

Research Article

Sensitivity of Nafion Films to Organic Substances, Especially Ketones

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This work shows the possibility to employ sulfonated tetrafluoroethylene-based fluoropolymer-copolymer, commercially known as Nafion, as a sensible layer on sensors to detect organic solvents such as ketones. The detection and evaluation of ketone corpuses is very important for multiple applications on medicine, specially to detect and evaluate *diabetes mellitus* from the breath of patients. Nafion is a very stable copolymer, easily available and relatively inexpensive. This allows us to envision the possibility of having cheap and reliable sensors to detect vapors of these substances based on this copolymer. The main result of the present work is that Nafion can protonate gaseous ions from organic solvents, such as acetone and similar substances, which modify its electrical properties, presenting a differentiated behavior according to the chemical nature of these substances, which could lead to their identification, designing an electrical nose, because each behavior is a fingerprint of the substance to detect. Then, this material can be used in the design of electrical sensors, which can be inexpensive, reliable, and chemically stable, representing an excellent alternative to ceramic sensors.

1. Introduction

Fluorinated copolymers have currently a number of applications, other than in fuel cells. For example, Huang et al. [1] developed a fluorinated PIL copolymer-based adhesive with versatile adhesion ability and high transparency; Xiaoyan et al. [2] study the antibacterial and superhydrophobic hemostatic properties of fluorinated random copolymer composite nanocoatings; Alduraiei et al. [3] report fluorinated thin-film composite membranes for nonpolar organic solvent nanofiltration, etc. However, the most popular application is in fuel cells, especially as Nafion.

Nafion is a widely used copolymer that although fairly well researched for decades as a material for fuel cell membranes, it was hardly considered for chemical sensors. However, its properties make it an interesting material for these applications opening new developments to design reliable and cheap sensors, useful in military and industrial applications.

Specifically, Nafion is an American copolymer developed by DuPont (Nafion is a registered trademark of EI DuPont

De Nemours & Co.). It is a random copolymer composed of an electrically neutral semicrystalline polymeric backbone (polytetrafluoroethylene (PTFE)) and a side chain attached with a pendant ionic group, SO_3^- (polysulfonate vinyl ether), which is associated with a specific counter ion (e.g., $\text{SO}_3^- + \text{H}^+ \rightarrow \text{SO}_3\text{H}$). The nature of the pendant group and the covalently linked backbone results in a natural phase separation, which is enhanced by solvation (upon the addition of water or solvent molecules). This separate phase morphology gives Nafion its unique ion transport capabilities ([4–6]). Indeed, it is in essence a copolymer with mechanical and transport functionalities governed by its morphology. However, this morphology also depends on the various interactions and the balance of chemical/entropic energy generated by its environment. Hence, it is interesting to be used in sensor design.

Nafion has the characteristic of being a superacid catalyst, the combination of the fluorinated skeleton, the sulfonic acid groups, and the stabilizing effect of the polymeric matrix, making Nafion a very strong acid, with pK_a -6. Due to this property, it is possible to activate carbonyl

groups of a series of organic substances by protonation, increasing their electrical conductivity. This makes this copolymer an interesting material for detecting those substances in the environment, and even in human breath, by evaluating their changes in electrical properties.

As mentioned, Nafion is widely used in fuel cells, as it is ideal for proton exchange membranes thanks to its electrical properties and its excellent thermal and mechanical stability.

In this work, the electrical response of moistened Nafion films when they are exposed to organic solvents is evaluated. Especially for its eventual application on the sensitive section of sensors of these solvents.

Specifically, in this article, we present a first study of the reaction and the consequent change in physical properties of moistened Nafion, when it is exposed to organic solvents, such as acetone and isopropanol, in the perspective of designing new chemical sensors for organic vapors of this kind.

As mentioned, the ionic conductivity of Nafion increases with its level of hydration. Indeed, the exposure of Nafion to the humidified environment increases the number of water molecules associated with each of sulfonic acid group (SO_3H), promoting its solvation, and therefore the dissociation of the protons from this group. Dissociated protons "jump" from one acid site to another through mechanisms facilitated by water molecules and hydrogen bonds [4], modifying the electrical properties of Nafion. Therefore, in this study, we will use this copolymer moistened. However, in subsequent work, we will use solid electrolytes and water-free Nafion.

The main hypothesis of the present work is that Nafion can protonate gaseous ions from organic solvents, such as acetone and similar substances, which will modify their electrical properties.

Figure 1 illustrates how the carbonyl group of acetone protonates in an acid medium, leaving an electronic hole in the Nafion, which increases its conductivity. Equation (1) is the chemical structure of the Nafion that, in the proposed system, functions as an acid catalyst. Eq. 2 illustrates the general reaction of acetone together with ambient water to form a diol by means of acid catalyzed reaction produced by Nafion. It is important to note that Nafion works just as a catalyzer.

The latter is very useful in the detection of organic vapors. Likewise, it can present a differentiated behavior according to the chemical nature of these substances, which could lead to their identification, because each behavior is a fingerprint of the substance to detect.

If the above hypothesis is true, then this material can be used in the design of electrical sensors, which can be inexpensive and reliable.

2. Experimental

2.1. Materials Used. For this work, Nafion perfluorinated resin (CAS 274704) was used in a 5% solution in low aliphatic alcohols and water (15 to 20% water), provided by Sigma-Aldrich México, under product number 274704.

A thin film of this polymer was distributed on a 100 * 160 mm Kelan brand phenolic plate with part number 14339 provided by Newark Mexico. Acetone technical grade

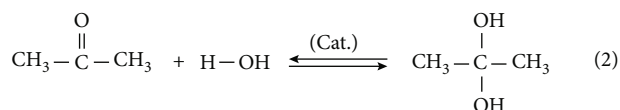
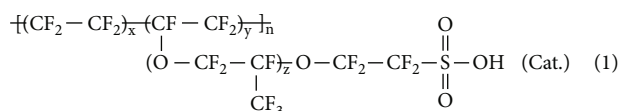


FIGURE 1: The carbonyl group of acetone protonates in an acid medium, leaving an electronic hole in the Nafion, which increases its conductivity. Equation (1) is the chemical structure of the Nafion that in the proposed system functions as an acid catalyst. Eq. 2 is the general reaction of acetone together with ambient water to form a diol by means of acid catalyzed reaction produced by Nafion.

provided by J. T. Baker México (CAS 2432-08) was used as the substance to be detected.

2.2. Preparation of Samples. The samples were prepared using as a base a phenolic printed circuit board, which has a copper-coated side. This face was sectioned into 10 * 20 mm rectangles. Subsequently, a center groove was performed lengthwise to the plate to have a 1 mm gap between the copper sections where these sections are used as the sample electrodes. The preparation process is illustrated in Figure 2, and the thickness of the film is obtained in Figure 3. A copper cable is welded to this plate at the corners of each electrode, to allow connection with the measurement equipment. Subsequently, the copper surface is polished with a No. 4000 sandpaper, and the excess material is removed with a delicate task towel impregnated with isopropyl alcohol. Subsequently, 250 μl of Nafion resin is spread over the plate on the copper face. After waiting for the excess solvent to evaporate, without accelerating its extraction since this directly impacts the electrical conductivity properties of Nafion [7], a Nafion film of about 3.0 μm thick is obtained.

The calculation of gas concentration in the test chamber was performed as follows: (a) the apparent density of a granulated material ELVAX 460 by DuPont was determined, taking a 500 ml burette, and filling it with this material, and subsequently weighing it. Its apparent density was calculated, being 0.552 g/ml. After this, the chamber was flooded with the granulated material up to its edge, and the material was removed from the chamber to be weighed, obtaining a total weight of the granulated material of 5001 g and an apparent volume of 9060 ml or 9.06 l. With this and density at the conditions of room temperature and atmospheric pressure, the weight of air contained in the chamber was calculated, which is 9.0612 g. This data together with the added volume of acetone and its respective density, a weight-on-weight percentage of the analyte is obtained, which for this study was 1.1, 2.2, 3.3, and 4.4, which, expressed in ppm, are 11,000, 22,000, 33,000, and 44,000.

2.3. Methodology. In Figure 4, the equivalent circuit of the connection system is shown. A Tektronix brand power supply, model PS280, was used to power the measurement

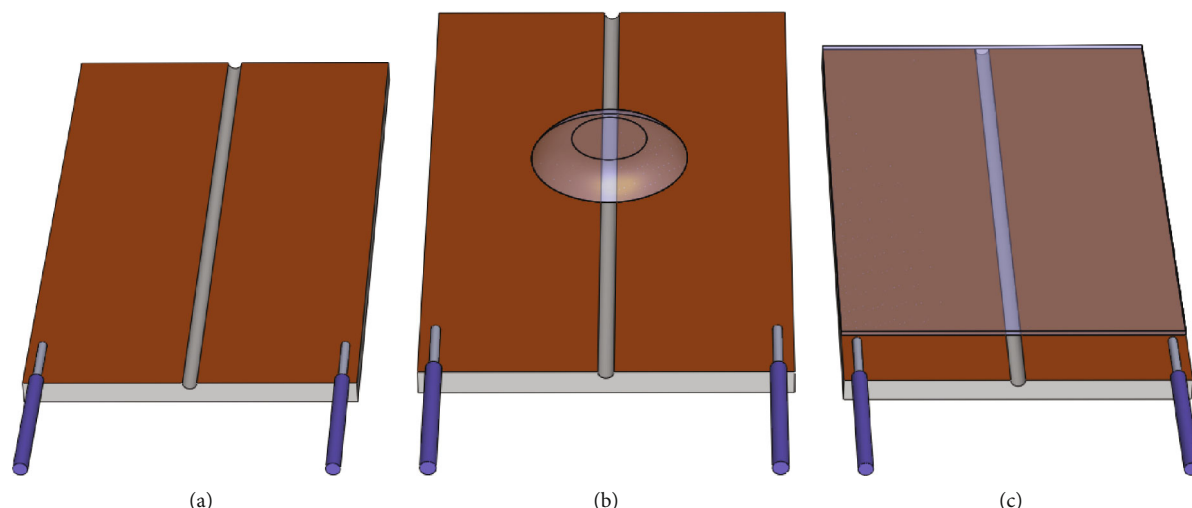


FIGURE 2: Graphic representation of the manufacture of the sensor. (a) Temple made with cuts and welding of cables for each electrode. (b) Deposition of Nafion in the manufactured template. (c) Sensor made with the Nafion film spread over the effective area and evaporated excess solvent. The samples were prepared using as a base a phenolic printed circuit board, which has a copper-coated side. This face was sectioned into 10×20 mm rectangles. Subsequently, a center groove was performed lengthwise to the plate to have a 1 mm gap between the copper sections where these sections are used as the sample electrodes. A copper cable is welded to this plate at the corners of each electrode, to allow connection with the measurement equipment. Finally, a Nafion film of about $3.0 \mu\text{m}$ thick is obtained.

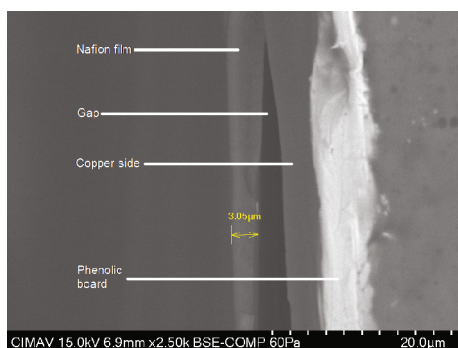


FIGURE 3: Microphotography of the Nafion film thickness. The Nafion film is shown in its dry state, slightly separated from the phenolic board, to measure its thickness.

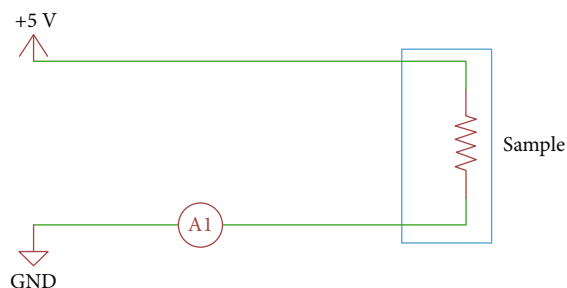


FIGURE 4: Equivalent circuit of the detection system: (+5 V) supply voltage, sample, (A1) Ammeter, and (GND) circuit ground.

system. The current in the circuit was measured with a 6.5-digit precision multimeter, Agilent, model 34411A.

To achieve controlled atmosphere conditions with specific vapor concentrations, a closed chamber of our own

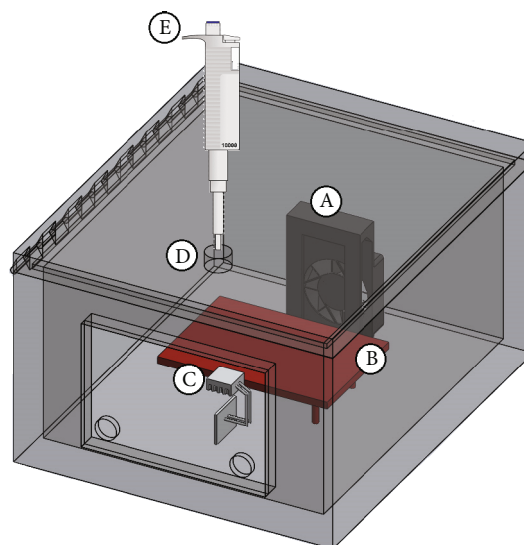


FIGURE 5: Schematic diagram of the closed test chamber: A fan, B sample plate, C evaporation resistance, and D sight glass.

manufacture was used, which has a dissipation resistance of 22 Ohms of 2 Watts, as a heating element, and a 12 V fan to homogenize the internal atmosphere of the chamber (Figure 5).

The samples were placed, one by one, in the controlled atmosphere chamber (Figure 5), under initial conditions of $25 \pm 1^\circ\text{C}$ of temperature and $40 \pm 1\%$ of relative humidity. In this chamber, the sample was connected to the voltage source at 5 volts and the multimeter to measure electric current (Figure 4). The measurement was carried out with a period of 20 seconds without applying voltage, and then, voltage

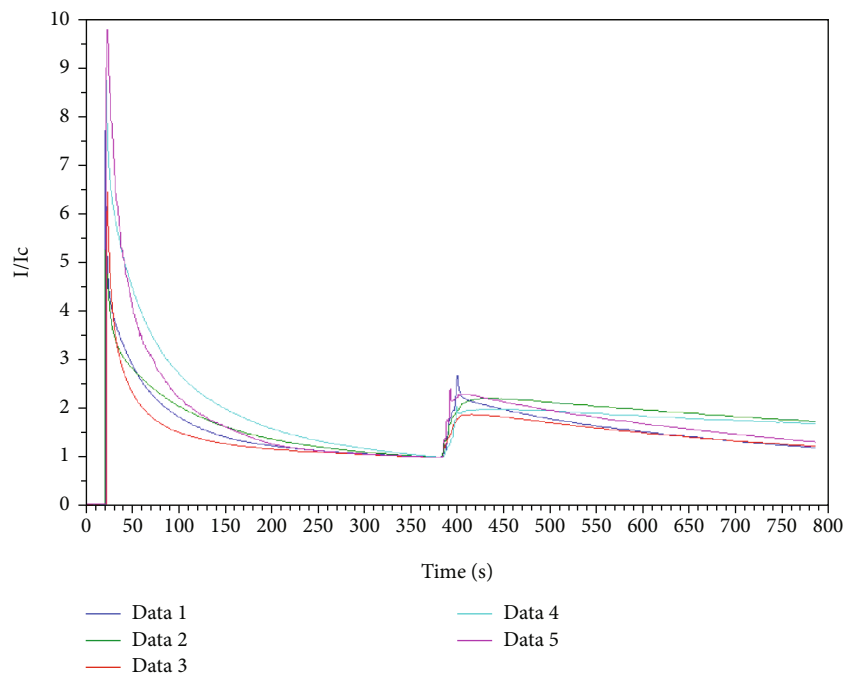


FIGURE 6: Example of 5 repetitions of the Nafion response to a concentration of 4.4% acetone, where it is shown the typical error of about $\pm 5\%$ on our tests. Subsequent tests presented very similar experimental errors. As can be seen, the tests are quite reproducible. For the sake of clarity in the curves, we do not present this type of data dispersion y the following curves.

from the adjustable external source is applied for a period of 6 minutes to achieve signal stabilization. Subsequently, employing a micropipette, the quantity of solvent corresponding to each test is administered. The concentrations evaluated range from 1.1 to 4.4% *w/w* (ketone/air). This is achieved by pouring each substance directly into the evaporation resistance of the chamber. The data are recorded and analyzed.

Different concentrations in % *w/w* were calculated according to the following:

$$C_A = \frac{V_A * \rho_A}{V_A * \rho_A + W_{Air}} * 100, \quad (1)$$

where C_A is the concentration of the corresponding substance in percentage (% *w/w*), V_A is its volume added to the chamber (ml), ρ_A is its density (g/ml), and W_{Air} is the weight of the air contained in the chamber (g).

To homogenize the concentrations in the chamber, a fan located at the bottom of the controlled environment chamber was used.

3. Results

The evolution of the resistivity of each sample is shown in Figures 5–9 [8–10]. These graphs show the behavior of resistivity as a function of time. It is worth mentioning that in this study, we used previously moistened Nafion, with an initial moisture percentage of 40%. Therefore, the initial increase in resistivity is due to the evaporation of the water physisorbed by Nafion (we are currently working on finding

a solid electrolyte that does not present this problem). This increase continues indefinitely, but for our purposes, we consider that after 380 s, the film was stable enough to perform the experiments with acetone, isopropanol, and water vapors. So at that period of time, these substances were added to the evaporation resistance (Figure 5(c)) for their dissemination in the chamber. Four different concentrations of acetone and isopropanol were employed (1.1, 2.2, 3.3, and 4.4%) for the tests.

Regarding the error of the measurements in the experimental stage, Figure 6 shows an example of the 5 repetitions performed for each test. This example corresponds to the test at 4.4% *w/w* of acetone. The error shown is $\pm 5\%$, which is similar in all the cases presented in the other tests. As can be seen, the tests are quite reproducible. Subsequent tests presented very similar experimental errors. For the sake of clarity in the curves, we do not present this type of data dispersion in the following curves.

Figure 7 shows the effect of acetone vapor on the resistivity of the Nafion film, with the four predetermined concentrations. A sharp decline in the resistivity of the film is observed. This drop is accentuated as the concentration of acetone increases (which allows us to sight the possibility of evaluating the concentrations of these vapors using Nafion as a sensitive material). Once a minimum resistivity is reached, a slight rise begins, because the film continues to lose water.

Figure 8 shows the response to isopropanol vapors, under the same experimental conditions as with acetone (this compound was chosen because it has great similarity to acetone without presenting the double bond, so it has a lower protonation capacity). The responses are similar in

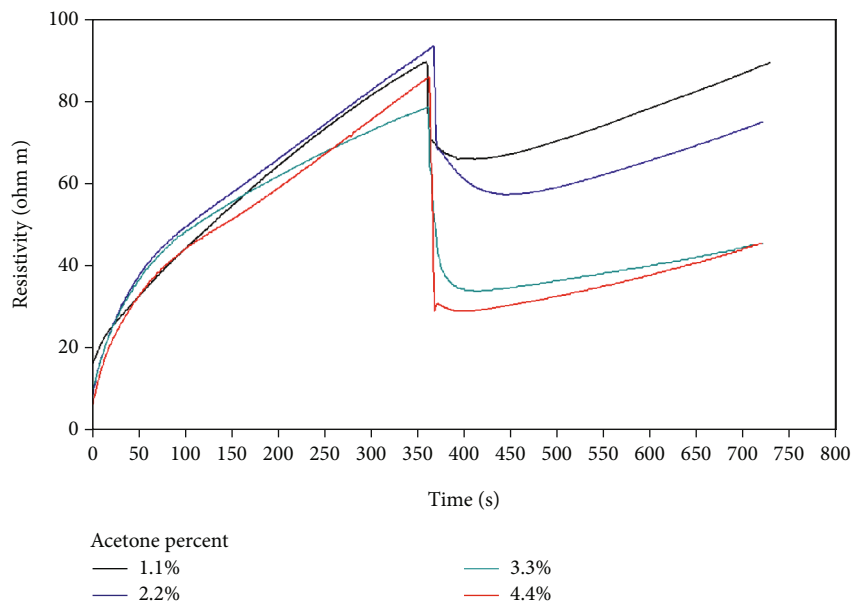


FIGURE 7: Change in resistivity of wet Nafion with acetone vapors. Vapors were added at 380 s.

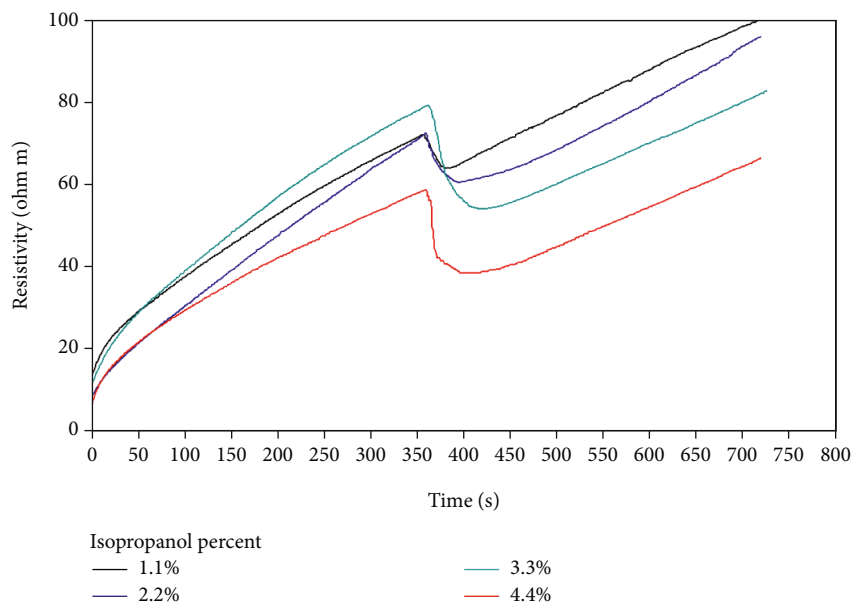


FIGURE 8: Change in resistivity of wet Nafion with isopropanol vapors. Vapors were added at 380 s. Note how the change in resistivity it is much less significant than with acetone.

shape to those obtained with acetone vapors, but with a considerably lower resistivity drop, approximately one order of magnitude. This means that the sensitivity of the sensor is specific and large enough to implement a sensor array, allowing to distinguish between different received vapor stimuli. Likewise, as for acetone, the decrease in resistivity also depends on the concentration of the substance in question, and therefore, it is possible to evaluate it using a suitable arrangement on a chemical sensor.

In Figure 9, the behavior of resistivity is compared with acetone, isopropanol, and water, when they are added at a

concentration of 4.4% *w/w*, at 380 s. It is observed that the sharpest drop in resistivity is with acetone, followed by isopropanol, and lastly with water (although the drop with water is longer).

4. Discussion

Also, it is too early to have a full explanation of the reaction involved; however, we have the following hypothesis; the acid attack of the Nafion breaks the double bond of the acetone, leaving an ion that increases the electrical conductivity

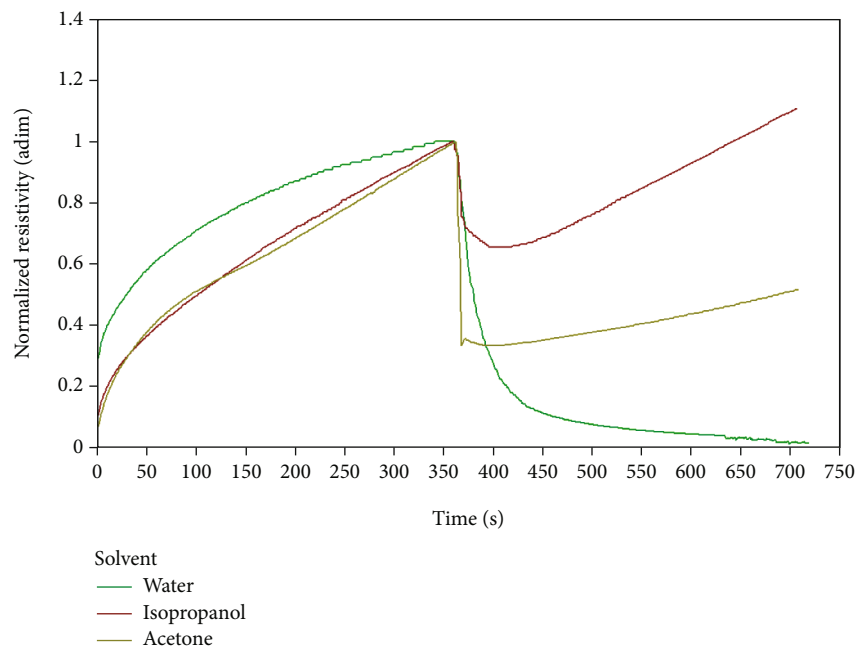


FIGURE 9: Comparison of the evolution of the electrical resistivity through the Nafion film with the vapors of acetone, isopropanol, and water at a concentration of 4.4% *w/w*.

in this polymer. The ion produced combines with the water forming a diol, which eventually dehydrates and returned back to acetone. This mechanism is similar to that reported by Patra et al. [11].

Indeed, initially, during the hydration process of the samples (before testing), it is well documented that [12–30] as the film absorbs water, the protons (H^+) dissociate from the sulfonate sites, SO_3^- , they are solvated, mobilized by the water molecules (forming ions like $H_9O_4^+$). This bound water and its solvation process are associated with the reduction of its resistivity, since bound water molecules improve phase separation and form ion-rich hydrophilic domains in the film. With the adsorption of two or more water molecules, it is believed that an interconnected network of domains is formed, which marks the percolation threshold, giving the film its ion and water transport functionalities. The adsorption process continues from 5 to 6 water molecules that form multiple layers of solvation around a fixed site of sulfonic acid ($SO_3^- - H^+$) and after dissociation around $(H^3O)^+$. At higher relative humidity values, the additional water molecules cause a greater growth and connectivity of the hydrophilic domains. This process is reinverted from the moment the sample begins to lose moisture, especially when it is placed in the test chamber, which is why the initial resistivity of the film increases over time.

Then, when acetone (or similar organic solvents) is added, as a liquid that evaporates inside the test chamber, solvent ions are naturally produced, especially acetone ones, which have a double bond in their molecule (and to a lesser degree in isopropanol).

These ions are easily protonated by Nafion, generating electrical holes in its structure. Thus, when the organic solvents tested (acetone and isopropanol) are added to the

Nafion film, a decrease in its electrical resistivity is observed (see Figure 1), like when water is added.

It should be mentioned that the effect of humidity is doubled since it generates a first generation of holes, thanks to the consequent protonation, and allows ionic conduction through the percolating network that is formed inside the Nafion.

In this first work, water was used to form an electrolyte, but it has the disadvantage of evaporating very easily. We are currently selecting solid electrolytes, such as “chitosan dissolved with glycerol,” to avoid this problem and be able to employ Nafion in a dry state.

Also, it must be mentioned that Nafion alone cannot identify with exactitude acetone from other gases. To do this, an array of polymers that give different responses to the same substance is normally designed, which allows obtaining a chemical fingerprint, with which to identify the substance in question. The methodology to do that has been very well described by Verma and Panda [31]. In order to prepare a chemical sensor with this polymer, which would be capable to identify the acetone from other gases in a selective fashion, it is necessary to prepare a battery of different blends of Nafion with other polymers, to obtain a chemical fingerprint that permits to perform this task. Currently, we prepared and tested such blends, and we expect to publish the results in a following paper.

5. Conclusion

On the basis of the present results, we can conclude that humidified Nafion protonates gaseous ions from organic solvents, such as acetone and similar substances, in an efficient way. This effect changes its electrical properties, presenting a differentiated behavior according to the chemical nature of these

substances, which could lead to their identification, because each behavior is a fingerprint of the substance to detect.

Concerning the reactions involved, we have the following main hypothesis; the acid attack of the Nafion breaks the double bond of the acetone, leaving an ion that increases the electrical conductivity in this polymer. The ion produced combines with the water forming a diol, which eventually dehydrates and returned back to acetone. This mechanism is similar to that reported by Patra et al. [11].

On the other hand, it is important to indicate that there are a number of advantages to have a polymeric sensitive material for organic solvents: indeed, currently most substances sensitive to acetone are ceramic or made on metal oxide. This has two drawbacks: (a) they must be heated, so a heating platform must be introduced to make them work, which is very cumbersome. (b) Also, they are not flexible, so they are difficult to integrate to modern fully flexible devices. Due to the above, they are also fragile, which represents a problem for modern electronics. In contrast, Nafion is a polymer, which works at room temperature, and is flexible and ductile, making it ideal for modern devices. This allows us to envision the possibility of having cheap and reliable sensors to detect vapors of these substances.

Data Availability

In this first paper we do not have more data than those reported in the same paper.

Conflicts of Interest

No conflicts of interest are present for any author in this paper.

Acknowledgments

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