



RESEARCH ARTICLE

Effect of the doping time of the 1-butyl-3-methylimidazolium ionic liquid cation on the Nafion membrane properties

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Summary

Nafion membranes were prepared by incorporating in the polymer matrix the 1-butyl-3-methylimidazolium (BMI⁺) ionic liquid cation at different doping levels. Increasing the doping time of the membranes with the ionic liquid results in increased incorporation of the BMI⁺ cation but a decrease in the bulk conductivity. The thermogravimetric analysis shows that the BMI⁺ cation incorporation increases the thermal stability of the membranes. The higher discharge efficiency of the fuel cell at 80°C was obtained by using Nafion membrane after 15 minutes of doping in the ionic liquid solution.

KEYWORDS

ionic liquid, Nafion, PEMFC, proton exchange membrane

1 | INTRODUCTION

Recently, proton exchange membrane fuel cells (PEMFCs) have received increased attention due to their efficiency in clean energy production through direct conversion of chemical energy into electrical energy. Fuel cells have many advantages over fossil fuels, such as high efficiency, low or zero carbon emissions, and simplicity when compared with conventional energy conversion technologies.¹ The choice of the proton conducting membrane for a PEMFC depends on a series of factors to enable the ionic transport between cathode and anode. Some of the main features required are thermal stability at high temperatures, high proton conductivity, and high humidity. The polymers of the perfluorosulfonic class are the most used in the PEMFCs, and among those the most used is Nafion. The Nafion membrane is highly proton conductive when the PEMFC operates at low temperatures ($T < 80^\circ\text{C}$) and high humidity.^{2,3} At high temperatures, these membranes are vulnerable to loss of conductivity due to loss of water.^{4,5}

To increase the efficiency of Nafion in PEMFC, the use of ionic liquids (ILs) as electrolytes has been studied and several works have been reported.⁴⁻⁸ These materials have properties such as thermal and chemical stability, high ionic conductivity, and negligible vapor pressure.^{9,10}

It is worth to note that the cation exchange of Nafion with imidazolium based ILs improves the thermal stability and the water retention ability of the membrane.¹¹

Herein are described the study of the incorporation of the BMI⁺ IL cation in the Nafion membrane, the effects of doping time on mechanical and thermal properties, as well as the fuel cell performance of the pure membrane and the membranes that exhibit higher conductivity after doping.

2 | EXPERIMENTAL

The 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF₄) IL was synthesized by using previously described procedures.¹¹⁻¹⁴ The purity of the IL was

checked out by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. The Nafion-117 membrane was purchased from Dupont (EW 1100, thickness 183 μm). The Nafion membranes were pretreated, for elimination of impurities, by immersion in 3% (vol/vol) H_2O_2 aqueous solution, deionized water, and 1.0 mol L^{-1} H_2SO_4 aqueous solution. Each stage of this treatment lasted 1 hour at 80°C , and afterward, the membranes were stored in deionized water until their use.

Doping of the membranes was performed by using sample pieces of 2 cm \times 2 cm, previously vacuum dried at 80°C for 24 hours. These samples were then immersed in a Petri dish containing 20 mL of 0.1 M aqueous solution of BMI.BF₄ IL at room temperature. After the preset immersion times, the membranes were washed in deionized water and dried again under vacuum at 80°C for 24 hours.

The doping level of Nafion membranes was determined gravimetrically. The exchange degree (λ) was calculated as a molar ratio between the IL cation and the sulfonic acid of the Nafion units. This amount is calculated by using Equation (1)¹⁵:

$$\lambda = \frac{W_E - W_d}{139.2} \times \frac{1100}{W} \quad (1)$$

where W_E is the exchange membrane weight, W_d is the dry N117 membrane weight, and 1100 and 139.2 are the average molecular weights of the N117 and the BMI⁺ cation, respectively.

The samples were given designations according to doping time in IL solution, as shown in Table 1.

The samples were investigated by using attenuated total reflectance Fourier transform infrared (ATR-FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM), thermogravimetric analysis (TGA), oxidation stability test (Fenton's test), conductivity measurements, and PEMFC performance.

The ATR-FTIR spectra were carried out by using a Bruker Alpha-P spectrometer in the scanning range of 4000 to 500 cm^{-1} . The XRD analyses were made by using an XRD by Rigaku with a solid detector and Cu K α radiation source at 40 kV and 40 mA. The 2θ varied between

TABLE 1 Doping time in ionic liquid solution of Nafion 117 samples

Sample Designation	Doping Time (min)
N117	0
NBMI2	2
NBMI15	15
NBMI90	90

5° and 60° . Atomic force microscopy imaging was performed with a Shimadzu SPM-9600 scanning probe microscope and Pico View 1.14 software (Key-sight Technologies). Thermogravimetric analysis was performed on a TA Instruments Q-50 apparatus in a temperature range from 15 to 700°C under nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$.

The swelling (S) of the NF, NBMI2, NBM15, and NBMI90 membranes was determined by the mass difference between the fully hydrated membrane and the completely dry membrane. The membranes were dried at 80°C under vacuum for 24 hours, weighed and immersed in deionized water for 24 hours at 80°C . After this time, the membranes were wiped with blotting paper to remove the surface water and were weighed right thereafter. The swelling (S) was calculated gravimetrically, using Equation (2):

$$S(\%) = \frac{W_s - W_d}{W_d} \times 100\% \quad (2)$$

where W_s and W_d are the masses of the wet and dry membranes, respectively.

The samples were tested for leaching (L) of the BMI⁺ IL cation. Before this experiment, the membranes were dried at 80°C under vacuum and then immersed in deionized water at 80°C , both processes lasting 24 hours. After this time, the membranes were dried by using tissue paper and then dried in a vacuum at 80°C for 24 hours and weighed. The leaching of the IL cation in the composite membranes was calculated gravimetrically by using Equation (3):

$$L(\%) = \frac{W_i - W_f}{W_f} \times 100\% \quad (3)$$

where W_i is initial mass and W_f is the mass after immersion in deionized water.

The oxidation stability test was performed by using a 3% H_2O_2 solution and 4 ppm of Fe (II). The membranes were cut into pieces of 1.0 cm \times 2.0 cm, weighed (weight O_1), placed in 20 mL of the solution, and kept at 80°C for 24 hours. After this time, the sample was collected by filtering and cleaned with deionized water several times and dried in a vacuum oven at 80°C for 24 hours. Then, the membrane was weighed (weight O_2). The oxidative stability (OS) was calculated by using the Equation (4)¹⁶:

$$OS(\%) = \frac{O_1 - O_2}{O_1} \times 100\% \quad (4)$$

where O_1 and O_2 are the weights as indicated above.

The proton conductivity of the membranes was determined by using electrochemical impedance spectroscopy by using an Autolab PGSTAT30 potentiostat. The proton

conductivity was measured in the open-circuit potential with an amplitude of 0.01 V and a frequency range from 10 Hz to 100 kHz. Before the conductivity measurements, all samples were hydrated by immersion in deionized water for 24 hours at room temperature to achieve swelling equilibrium. A 20 mm × 15 mm membrane sample was clamped by the edges between stainless steel electrodes and placed in a cell with controlled temperature and relative humidity (RH). The membrane was equilibrated at 100% and 60% of RH for conductivity measurement at 25°C and 80°C, respectively. The conductivities (σ) of the samples in the longitudinal direction were calculated by using Equation (5)¹⁷:

$$\sigma = \frac{l}{RdW} \quad (5)$$

where l is the distance between the electrodes, d and W are respectively the thickness and width of the sample, and R is the resistance value (Ω) obtained at the maximum frequency value, where imaginary Z tends to zero.

Membrane electrode assembly was prepared with gas diffusion electrodes with 4.84 cm² of active area loaded with 0.4 mg cm⁻² Pt and by hot pressing the electrodes onto the membranes at 125°C and 50 kgf cm⁻² for 2 minutes. The measurements were performed with the unit cell at 80°C by using a fuel cell test station (ElectroCell/ ECT 500) with independent H₂ and O₂ feeds saturated with water at 95 and 85°C, both with backpressure of 2.0 bar.

3 | RESULTS AND DISCUSSION

The doping of Nafion membranes with BMI.BF₄ for a fuel cell has been described as an effective way to improve the performance of these devices, but the mechanism of such beneficial effect is not yet very clear. The doping process can be done by the application of 2 protocols¹⁸: (i) using deionized water washing, to remove any residual IL, and (ii) without washing, to compare the amount of methylbutyl-imidazolium cation (BMI⁺) incorporated in the membranes and the amount of IL adsorbed on the surface of the Nafion. The first procedure must be tested because it must be taken into account that the IL could be incorporated by cation exchange, physical adsorption, or both. Those protocols were performed by immersing the membrane samples into a BMI.BF₄ 0.1 mol L⁻¹ solution, at room temperature.

The doping reaction consists of replacing the available H⁺ protons in the -SO₃H groups with the BMI⁺ cations present in the BMI.BF₄ IL. The results obtained with both procedures are shown in Figure 1.

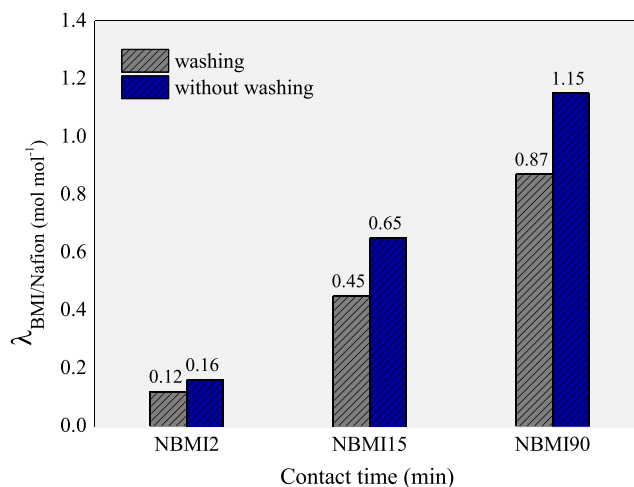


FIGURE 1 The molar ratios of NBMI samples using a BMI.BF₄ 0.1 mol L⁻¹ aqueous solution for incorporation with and without washing with deionized water [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 1 shows that the incorporation of the BMI⁺ cation into the Nafion membrane, which is a result of the kinetics of the doping process, depends on the time during which the membranes were immersed in the IL solution. It can be seen that the molar percentage of the absorbed IL that was removed by washing with water ranged from 4 to 28 mol%. In addition, the results show that, when the doping time exceeds 1 hour, a doping of more than 80 mol% of IL was obtained for both procedures, indicating high doping of the membranes by replacing H⁺ ions by BMI⁺ cations.¹⁹

Figure 2 shows the ATR-FTIR spectra of N117 and Nafion-doped membranes.

The figure shows that both pure and doped membranes present 2 characteristic bands at 1200 cm⁻¹ and 1145 cm⁻¹, corresponding to -CF₂ groups and a band at 733 cm⁻¹ for -CF₃ groups.²⁰ The bands at 1055 cm⁻¹ and 970 cm⁻¹ are attributed to the symmetrical stretching of the S=O bands of sulfonic acid and the C-O-C groups.^{21,22} These results indicate that doped membranes preserve those characteristic bands, as it can be seen in the ATR-FTIR spectra.

Figure 3 shows the XRD patterns of pure Nafion (N117) and Nafion-doped (NBMI2, NBMI15, and NBMI90) membranes.

The pure N117 membrane shows 2 main peaks at 18.5° and 40.8°, which are consistent with those reported in literature.²³ The broad peak at 18.5° was related to the crystalline scattering of the polyfluorocarbon chains in Nafion membranes. It is possible to observe that, with a longer doping time of the Nafion membrane in BMI.BF₄ 0.1 mol L⁻¹ aqueous solution, the peak undergoes a widening and a decrease in the intensity, showing a decrease

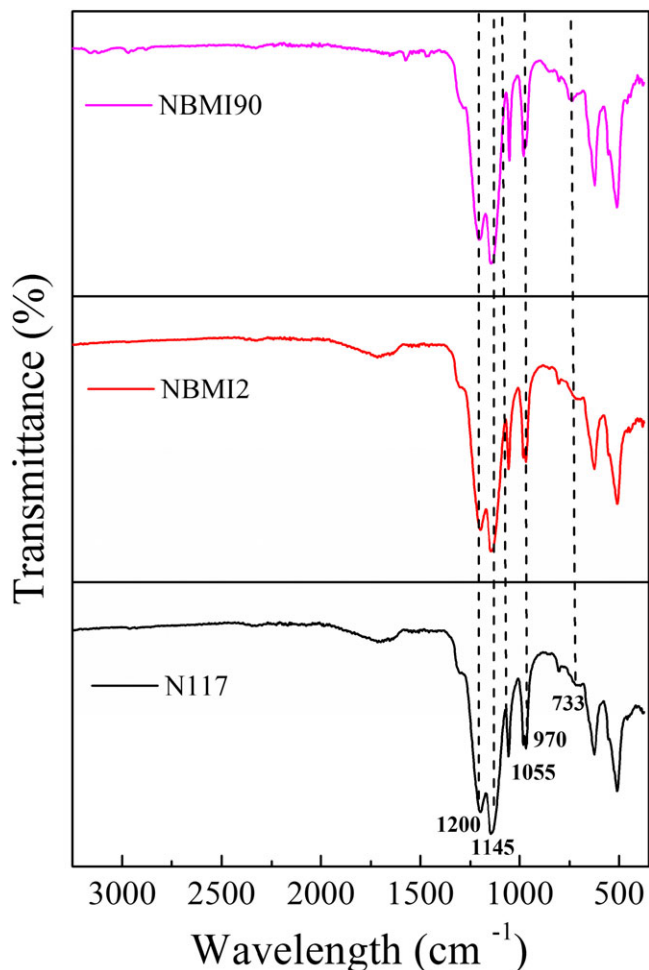


FIGURE 2 Attenuated total reflectance Fourier transform infrared spectra of pristine N117 and NBMI2 and NBMI90 membranes [Colour figure can be viewed at wileyonlinelibrary.com]

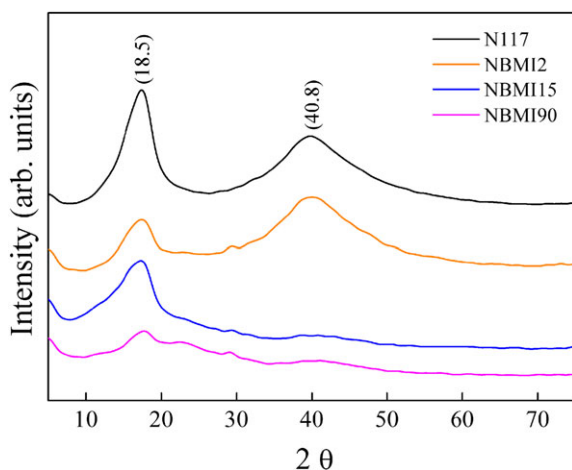


FIGURE 3 X-ray diffraction pattern of N117, NBMI2, NBMI15, and NBMI90 membranes [Colour figure can be viewed at wileyonlinelibrary.com]

in the crystallinity of the structure. During the doping time, the second main peak undergoes a widening at 2 minutes of doping, and at 90 minutes, this disappears, showing a probable change in the structure with the cation exchange.

The morphology of pure N117 and doped membranes were examined via AFM microscopy. Figure 4 shows the AFM images of the N117 and the doped membranes with different doping levels in IL solution.

As shown in Figure 4, the average surface roughness of the pure N117 membrane reduced from 2.45 ± 0.11 to 1.52 ± 0.11 nm when the doping time in the IL solution was 2 minutes. However, when the doping time increases to 15 minutes, the roughness increases greatly, to 13.33 ± 0.12 nm. On the other hand, when the doping time was 90 minutes, roughness decreases again to 1.53 ± 0.12 nm. All these changes in morphology can be associated with phase rearrangement of hydrophilic and hydrophobic regions in the Nafion membrane microstructure during the formation of the bond between the $-\text{SO}_3$ group and the BMI^+ cation when the membrane was immersed in the IL solution.

Figure 5 shows TGA curves for (A) BMI^+BF_4 IL and pristine N117 with (B) NBMI2 and with (C) NBMI90 membranes.

Figure 5 shows that the BMI^+BF_4 IL presents only 1 decomposition stage, which starts at approximately 350°C . The N117 membrane and NBMI2 membrane, doped for 2 minutes, show 2 stages of degradation in the TGA curve. The first stage is around 329°C and 400°C , which is attributed to the decomposition of the sulfonic group,²⁴ and the second stage, around 409°C and 450°C , is due to the degradation of C–F in the Nafion.²⁵ The NBMI90 membrane, doped for 90 minutes, shows only 1 degradation stage at approximately 350°C , which is attributed to the decomposition of the sulfonic group. The results show that the addition of BMI^+ cation in the Nafion membranes causes an improvement in thermal stability.²⁶

Figure 6A shows the swelling of the N117 and the membranes doped with BMI^+BF_4 IL at 80°C . It can be observed that the swelling decreases when the amount of IL in the membrane is increased. The insertion of the BMI^+ cation into the membranes may be leading to the formation of a more compact film due to the formation of pores and channels, indicated by the low water retention.

The leaching out of the doped samples, shown in Figure 6B, was done to assess how easily the water can leach out the BMI^+ cations from the polymer. It was observed a clear tendency that with the increase of amount of BMI^+ cation, the leach out increases too, but not significantly. One explanation for the cation leaching

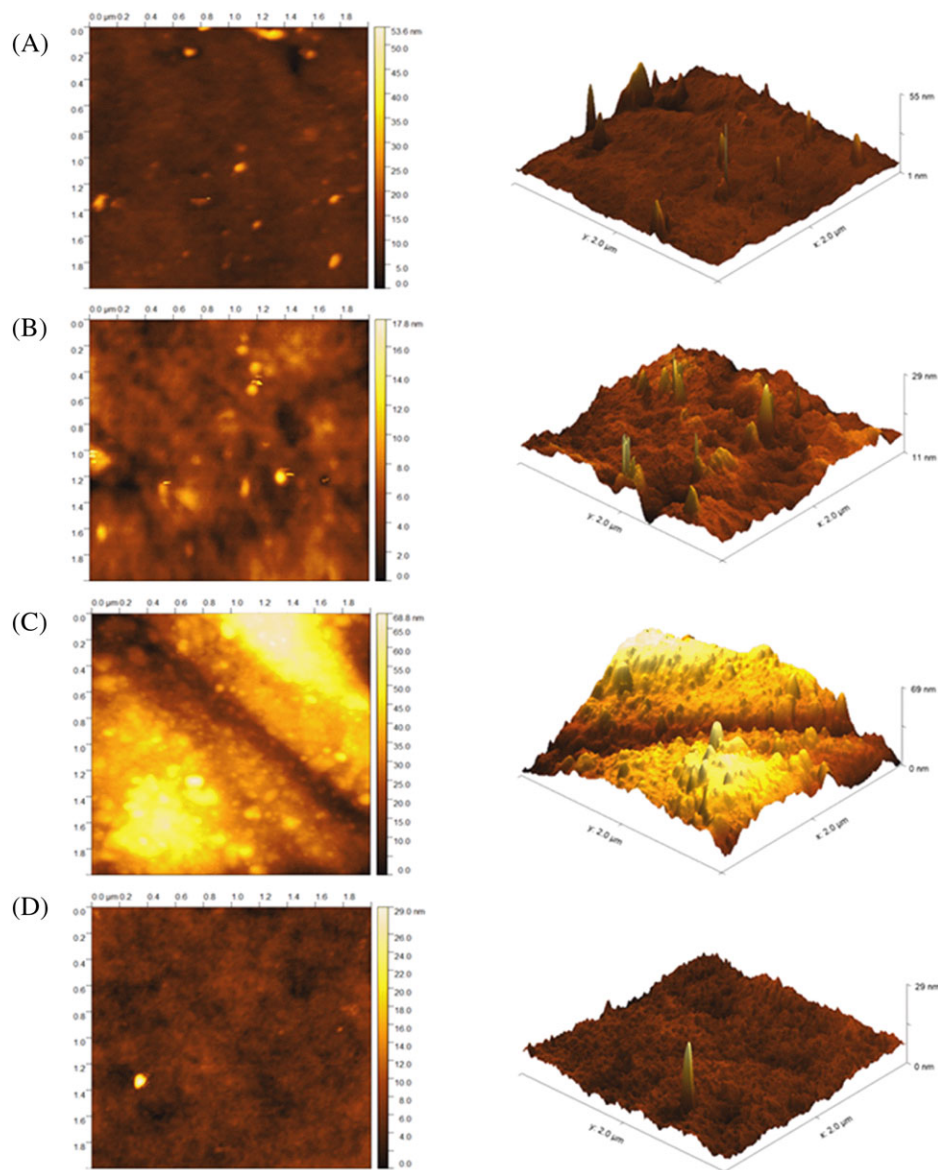


FIGURE 4 Atomic force microscopy images of pristine (A) N117, (B) NBMI2, (C) NBMI15, and (D) NBMI90 membranes [Colour figure can be viewed at wileyonlinelibrary.com]

of the membranes may be that the viscosity of the BMI⁺ decreases with increased temperature, thus increasing its fluidity.

Figure 6C shows the oxidation stability of all samples. The chemical stability of proton exchange membranes is affected during operation of the fuel cell because radicals like HO[•] and HOO[•], which can induce the membrane degradation, are produced inside the cell.²⁷ The results show that when the membranes were exchanged with the BMI⁺ cation, the weight losses for NBMI2, NBMI15, and NBMI90 were 9.1%, 8.9%, and 1.4%, respectively, while for N117, the loss was 9.4%. The NBMI2 and NBMI15 membranes presented weight loss equivalent to N117, but the loss for NBMI90 was almost 7 times smaller than that of N117. This is evidence that the doping time directly influences an increase of oxidation stability of

the membranes. When compared with pure Nafion, the exchanged membranes exhibit better oxidation resistance. The reason could be the role of the BMI⁺ cation in the interaction of sulfonic acid group against the diffusion of H₂O₂.

Figure 7 shows the conductivity of all membranes varying the doping time as a function of temperature and RH.

The figure shows that the conductivity increases from 0.040 S cm⁻¹ to 0.050 and 0.114 S cm⁻¹ when the membrane is doped during 2 and 15 minutes, respectively, at 25°C and 100% of RH. When the temperature is raised to 80°C and the RH is reduced to 60%, the conductivity of the pure membrane increased to 0.090 S cm⁻¹. However, the conductivity of NBMI2 and NBMI15 membranes increased to 0.094 and 0.181 S cm⁻¹. Nevertheless, the

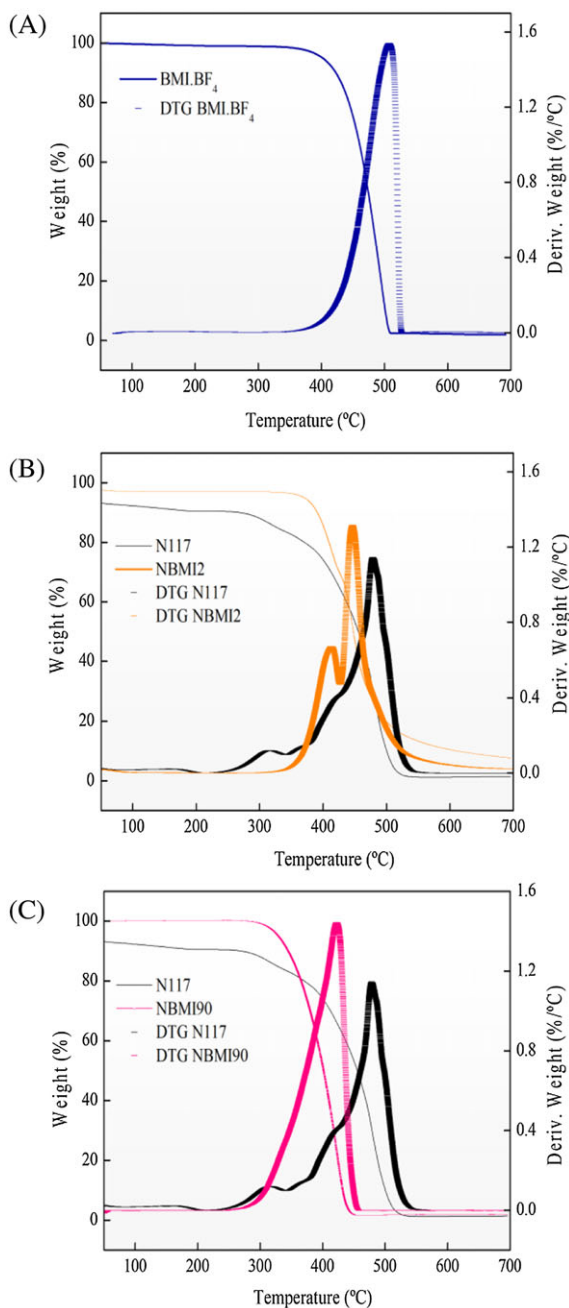


FIGURE 5 Thermogravimetric curves of BMI.BF₄, N117, NBM12, and NBM190 membranes [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

NBM190 membrane, doped during 90 minutes, has a lower conductivity than N117 at both temperatures, 0.025 and 0.03 S cm⁻¹, respectively. This decrease in conductivity of the membrane with longer doping time may be related to the increased amount of BMI⁺ cations in the Nafion channels, thus causing a greater blockage within the membrane channels, increasing resistivity, that is, reducing conductivity. According to Sun and Zhou,²⁸ the BMI⁺ cation can form clusters within the Nafion membrane, which may be the cause of the

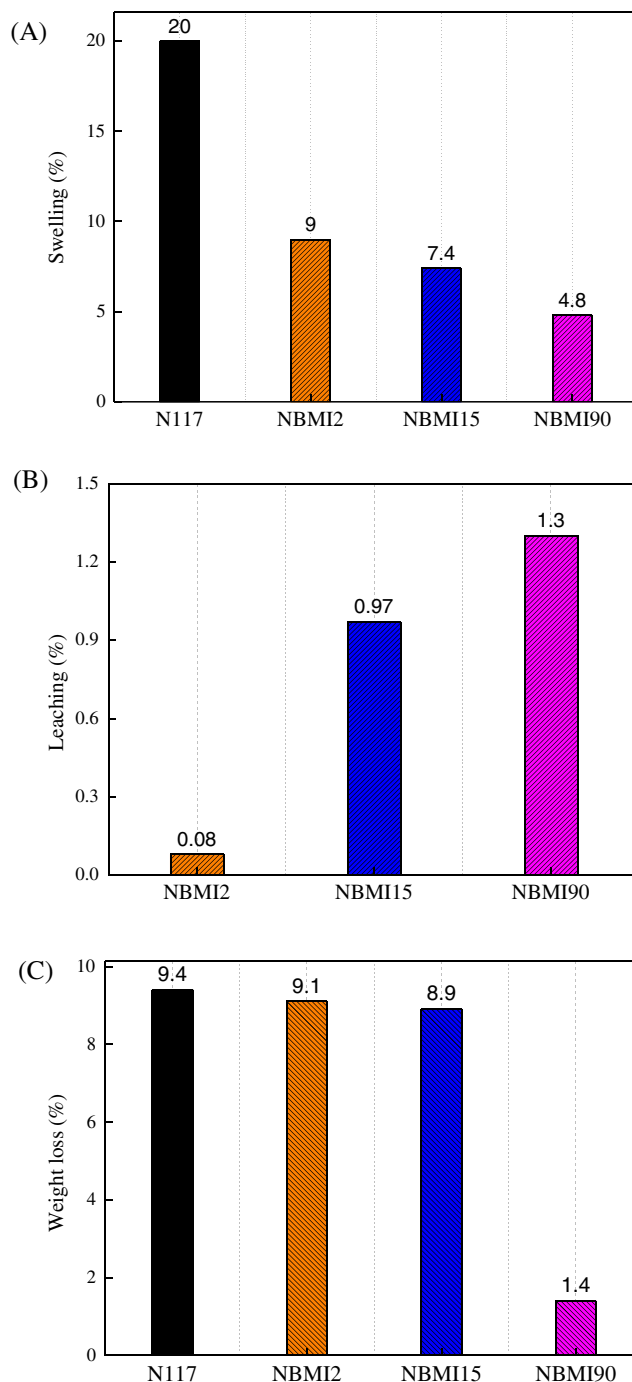


FIGURE 6 A, Swelling of N117, NBM12, NBM15, and NBM190 membranes at 80°C for 24 hours; B, leaching out of NBM12, NBM15, and NBM190 doped membranes at 80°C for 24 hours; and C, oxidation stability of N117, NBM12, NBM15, and NBM190 membranes in Fenton's test at 80°C for 24 hours [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

decrease in the membrane conductivity when the doping time is greater than 15 minutes. Another possibility is that, with the replacement of H⁺ ions by these cations, there is an increase in membrane resistance and consequently there is a reduction in ionic conductivity as well as proton mobility.²⁹

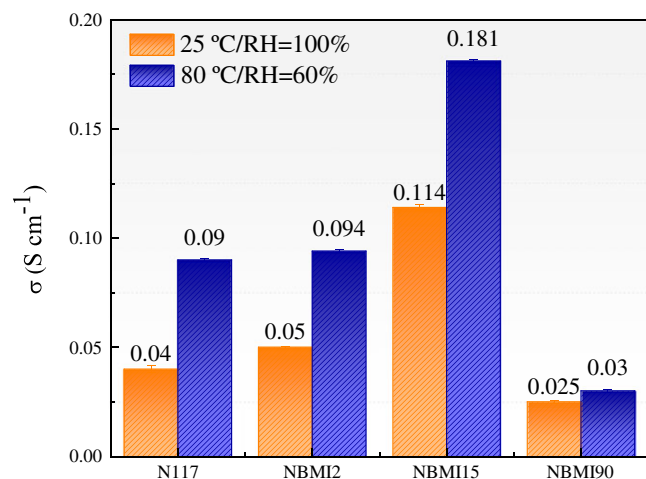


FIGURE 7 Ionic conductivity of N117, NBMI2, NBMI15, and NBMI90 membranes at 25°C/RH = 100% and 80°C/RH = 60% [Colour figure can be viewed at wileyonlinelibrary.com]

The results showed that Nafion membranes doped during 2 and 15 minutes are promising to have their performance evaluated in PEMFC. Figure 8 shows the potential and power density curves as a function of the current density for the N117, NBMI2, and NBMI15 membranes, obtained during the discharge of PEMFC at 80°C.

The potential vs current density shows that the ohmic resistance increases during discharge in the following order: NBMI2 > N117 > NBMI15. The ohmic resistance is related to the conductivity of the membrane and therefore with the ease of transport of H⁺ ions between the anode and the cathode of the PEMFC. It can be observed that the presence of lower concentration of BMI⁺ cations increases the membrane ohmic resistance when compared with the other samples. However, when doping time increases to 15 minutes, the ohmic resistance decreases, thus reducing the Joule effect and facilitating the discharge process. The power density vs current density curves show that the maximum power density

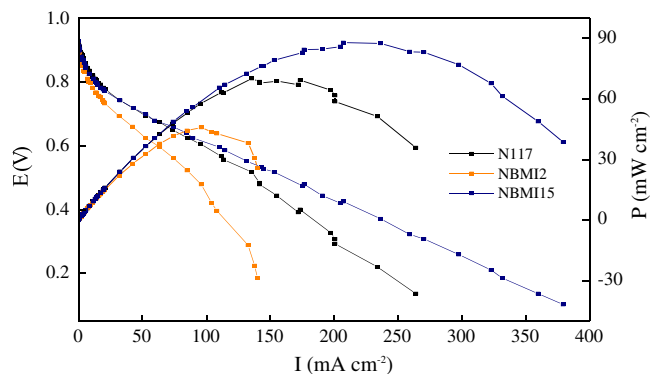


FIGURE 8 Voltage and power density curves as a function of the current density for the N117, NBMI2, and NBMI15 membranes in proton exchange membrane fuel cell at 80°C [Colour figure can be viewed at wileyonlinelibrary.com]

follows the order NBMI15 > N117 > NBMI2. The higher power value achieved with the use of the NBMI15 membrane is a result of the higher discharge current value obtained due to its lower ohmic resistance.

The values of open circuit potential (OCP), maximum current density, maximum power density, and respective current obtained from the PEMFC discharge tests are presented in Table 2.

The OCP values of all the samples were practically the same. Doping the Nafion membrane with a small amount of IL (NBMI2) decreases the maximum current density and the current density at the maximum power density when compared with the pristine membrane (N117) and the NBMI15 membrane. However, when the doping time is increased to 15 minutes (NBMI15), both values increase, even if compared with the membrane without IL. Because of the conductivity values displayed in Figure 8, this better performance of NBMI15 was already expected.

Hao et al.³⁰ used the same doping method for the Nafion (NRE212) membrane. This membrane was doped with 1,2,4-triazolium methanesulfonate (C₂H₄N₃⁺CH₃SO₃⁻, [Tri][MS]) protonic IL. Two [Tri][MS]/Nafion composite membranes were prepared by immersing Nafion membranes into molten [Tri][MS] at 150°C for 7 and 36 hours. A single cell membrane electrode assembly with the [Tri][MS]/Nafion membrane 36 hours with Pt loading of 0.5 mg cm⁻² was tested at 140°C and 150°C under anhydrous conditions. The results show that the OCP was 0.74 and 0.60 V for [Tri][MS]/Nafion and Nafion membranes, respectively, for both temperatures. The highest power densities of the [Tri][MS]/Nafion membrane were 3.20 mWcm⁻² at 140°C and 4.90 mWcm⁻² at 150°C, while for the Nafion membrane the values were 1.00 mW cm⁻² at 140°C and 1.06 mWcm⁻² at 150°C. The highest current density values of the [Tri][MS]/Nafion membrane were 29.4 mA cm⁻² at 150°C and 36.6 mA cm⁻² at 150°C, and the value found for the Nafion was approximately 5 mA cm⁻² for both temperatures. The values found for these parameters with the use of the NBMI15 membrane were higher, probably due to the lower ohmic resistance

TABLE 2 Open circuit potential (OCP), maximum current density (i_{max}), maximum power density (P_{max}), and current density at the maximum power density (i at P_{max}) values of all tested samples in a proton exchange membrane fuel cell

Sample	OCP (V)	i_{max} (mA cm ⁻²)	P_{max} (mW cm ⁻²)	i at P_{max} (mA cm ⁻²)
N117	0.92	264	80	156
NBMI2	0.91	140	66	97
NBMI15	0.93	379	93	237

obtained by the incorporation of the BMI⁺ cations. The comparison of the results shows that the doping of Nafion membrane with BMI⁺ cation during 15 minutes is more promising for PEMFC at temperatures above 80°C and under anhydrous conditions.

4 | CONCLUSIONS

It has been shown that the incorporation of the BMI⁺ cation into the Nafion membrane depends on the time during which the membrane is immersed in the IL aqueous solution. The results obtained by conductivity measurements at 25°C and 80°C showed that a doping time of 15 minutes decreases the resistance and increases the proton conductivity the most. For the NBMI90 sample, the resistance increases, evidencing that, with a long doping time, a tighter network of clusters is formed, which hinders the movement of H⁺ ions that would promote greater proton conduction in the membrane. X-ray diffraction patterns and AFM images show that the BMI⁺ cation was properly incorporated. Thermogravimetric analysis demonstrated that the doping increases the thermal stability of the membranes.

Comparing the results of the PEMFC system with pure Nafion membrane, the system using Nafion membrane doped during 15 minutes working at 80°C increases the current density by 40% and the power density by 50%.

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