with Cu tube ($\lambda = 1.54 \text{ \AA}$), applying an angular range of 1.5 to 50° , with increments of 0.05° , and power of 14 kW , aiming to confirm the halloysite modification.

The morphology and distribution of particles in the membranes were evaluated by using SEM JSM 6060 (Jeol).

For the mapping and determination of the chemical composition of some elements of the sample, SEM - EDX JSM-5800 (Jeol) was used.

The thermal behavior of the membranes was analyzed by DSC Q20 (TA Instruments), in the interval of 20°C to 350°C at the heating rate of $10^\circ\text{C}/\text{min}$, under N_2 atmosphere, by using 5mg of the sample. Thermal stability was checked by TGA 2050 (TA Instruments), at a temperature range from 20°C to 1000°C , under the heating rate of $20^\circ\text{C}/\text{min}$ and N_2 atmosphere [14]. Ethanol permeability in the Nafion®

composite was measured in a two-compartment acrylic cell, with a permeation area equal to 3.9 cm^2 . DM 5000 peristaltic pumps (Provitec) were used to keep a flow of 10 mLmin^{-1} outflow to fill up the two compartments, one with 1 mol.L-1 ethanol solution and the other with deionized water. The samples were collected after a flow of 15 minutes, in triplicate, and analyzed in a gas chromatographer, CP 3800 (Varian), with ionizing flame detector. Water absorption is a priority related to protonic conductivity, therefore, the water content control is an important factor for the membrane optimization [15]. For water absorption determination, the samples were previously dried at 100°C for one hour in an oven; afterwards, they were weighed and immersed into a recipient with deionized water for 24 hours at ambient temperature. After the sample was weighed again and the absorption percentage was calculated:

$$\% \text{ Water} = \frac{m(\text{humid}) - m(\text{dry})}{m(\text{dry})} \times 100 \quad (1)$$

For the accuracy of the results obtained in this test, a 90% reliable interval was calculated.

III. RESULTS AND DISCUSSION

In this work, three composite membranes of different compositions were prepared. They were made from Nafion® polymer with the addition of kaolin, halloysite and modified halloysite as fillers as described in the procedures, all of them prepared with three concentrations of 0.5, 1.0 and 1.5% by weight. The fillers addition was made with the view of decrease the alcohol molecules cross over.

A. Characterization by XRD

The samples with 1.5% by weight of Halloysite and 1.5% by weight modified Halloysite were analyzed by X-ray diffraction (DRX). In the diffractograms presented in Fig. 1, it can be observed that the first diffraction peak of the Nafion®/Halloysite composite that appears at 5.3° is displaced to a smaller angle θ of 2.5° when used Nafion®/ modified Halloysite composite. This behavior may represent an interlay of halloysite particles in the composite through the deviation of the halloysite layers due to the separation of the minerals layer [16], [17].

Another spectrum change observed is that the third peak of the two composites shows an important intensity increase to the modified halloysite if compared to the non-modified halloysite, although the peak was not displaced in relation to the original angle. It's also observed that the crystallites in the composite do not have homogeneous sizes, provided that some peaks are narrow, indicating large crystallites and others are wide, a characteristic of small crystallites.

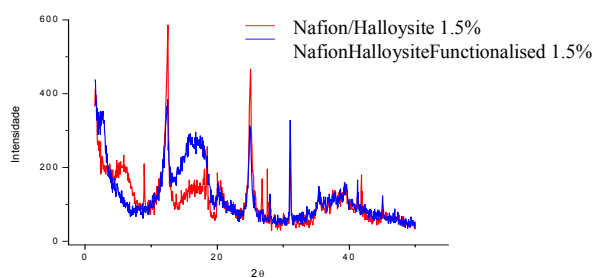


Fig. 1 XRD Diffractogram composite membrane Nafion / halloysite 1.5% compared to Nafion / 1.5% modified halloysite

B. Characterization by SEM/EDS

The particle distribution in the composite matrix can be observed in Fig. 2. In the Nafion®/Kaolin composite membranes, the kaolin particles are homogeneously distributed in the polymeric matrix, according to Fig. 2 (a); however, there was a variation in the particle distribution for different concentrations of clay mineral. The EDX spectrums, in each micrograph, show the exact analysis of the visualized particles. Through this analysis, it's possible to determine the particle qualitative composition, thus confirming its clay mineral characteristics.

According to the literature available [18], kaolin participates in inorganic connections of membranes, promoting the particle dispersion and the membrane formation. Nevertheless, in large quantity, it can deteriorate the homogeneous dispersion system and induce defects in the membrane structure. In the Nafion®/Halloysite composite membranes micro-cavities were observed, and are marked by arrows in Fig. 2 (b). The cavities size increased as halloysite concentration increased, thus agreeing with Ismail [19] findings that the increase of halloysite proportion has led to important defects on the material surface. Li [8] proposed that small voids and cavities may be formed between the crystals and the polymeric matrix, being clear that the more load incorporated in the membrane, the more voids would occur due to the poor interfacial compatibility between the mineral and the polymeric matrix.

The membranes that contained kaolin presented better formation than those that used halloysite, what may be related to attractive force or interfacial adhesion of the clay mineral to the polymer.

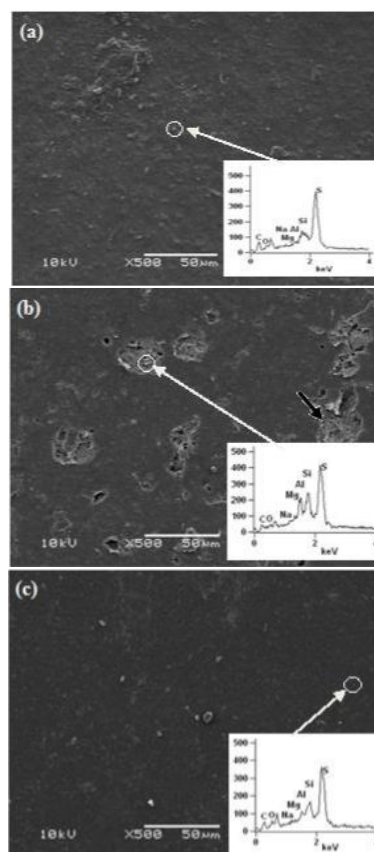


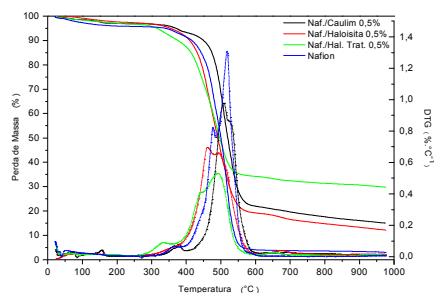
Fig. 2 SEM micrographs of composite membranes: (a) Nafion / kaolin 1.0%, (b) Nafion / halloysite 1.0%, (c) Nafion / 0.5% modified halloysite

The differences between kaolin and halloysite are due to the lamella stacking direction and the location of the octahedral vacancy sites between sequential lamellas. The micrograph of the modified Nafion®/Halloysite membrane is shown in Fig. 2 (c). This membrane shows better homogeneity and allowed good distribution of particles resulting in a well-formed membrane for all the clay mineral concentrations. When the halloysite agglomerates are very large, they tend to migrate to the bottom of the cast recipient leading to heterogeneity of the membrane. Therefore, by improving the mixture methods, such as modifications on the surface of the membranes and chemical treatments, it is expected better homogeneity of the nanocomposites with reduction of the agglomerates, leading to an improvement of the polymer-halloysite interfacial adhesion [20].

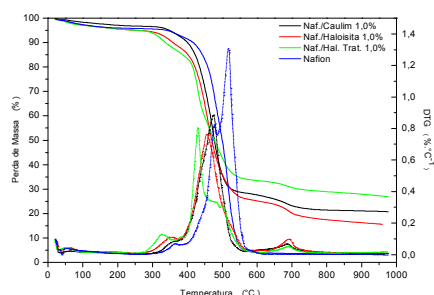
C. Thermal Characterization (TGA and DSC)

The thermal behavior of the obtained membranes, as well as the pure commercial Nafion® membrane, can be observed in Fig. 3. The TGA curves show mass loss for all the membranes at the temperature of around 100°C due to the water evaporation. The mass loss maximum temperature and percentage varied with the membrane humidity level and its interaction degree with the mineral components. The 0.5, 1.0

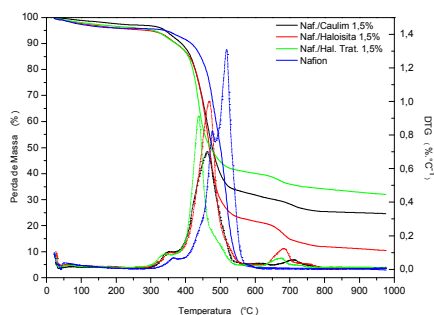
and 1.5 Nafion®/Kaolin and Nafion®/Halloysite membranes presented mass loss of around 70% regarding the polymeric chain. This mass loss occurred at 509°C for 0.5% Nafion®/Kaolin membrane and at the average temperature of 465°C for the other membranes. In these samples there was a mass loss of around 7% at 690°C regarding the inorganic load decomposition.



(a)



(b)



(c)

Fig. 3 TGA Mass loss curve from Nafion® membrane and Nafion® composite membranes containing the ratio Nafion® /nanoclay of 0.5% (a), 1.0% (b) and 1.5% (c).

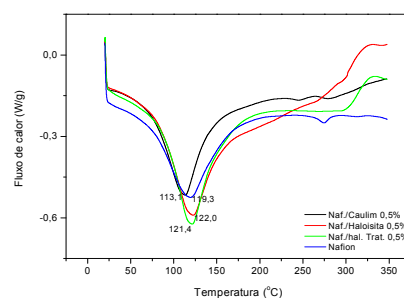
The larger quantity of Nafion composite membranes residue (10 to 25%) in relation to Nafion® membrane (around 3%) may have occurred due to the carbonization of the polymeric chain because of the presence of clay minerals and their refractory characteristics.

The modified Nafion®/Halloysite composite membranes presented mass loss similar to those of the Nafion® membrane analyzed. Besides the first decrease in mass was related to

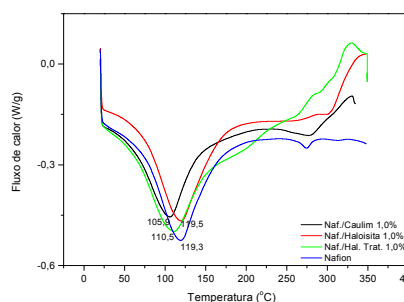
water loss, the membranes presented a second event of mass loss around 334°C with a mass loss between 5 and 11%, related to the decomposition of the sulfonic groups, and they presented a third event with greater mass loss ($\approx 56\%$) at an average temperature of 438°C, related to the polymeric chain degradation. The Nafion® composite membranes presented a last event related to the inorganic load: the higher the temperature and mass loss percentage, the higher the percentage of the clay mineral in the membrane composition. The residue of Nafion® composite membranes with modified halloysite was over 25% what shows more interaction of this clay mineral with the polymeric matrix leading to its carbonization.

The Nafion® membrane decomposition occurs according to three events: the first from 250 to 400°C, due to the desulphonation process; the second between 400 and 500°C, due to the side chain decomposition, and the third between 500 and 600°C, due to the Teflon copolymer main chain decomposition [21].

The Nafion® membrane and the Nafion® composite membrane containing 0.5, 1.0 and 1.5% of clay mineral were also analyzed by DSC and their endothermic peaks occurred between 105 and 122°C, due to the evaporation of the water linked to the hydrophilic groups present in the membranes.



(a)



(b)

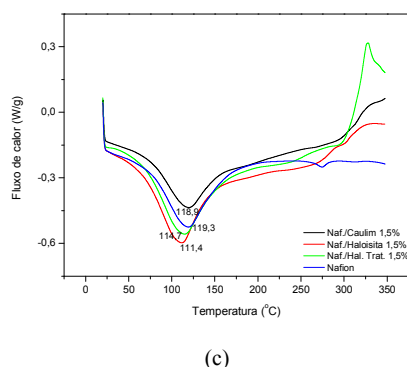


Fig. 4 DSC curve from Nafion® membrane and Nafion® composite membranes containing the ratio Nafion® /nanoclay of 0.5% (a), 1.0% (b) and 1.5% (c)

Table I shows the temperature corresponding to the maximum of the endothermic peak and the evaporation heat (ΔH_{evap}) regarding the peak area in relation to the sample mass analyzed. The bigger the water molecules interaction with the substrate, the higher the maximum temperature will be. The difference between ΔH_{evap} values is due to higher or lower humidity level of the membrane and it depends on the drying process and residual water level or humidity. Nafion® vitreous transition temperature (T_g) is around 110°C and it was not observed because of the water evaporation endothermic peak. According to Mothé [22], a polymer's vitreous transition temperature is the temperature in which the molecular chains gain enough energy to overcome the attractive forces and present chain segment mobility.

TABLE I
THE MAXIMUM TEMPERATURE RANGE AND ENTHALPY OF EVAPORATION (ΔH_{EVAP}) OF BOUND WATER AND THE NAFION® MEMBRANE COMPOSITES AND NAFION®

Membrane	Composition (wt %)	T max (°C)	ΔH_{cure} (J/g total)
Nafion/Kaolin	0.5	113.11	110.40
	1.0	105.93	64.07
	1.5	118.98	72.13
Nafion/Halloysite	0.5	121.98	122.90
	1.0	119.50	100.00
	1.5	111.40	116.70
Nafion/Halloysite Functionalized	0.5	121.39	137.60
	1.0	110.55	78.95
	1.5	114.69	131.90
Nafion	-	119.27	94.49

Semi-crystalline polymers when cooled down from the melting temperature present exothermic peak or crystallization temperature (T_c), which was not evaluated in Nafion® membrane and the other membranes studied due to either mass loss or decomposition when the temperature is lower than that to melt the crystallites. It was observed an endothermic peak of crystalline fusion in the Nafion® membrane at temperatures in the range of 250 to 280°C. This peak was not observed in the Nafion® composite membrane due to the decomposition

of the membrane components at this temperature, as observed at TGA curves.

D. Ethanol Permeability

The fuel transportation within Nafion® composite membrane occurs mainly through the pores, ion agglomeration and the connection among the ions on the channels [7]. The clay minerals added may interact with the hydrophilic part and with the ion channels causing a change in the membrane microstructure, increasing the tortuosity of the channels to convey the fuel. The ethanol permeability decrease (Fig. 4) occurred mainly in the Nafion® composite membrane produced with the functionalized halloysite.

Considering the Nafion® composite membranes/functionalized halloysite, there has been a reduction of ethanol permeability of approximately 63%. The results obtained, show a small tendency for the ethanol permeability to diminish with the increase of the filler added. The fuel permeability diminishment may be attributed to the fact that the presence of nanoparticles blocks the channels on Nafion® surface and reduces the size of the internal channels, thus suppressing the membrane's swell and, consequently, increasing the resistance to ethanol diffusion [9]. The Nafion®/Kaolin and the Nafion®/Halloysite membranes presented permeability reduction of around 48% to 50% respectively.

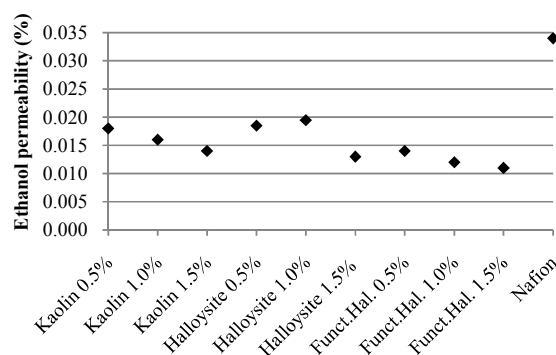


Fig. 5 Ethanol permeability of each Nafion® composite membrane obtained

E. Water Absorption

Nafion® membrane 177 presents water absorption between 24 and 26%, according to [23] and [24]. On Table II the values obtained for water absorption of the samples tested are presented. The water absorption results from this work show that the values obtained for the composite membranes examined were below the theoretical value. According to results presented by [25], the water absorption of the composite modified with clay mineral was lower, which can be due to a better dispersion of the polymeric matrix particles.

TABLE II
WATER ABSORPTION BY NAFION® COMPOSITE MEMBRANES

Membrane	Composition (wt %)	Water Absorption (%)
Nafion/Kaolin	0.5	19.09 ± 2.55
	1.0	15.26 ± 4.75
	1.5	16.22 ± 5.04
Nafion/Halloysite	0.5	15.83 ± 3.25
	1.0	14.36 ± 1.03
	1.5	14.45 ± 0.70
Nafion/Halloysite Functionalised	0.5	13.64 ± 1.21
	1.0	12.28 ± 4.19
	1.5	10.95 ± 0.92

The water absorption capability of the membranes is directly related to the balance among: the osmotic pressure that leads to the ionic species dilution; the water-polymer interfacial energy; and the elastic deformation of the polymeric chains in order to settle the ionic groups in the water-polymer interface [26].

IV. CONCLUSION

The particle dispersion of the clay minerals added to the polymer was suitable for the formation of homogeneous membranes, despite the presence of micro-cavities in the Nafion/Halloysite composite membranes. The thermal behavior of the Nafion® composite membranes obtained was not significantly altered by the addition of clay minerals. All membranes remained stable up to a temperature of 325°C, which is a good parameter for the application of the membranes in proton exchange membranes Fuel Cell. Ethanol permeability decreased in all Nafion® composite membranes obtained, specially the Nafion®/Halloysite membranes modified at around 60%. The size of the filler particles added to Nafion® has influenced the cross-over of ethanol. The smaller is the particle, the higher the retention of ethanol molecules.

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