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New Composite Membranes for Application in a PEM Electrolyser

Jesús Ferre, **Sergio Mollá**, **Jessica Calleja**, **Leire Zubizarreta**,
Energy Technology Institute (ITE), Av. Juan de la Cierva 24, Parque Tecnológico de Valencia, 46980 Paterna-Valencia, Spain

1 Introduction

Water electrolysers using proton exchange membranes (PEM) offer high prospective potentialities for the production of pure hydrogen. This application can produce hydrogen from energy sources and can contribute to reduce CO_2 emissions [1]. The performance of a PEM electrolyser is strongly related to the characteristics of the membrane and electrodes assembly, membrane electrode assembly (MEA), where the electrochemical reaction takes place. Generally, Nafion® membrane, a perfluorinated sulfocationic polymer, is used as proton conductive polymer electrolyte in PEM electrolyser systems. To improve some drawbacks of Nafion® polymer, composite membranes using additional reinforcements such as metal oxides or other reactive has been added to the Nafion polymer [2].

Particularly interesting are Nafion®-conducting polymer composites in which the ionomer, besides behaving as host network for the conducting polymer, provides doping anions and protons, both being essential to electronic conductivity in polyaniline (PANI) [3-4]. Composites of Nafion-PANI have shown good conductivity properties, and moreover, it has shown the possibility to work at high temperature, which means an increment in the performance of reaction [5-6].

In this work, PANI intercalations have been produced by in-situ polymerization of aniline in Nafion®. Membranes with different polymerization times were synthesized at ambient temperature to evaluate the optimum thickness of PANI layer. In this sense, two acid solutions containing an oxidant and aniline respectively were contacted with both faces of a commercial Nafion® membrane.

The properties of the obtained membranes were characterized by different techniques. Water uptake and the ion-exchange capacity (IEC) were determined in the different membranes. Impedance spectroscopy measurements were used to obtain the impedance of membranes and to calculate the protonic conductivity.

Finally, a test bench with a two-cell electrolyser was developed in order to study the performance of the Nafion-PANI membranes was evaluated in a two-cell electrolyser. A range of temperatures between 50-90ºC was used to determine the polarization curves.

The results obtained show that the reaction time of polymerization of aniline affects to the final properties of the membranes, furthermore these properties directly influence on the membrane performance in an electrolyser.

2 Experimental and results

2.1 Polyaniline synthesis

The composite membranes of Nafion-PANI were prepared by means of aniline polymerization within the Nafion network in acid medium. A vertically fixed membrane of Nafion N115 was placed between solutions of 0.01 M $FeCl_3$ in 0.5 M H_2SO_4, and 0.01 M aniline in 0.5 M H_2SO_4, as schematically shown in Figure 1. In acid medium, aniline exists as phenylammonium cations acting as counterions for the sulfonic groups, thus being protons in the membrane exchanged with aniline cations (An^+). Fe^{3+} ions act as redox-catalyst oxidizing aniline. The colour intensity depends on the balance between oxidized (doped) and reduced (undoped) forms of polyaniline and the exposure duration in working solutions [3]. Composite membranes were obtained using different polymerization times and ambient temperature.

The membranes were equilibrated in a 2M HCl solution overnight. The acidic membranes were further washed several times with distilled water.

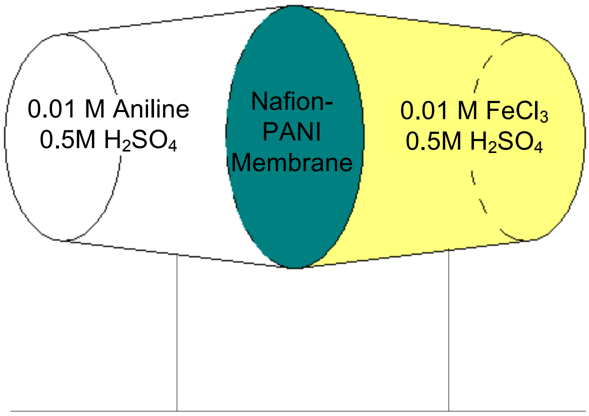

Figure 1: Diagram of reactive system used for polymerization of aniline in the Nafion® network. The membrane was vertically placed between two solutions.

Table 1: Water uptake and ion-exchange capacity (IEC) of Nafion and Nafion-PANI membranes with different polymerization times.

Membrane ($t_{polymerization}$)	Water uptake (kg water/kg wet membrane)	IEC (equiv. H^+/kg wet membrane)
Nafion	0.28	0.92
PANI 1h	0.24	0.91
PANI 5h	0.24	0.88
PANI 8h	0.28	0.85
PANI 24h	0.22	0.72
PANI 168h	0.20	0.64

2.2 Water uptake

A piece of washed membrane was dried at 90ºC during one hour, determining the dry mass of membrane. Then the piece of membrane was submerged in distilled water at 70ºC during one hour and afterwards superficially dried by gently blotting filter paper and weighed. The values of water uptake are collected in Table 1 and show that this parameter is practically independent on the aniline content of the composite membranes. Similar results have recently been reported for alike membranes [3-7].

2.3 Ion-exchange capacity

The washed membranes were equilibrated with a 2 M sodium chloride solution; the protons were exchanged by sodium cations and then titrated with a 0.01 M sodium hydroxide solution. The values of the ion-exchange capacities of the membranes are given in Table 1, and show that this parameter decreases with the aniline polymerization time, decreasing in linear mode during the first 24 hours.

2.4 Impedance spectroscopy measurements

The electrochemical technique of impedance spectroscopy is based on the analysis of response of an electrochemical system (the membrane) with the application of alternating current with variable frequency. This response is the impedance, a complex variable, which is represented through the modulus value, $|Z|$, and the phase angle, Φ, versus the frequency, a representation known as Bode diagram. The fundaments of this technique can be consulted in [3].

This study was realized for several membranes using different temperatures, i.e. 25, 50, 70 and 90 ºC. In Figure 2 it is shown the Bode diagram for different membranes at 70ºC. In this chart it can be observed that the value of modulus of impedance approaches to a constant value when the phase angle approaches to zero. The value of impedance in this plateau is the corresponding to protonic conductivity by the expression:

$$\sigma = \frac{L}{R \cdot A} \tag{1}$$

In this expression, R is the impedance modulus, L is the membrane thickness and A is the membrane area.

The conductivity values for different membranes at temperatures between 25-90ºC are shown in Table 2. It is observed that the conductivity rises with temperature, furthermore the maximum values were mainly obtained with the Nafion-PANI membrane prepared with 5 hours of polymerization time.

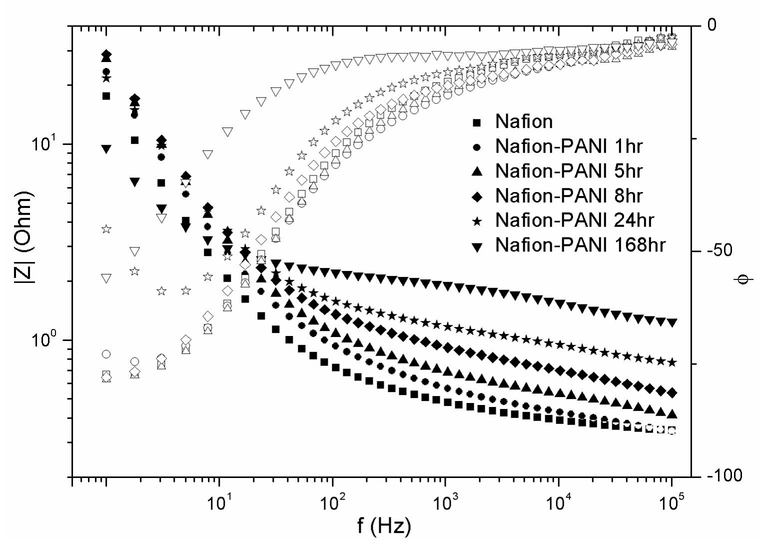

Figure 2: Bode diagram for different membranes at 70ºC. Filled and open symbols represent, respectively, the impedance modulus and the out of phase angle.

Table 2: Values of protonic conductivity, in S/m, as a function of temperature for Nafion-PANI membranes with different polymerization times.

$t_{polim.}$ (hr)	25ºC	50ºC	70ºC	90ºC
Nafion	2.4	2.3	3.8	3.5
PANI 1h	2.8	2.9	3.8	3.6
PANI 5h	3.4	2.8	3.3	4.9
PANI 8h	1.9	2.5	2.8	2.7
PANI 24h	1.7	2.6	2.1	2.8
PANI 168h	0.7	1.0	1.2	1.1

2.5 Electrolyser performance

The performance of the composite membranes in electrolysis operation was evaluated in a two-cell electrolyser with a circular active area of 28 cm^2. The electrolyser was mounted in a test bench developed to this aim and fed with ultrapure water. The tests were carried out at different temperatures, i.e. 50, 70, 80 and 90ºC, using membranes prepared with different aniline polymerization times, i.e. 3, 5, 8 and 10 hours. The membranes were coated with catalyst layers made up of Pt/C on the cathode and Iridium on the anode, deposited by FuMA-Tech GmbH (St. Ingbert, Germany), which are reported as suitable catalysts for electrolytic water splitting [8, 9].

The polarization curves were obtained with catalyst coated Nafion-PANI membranes as well as with a pristine Nafion® membrane for comparison. Voltage was stepwise incremented and current intensity recorded up to 6 V.

An interesting parameter is the specific energy consumption ES, which is defined as the amount of electricity (in kWh) required for the production of a given amount (for example one cubic meter) of hydrogen. It is expressed in units of kWh/Nm^3 [10]. In Figure 3 it is shown the evolution of this parameter versus the current density for the studied membranes at 70ºC.

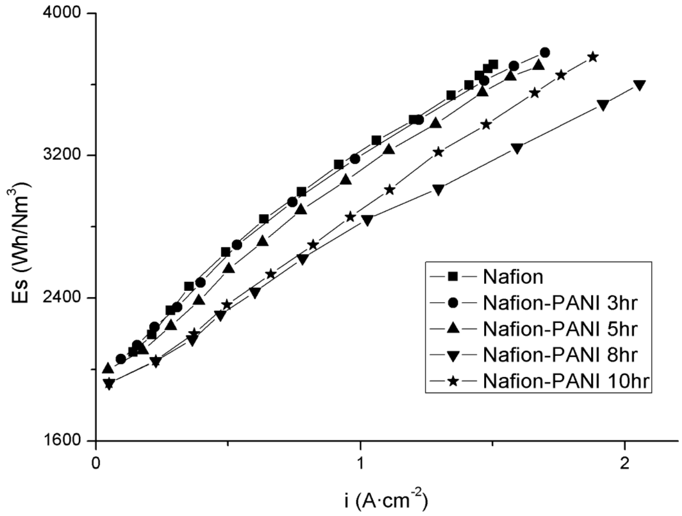

Figure 3: Specific energy consumption versus current density measured at 70ºC using different membranes.

The obtained results indicate that the quantity of polyaniline in Nafion, as a function of polymerization time, improves the electrolyser performance, although above 8 hours this effect is reversed.

3 Conclusions

The composite membranes of Nafion-PANI produced by in-situ aniline polymerization in the Nafion® network increase some properties as compared with pristine Nafion®. Their application in water electrolysis using PEM technology involves an increase in the system performance, due to the enhancement in membrane conductivity by the intercalations of conducting polymer in the structure.

The rise of the electrolyser performance is conditioned by the polymerization time used to obtain each membrane. The maximum value of performance was obtained at 8 hours of reaction time, however the maximum of conductivity was obtained at 5 hours. This indicates that the optimal point must be located within this range of polymerization times.

Acknowledgements

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