PREPARATION AND CHARACTERIZATION OF PVDF/PES/NAFION®117 MEMBRANES WITH POTENTIAL APPLICATION IN VANADIUM FLOW BATTERIES

PREPARACIÓN Y CARACTERIZACIÓN DE MEMBRANAS DE PVDF/PES/NAFION®117 CON APLICACIÓN POTENCIAL EN BATERÍAS DE FLUJO DE VANADIO

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Abstract

In this work the preparation of dense composite membranes, from blends of poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PES) and Nafion® 117, with possible applications in vanadium redox flow battery is reported. The composite Nafion® 117 membranes where prepared by the phase inversion method in controlled air atmosphere, and were characterized to determine their potential for use in energy conversion devices, as a lower cost alternative to the use of the commercial Nafion® membrane. The effect of the thickness on its morphological and cation exchange properties was evaluated, as well as the effect of the chemical composition of the membranes. The characterization of the membranes was carried out using analytical techniques: water uptake, thermogravimetric analysis (TGA), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), surface charge density (SCD), proton conductivity, as well as in the permeability of vanadium ions. From the six composite Nafion® 117 membranes prepared, five exhibited higher rejection of vanadium ions than commercial membrane and all prepared membranes showed a lower proton conductivity, ranging from 1 to 3 magnitude order.

Keywords: Polyvinylidene fluoride, polyether sulfone, vanadium redox flow batteries, Nafion® 117 membrane, cation exchange membranes.

Resumen

En este trabajo se reporta la preparación de membranas poliméricas densas, a partir de mezclas de polifluoruro de vinilideno, poliéter sulfona y Nafion® 117, con uso potencial en baterías de flujo de vanadio. Las membranas se prepararon mediante el proceso de inversión de fases en atmósfera de aire a temperatura controlada, como una alternativa más económica al uso de la membrana comercial de Nafion®. Se evaluó el efecto del espesor y de la composición química de la membrana sobre sus propiedades morfológicas y de intercambio iónico. La caracterización de las membranas se realizó mediante contenido de humedad, análisis termogravimétrico, microscopia electrónica de barrido, espectroscopía de infrarrojo con transformada de Fourier, conductividad protónica, densidad de carga superficial y permeabilidad a los iones de vanadio. De las seis membranas con Nafion® preparadas, cinco presentaron mejor desempeño en cuanto a restringir el intercambio de vanadio, no obstante, los valores de conductividad protónica de los materiales fueron menores con relación a la membrana comercial, desde 1 orden de magnitud hasta 3.

Palabras clave: Polifluoruro de vinilideno, poliéter sulfona, baterías de flujo de vanadio, membrana de Nafion®, membranas de intercambio protónico.
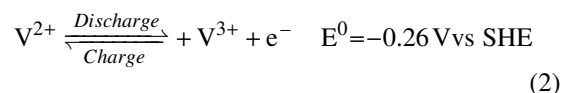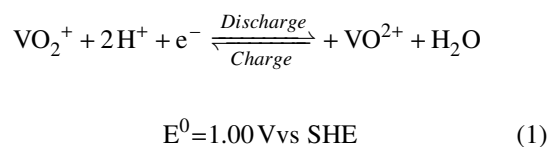
1 Introduction

Energy demand is a sensitive marker of the wellness and prosperity of the society, since energy consumption is involved in basic requirements needs and trivial aspects. An estimation of the energy source used to supply the energy demand around the world states that more than 80% proceeds from fossil and carbon sources, 10% comes from biomass, 6% is related to nuclear energy and the rest is attributed to renewable energy sources, such as tidal, solar, wind, hydroelectric, geothermic, etc. (Del Carmen, 2012). The substitution of the conventional energy sources by renewable energy is a mandatory task for the humankind, since the depletion of the global reserves and the emission of greenhouse effect gases is increasing year by year (Dominguez-Maldonado *et al.*, 2014).

On the other hand, is essential the development of energy storage devices that supply energy when an energetic deficit is detected. From those energy storage devices, batteries attract attention due to capability to storage a great quantity of energy, compared to other devices. There are many types of batteries, such as Li-ion (Qian *et al.*, 2018), Na-ion (Zheng *et al.*, 2018), metal-air (Tan *et al.*, 2018), lead-acid (Křivík, 2018), etc. Redox flow battery (RFB) is a novel storage device proposed by Thaller in 1975, which contains the redox pair species in aqueous solutions, thereby, few advantages are identified, such as durability and stability of the electrolyte (Nam *et al.*, 2016). Usually, the RFB consist of an electrochemical reactor divided by a cationic exchange membrane, where the electrolytes are stored in reservoirs and feeding to the anodic and cathodic compartment by pumps. From all RFB, the vanadium redox flow battery (VRFB) is the only battery where all ionic species are from the same element, this is quite convenient, since the crossover through the membrane can be reversible by imposing an electrochemical treatment to the respective electrolyte solution, unlike other RFB, where there is no manner to regenerate the electrolyte solutions. The VRFB was proposed by Skyllas-Kazacos (Sum and Skyllas-Kazacos, 1985; Sum *et al.*, 1985) the simple operation and remarkable stability of VRFB makes this technology suitable to combine with renewable energy sources in order to have more robust integrated energy systems, hence this device has received considerable attention due to its long cycle life, flexible design, deep charge-discharge

capability, etc. (Luo *et al.*, 2005). The reactions that take place in the cathodic (Eq. 1) and anodic (Eq. 2) compartment of the VRFB are (Kim and Park, 2017):

$$VO_2^+ + 2\,H^+ + e^- \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} + VO^{2+} + H_2O$$

$$E^0 = 1.00\,V\,vs\,SHE \qquad (1)$$

$$V^{2+} \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} + V^{3+} + e^- \quad E^0 = -0.26\,V\,vs\,SHE \qquad (2)$$

The performance of the VRFB depend upon operational parameters, the catalysts and the membrane (Xiao and Tan, 2018; Park *et al.*, 2016; Pu *et al.*, 2018). The charge balance is controlled by the proton migration through the membrane. The Eq. 1 shows that the reduction of VO_2^+ to VO^{2+} requires two protons hence, the proton exchange capacity will be a determining factor on performance of the membrane in the VRFB. Even if the crossover effect can be minimized in VRFB, since the electrolyte can be restored by an electrochemical treatment, the diffusion of the vanadium species trough the membrane by the osmotic process is an undesirable phenomenon, which leads to the polarization of the electrodes. Regarding to the desirables features of the membranes for VRFB application can be established the following: (i) low resistance for mass transport of water, (ii) high ionic conductivity, (iii) very low or null crossover of the vanadium cationic species.

Nowadays, there are commercial proton exchange membranes available in the market based on perfluorinated polymers for the use in fuel cells and RFB applications. From those membranes, Nafion®-based membranes exhibits a remarkable performance, however there are few aspects that worth to improve by adding either additives or preparing membranes with new methods and/or by using other monomers. Hwang *et al.* (2017) compared three commercial anion exchange membranes and two commercial cation exchange membranes in VRFB, all the commercial membranes exhibited VO^{2+} permeation values between 20 to 40 mM by 2 h of operation, except for the membrane from Asahi Glass Co., which reach 2.5 mM at the same conditions. Gindt *et al.* (2017) synthesized polysulfone membranes with either allyl sulfonate or styrene sulfonate groups, polymerized with a fluorinated monomer, the performance of the polysulfone membranes was

tested at VRFB and compared against the commercial Nafion® membrane. Ding *et al.* (2018) reported the use of three based polybenzimidazole membranes, which exhibited lower vanadium permeability than Nafion® membrane, however, the proton conductivity values of those membranes are lower than Nafion® membrane. Zhang *et al.* (2018) proposed a membrane based in quaternary adamantane containing poly(ether ketone) membranes, since the quaternary adamantane confers positive density charge at the surface of the membrane, those membrane exhibited an excellent performance in the VRFB, since the permeability to VO^{2+} ions was lower than nafion-based membranes, which is related to a lower self-discharge rate. On the other hand, Jung *et al.* (2018) prepared membranes with different blend containing sulfonated poly(ether ketone) (SPEEK), poly(vinylidene fluoride) (PVDF), and urethane acrylate (UA), the main idea of this research is combine the high proton conductivity of the SPEEK and the low vanadium permeability of PVDF features, introducing an amphiphilic group from the UA. The blended membranes exhibited a slightly performance improvement against Nafion® membrane. In this work the preparation of composite membranes, based on a matrix of PVDF/PES and Nafion® 117, as a conducting polymer, for applications in VRFB is reported. PVDF is a fluorinated polymer with excellent chemical and thermal properties, which makes it attractive for use as a support matrix; the PES also exhibits good chemical and thermal properties and favors the incorporation of the functional polymer in the internal structure of membrane and Nafion® 117 has high capacity of ion exchange that incorporates the ionic conductivity property to composite membrane. Six composite membranes (MN1-MN6) with different Nafion® 117content were prepared, which were thinner and 5 of them more selective to the vanadium crossover than the commercial membrane. However, the ionic conductivity of the composite membranes showed lower values for a content of 2%, 3% and 4% of Nafion® 117 evaluated.

2 Materials and methods

2.1 Materials

ACS-grade hydrocloric acid (37%), sulfuric acid (95-97%), magnesium persulfate, sodium hydroxide (≥97%), N-methylpyrrolidone (≥99%),

Poly(vinylidene fluoride), vanadium (IV) oxide sulfate (97%) and Nafion® 117 (~5% solution) were supplied by Sigma Aldrich, poly ether-sulfone (≥99%) was supplied by Ionic Company. Deionized water (DI) was obtained with a SYBRON/Barnstead purification system model 02610.

Preparation of PVDF/PES/Nafion® 117 polymeric solution

Different polymeric solutions were prepared by mixing different polymers, similarly to the procedure reported by Kumar *et al.* (2015) with minor modifications, for a total solids content of 16% w/w, using as solvent *N*-methyl-2-pyrrolidone (NMP). Briefly, an amount of NMP was transferred to a glass bottle and then the PVDF (8-12% w/w) and PES (2-4% w/w) were added and stirred until dissolving and then Nafion® 117 solution (5% w/w) was added for a 2-4% w/w, this solution was heated at 80 °C in a bath for a homogeneous stirring.

Composite membrane preparation

The polymeric solution was applied on a glass plate by the doctor blade method and the membrane was obtained by phase inversion method in air controlled atmosphere at 60 °C in an oven for 24 h. The casting knife gap was set at 0.254 mm y 0.127 mm, to evaluate the effect of membrane thickness on properties.

Polymeric solution was heated at 80 °C to keep solution homogeneous, the glass plate and casting knife were heated at 60 °C to avoid thermal shock of polymeric solution during application and favoring a homogenous distribution of polymeric film, this was found to be a critical step during composite membranes preparation. After 24 h of phase inversion, membranes were removed from glass plate and storage in deionized water at 10 °C for further use.

2.2 Composite Nafion® 117 membranes characterization

The thickness of membrane is a very important parameter, since some mass transfer resistance effects are attributed to the film thickness. The thickness was determined with a digital micrometer Mitutoyo, model 547-400S. A dry membrane sample of 5 cm × 5 cm was cut, the thickness of the membrane was determined from the average of the thicknesses of the four corners and the center of it.

Water uptake in the ion exchange membranes is an important parameter, since the proton exchange process requires a large amount of water to coordinate with the proton as it transfers through the membrane, nevertheless, the water content also contributes to the vanadium permeation, due to the hydrophilic behavior of VO^{2+} ion. The water absorption was carried out according to the following procedure: membrane samples were cut and the excess of water was removed and the weight was recorded. Subsequently, they were allowed to dry at a constant temperature of 100 °C for 4 h and the weight was recorded. The water content was calculated by the following equation:

$$Water\ Uptake = \frac{w_{wet} - w_{dry}}{w_{wet}} \times 100 \qquad (3)$$

where w_{wet} and w_{dry} are the weight of the wet and dry membrane, respectively.

FT-IR spectra of composite Nafion® 117 membranes were recorded using an attenuated total reflectance (ATR) technique with a spectrometer Perkin Elmer (Spectrum 100) in the range of 3000-650 cm^{-1}. Spectra were acquired with a resolution of 2 cm^{-1} and 16 scans.

Thermogravimetric analysis (TGA) was performed using an instrument TA model Q600, in O_2 atmosphere. The temperature range was from 40 °C to 800 °C, with a heating rate of 20 °C min^{-1}. The SEM technique was used to observe the surface morphology of the composite membrane by a TESCAN microscope, model VEGA3. Each sample was mounted on a support with carbon tape to secure the sample. The membranes were coated with gold by sputtering (SPI Sputtering Module) at 18 mA for 180 s prior to SEM analysis. The images were obtained using an acceleration voltage of 15 kV.

The determination of surface charge density (SCD) was carried out by an acid-base titration. Firstly a piece of membrane, area 120 cm^2, was mounted on a teflon plate, then 50 mL of HCl (1.0 M) was poured on the surface of the membrane to replace the mobile counter-ions by H^+. After 2 minutes, HCl solution was discharged and the membrane was washed with deionized water until reaching the pH value of deionized water. Following, it was poured on the surface 25 mL of NaOH (0.1 M) and it was left in contact with the membrane for 2 min, after this 20 mL of this solution was taken and transferred to a flask for titration with HCl (0.1 M), using phenolphthalein as indicator (1%). The surface charge density of the membrane is reported in meq Na^+m^{-2} and was determined by the difference in the number of milliequivalents (meq) of the NaOH solution before and after being neutralized.

The proton conductivity is an important parameter that evaluates the contribution of the functional groups and the structural characteristics of the polymer matrix, such as water content and the interaction between the ionic groups towards proton conduction. The evaluation of proton conductivity was performed using the electrochemical impedance spectroscopy technique. The EIS measurements were performed in an electrochemical cell of two electrodes connected at a potentiostat/galvanostat Biologic VMP-300, where the prepared composite membranes were placed as a separator, at distance of 2 mm of each electrode, in aqueous H_2SO_4 medium. Range of frequencies was 1 MHz-10 mHz and the voltage amplitude was 50 mV. This technique provides information on resistive phenomena related to resistance of mass and load resistance involved in the processes of flow batteries. The proton conductivity can be calculated by the following equation (Sang *et al.*, 2007).

$$\sigma = \frac{d}{RS} \qquad (4)$$

where σ is the conductivity (S cm^{-1}), d (cm) is the thickness of the membrane, S (cm^2) is the area of the sample in contact with the electrodes, R (Ω) is the electric resistance of the sample.

The permeability of V(IV), through the membrane, was determined in a cell, as shown in Fig. 1, where the reservoir on the right side was filled with 200 mL of 0.1 M $VOSO_4$ in 2.0 M H_2SO_4, while in the left compartment was filled with 200 mL of 0.1 M $MgSO_4$ in 2.0 M H_2SO_4. For electrolyte solution preparation, the reagents $VOSO_4$ (purity of 97%), H_2SO_4 (purity of 95-97%) and deionized water (conductivity of 0.798 μS/cm) were used. Both compartments were at constant magnetic stirring to avoid concentration polarization.
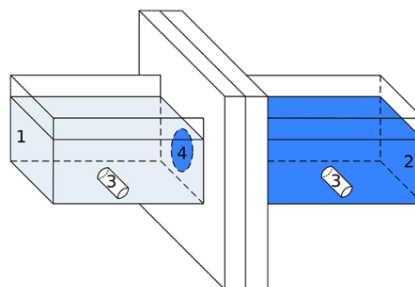

Fig. 1. Two-cell system to evaluate the vanadium permeation 1 $MgSO_4$, 2 $VOSO_4$, 3 magnetic stirrers, 4 Membrane.

The area of the membrane exposed was 28.27 cm^2. Samples were collected from the left compartment every 2 h, during the first 12 h and one last at 24 h. The concentration of V(IV) was determined with a UV Vis spectrophotometer (Varian, Cary 100 UVVis), at a wavelength of 762 nm. The relationship between the concentration of V(IV) in the left compartment, and the time can be described by the diffusion Fick's Law shown in the equation:

$$V_L \frac{dC_{L(T)}}{dt} = \frac{AP}{L}(C_R - C_{L(t)}) \qquad (5)$$

where V_L is the volume of the solution on the left compartment, A is the effective area of the membrane exposed to the solutions, P is the permeability of V(IV) through the membrane, t is the time, C_L and C_R are the concentration of V(IV) in the left and right compartments, respectively. Palomeque-Santiago *et al.* (2018) stablished that permeability and selectivity are important features in membrane processes, unfortunately, both parameters move in opposite directions, since an increase of the permeability disfavors the selectivity. Hence, the ion selectivity can be estimated by calculating the ratio between the proton conductivity (σ) and permeability of V(IV) through the membrane (P) (Fu *et al.*, 2016).

3 Results and discussion

3.1 Thickness and water uptake of composite Nafion® membranes

The thickness and percentage of water absorption of the PVDF/PES/Nafion®117 membranes are shown in Table 1. In addition, a commercial membrane of Nafion® was characterized and the results were compared with the synthesized membranes.
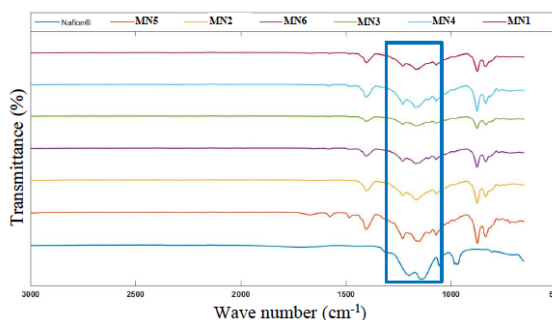

Fig. 2. FT-IR (ATR) spectra for composite Nafion® 117 membranes.

Is noteworthy that the thicknesses of the prepared membranes were considerably thinner than the Nafion® membrane, beside PVDF and PES are hydrophobic polymers. Hence, is expected that the water content value of those membranes are lower than the Nafion® membrane. From the synthesized membranes, the MN1 presented the highest water absorption and the MN4 has a lowest capacity of water absorption, this parameter is important during its application in the flow battery, since it will determine how much aqueous solution can remain inside the structure, a required condition to favor proton conductivity, this parameter is related to the porosity of the material, as well as to the chemical composition on the surface, which in turn determines the hydrophilicity/hydrophobicity of the film. The Nafion® membrane presented a relatively high value, although it is also the thickest membrane. On the other hand, when comparing the thicknesses of MN2 (40 μm) and the commercial Nafion® having similar thickness, but very different values of water absorption, this is related to the chemical composition and the morphology associated to it, since having the PVDF favors a denser structure, however the presence of PES and Nafion® 117 tends to increase the porosity and hydrophilicity of the material.
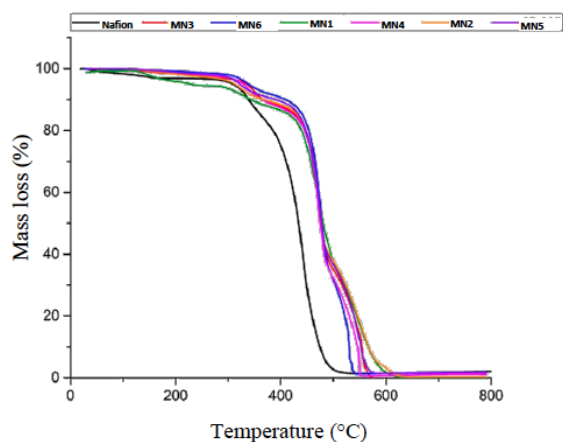
Table 1. Results of thickness and water content for composite Nafion® 117 membranes prepared.

Membrane	Chemical composition	Thickness, μm	Water content, %
MN1	(PVDF 12%/PES 2%/Nafion® 2%)	29	7.67
MN2	(PVDF 10%/PES 3%/Nafion® 3%)	40	3.32
MN3	(PVDF 8%/PES 4%/Nafion® 4%)	14	2.87
MN4	(PVDF 12%/PES 2%/Nafion® 2%)	11	1.57
MN5	(PVDF 10%/PES 3%/Nafion® 3%)	17	4.68
MN6	(PVDF 8%/PES 4%/Nafion® 4%)	6	2.87
NAFION®	Nafion®	50	15.82

Fig. 3. Thermograms for composite Nafion® 117 membranes. O$_2$ atmosphere.

3.2 FT-IR analysis

FT-IR spectroscopy was used to corroborate the differences in the surface of composite membranes due to different chemical composition of membranes. The results are shown in Fig. 2. According to the spectra of IR, all the synthesized membranes present additional signals to those of the Nafion® commercial membrane. The peaks that appear towards 835 cm^{-1} correspond to aromatic rings of PES, signals at 1485 cm^{-1} and 1576 cm^{-1} are associated with the asymmetric stretching of the C=C bond in PES (Jalali *et al.*, 2016), so the peak at 1235 cm^{-1} is related to aromatic ether stretching (C−O−C). Typical asymmetrical and symmetrical stretching peaks at 1150 cm^{-1} and 1205 cm^{-1} correspond to CF$_2$ groups of Nafion® and the characteristic signal at 1402 cm^{-1} is attributed to −CH$_2$− groups on PVDF, similarities in the FTIR spectra where founded by Kumar *et al.* (2015). Differences between FT-IR spectrum for each membrane are related to different chemical composition becoming difficult a specific assignment of all signals observed in each spectrum.

3.3 Thermogravimetric analysis

The thermal stability of the membranes was determined from the TGA (Fig. 3), the membranes were stable up to 575 °C. In comparison with the Nafion® membrane, it is observed that the thermal stability of the composite membranes increases approximately 100 °C, moreover, increasing the percentage of polymers added, thermal stability of

the membrane is enhanced. This result suggests a good interaction between the chains of polymers at the time of mixing (blend), which increases the thermal properties with respect to the polymers by themselves.

The differences in the decomposition temperatures between the composite materials are due to the different chemical composition of the polymeric solution, which suggests a good homogeneity in the structures of the composite Nafion® 117 membranes prepared.

On the other hand, a greater thermal stability of the membranes suggests greater mechanical stability. The MN1 and MN2 composite Nafion® 117 membranes showed a slightly higher decomposition temperature (~585 °C), where for MN1 is consistent to PVDF highest content in the composition, and for MN2 could be related to its thickness (40 μm), considering that this analysis implies the heat transfer in the sample.

3.4 Scanning electron microcopy

The superficial micrographs of the membranes are presented in the Fig. 4. In the micrographs the appearance of the membranes synthesized with the polymer mixtures is showed, detecting some grains smaller than 5 μm formed during the thermal treatment of phase inversion.
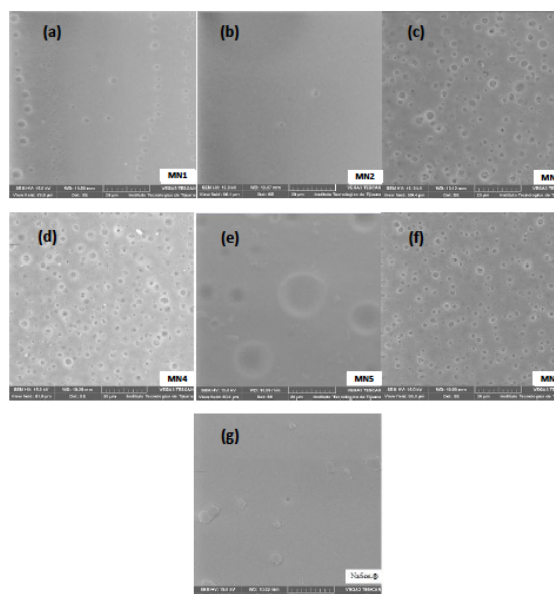

Fig. 4. SEM micrographs for composite Nafion® 117 membranes: (a) MN1, (b) MN2, (c) MN3, (d) MN4, (e) MN5, (f) MN6 and (g) Nafion®.

Likewise, it is observed that for membranes MN2 and MN5 with composition (PVDF 10%/PES 3%/ Nafion® 3%) have a more homogeneous surface structure, while for membranes MN1, MN3, MN4 and MN6 can be observed a pore-like pattern, this fact suggests that there is a greater surface apparent porosity on this membranes. These characteristics can be attributed to the chemical composition of the polymers used and to the membrane preparation method. It can be observed that in the membranes MN1 and MN4, as well as MN3 and MN6, which have the same polymeric solution composition, they show a similar morphology, independently of the thickness. However, membranes MN2 and MN5, in spite of having the same chemical composition exhibit different morphology, which is attributed to the thickness of the membrane, since a greater thickness allows the surface to have less surface tension, allowing greater formation of imperfections during phase inversion. The term surface apparent porosity refers that, even this materials, exhibit a pore-like pattern on the surface they must be internally dense, otherwise some parameter as vanadium ions crossing and proton conductivity would be too high, and results indicate the opposite. The membranes reported in this work exhibited a smoother surface compared to the SPEEK/Nafion®-based membranes reported by Seden *et al.* (2014).

3.5 Surface charge density and proton conductivity

The proton exchange capacity of the membranes is determined by two conditions; water content of the membrane and surface charge density. Table 2 shows surface charge density and proton conductivity results of the composite membranes. According to these values the membranes MN4 and MN2 showed same surface charge density than Nafion®, this characteristic favors hydrophilicity and it depends of the chemical groups in surface as well as surface roughness, nevertheless, both MN4 and MN2 exhibited low values of water content, involving low proton conductivity value. The proton conductivity results reveal that Nafion® membrane presented the highest conductivity values (0.024 S cm^{-1}), followed by MN1 (0.0023 S cm^{-1}) and MN3 (0.0012 S cm^{-1}) composite membranes, but their surface charge density values ranged the lowest values among the composite membranes. The rest of membranes showed lower proton conductivity respect to the Nafion® membrane. This indicates that the composite membranes are more resistive membranes to H$^+$ exchange, explained by the lower water content and surface charge density values respect the Nafion® membrane. This is an undesirable feature, because the VRFB performance depends on proton conductivity. Fu *et al.* (2016) reported the preparation of SPEEK/PVDF/PES membranes, those membranes exhibited proton conductivities in the order of 10^{-2} S cm^{-1}, while the membranes prepared in this work are 10^{-3} S cm^{-1}, attributed to the low conductivity nature of the PES and PVDF, compared to Nafion®.

3.6 Vanadium permeability

The permeability to the vanadium ions of the membranes is clearly shown in the Fig. 5. The membrane MN5 showed the highest V(IV) permeability, comparing with the membrane MN2 (even, this membrane does not exhibit V(IV) at the left compartment after 24 h of the operation), having same chemical composition, this result is consistent with the thickness of membranes, where MN2 is the thickest membrane.

Table 2. Results surface charge density, proton conductivity, V(IV) permeability and ion selectivity of the composite Nafion® 117 membranes.

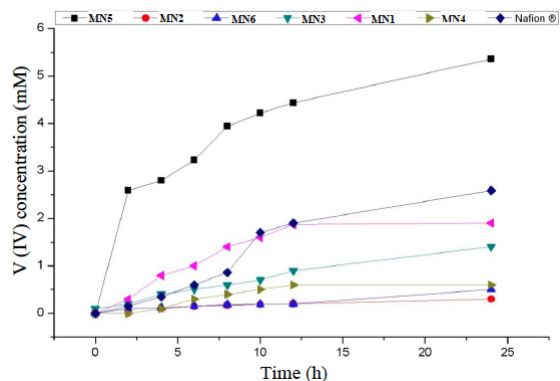| Membrane	SCD (meq Na$^+$ m^{-2})	σ (S cm^{-1})	V(IV) permeability (cm^2 min^{-1})	Ion selectivity (S min cm^{-3})
MN1	49.12	0.0023	5.3×10^{-7}	4.3×10^3
MN2	75.22	0.00063	5.8×10^{-8}	1.1×10^4
MN3	35.89	0.0012	9.3×10^{-8}	1.3×10^4
MN4	78.5	0.00054	7.2×10^{-8}	7.5×10^3
MN5	52.03	0.00036	2.7×10^{-6}	1.3×10^2
MN6	53.78	0.00032	1.4×10^{-8}	2.3×10^4
NAFION®	77.5	0.024	6.2×10^{-7}	3.9×10^4

Fig. 5. Vanadium (IV) permeability for composite Nafion® 117 membranes.

However, MN1 membrane showed a higher V permeability than MN4, both with same chemical composition, and MN1 with a higher thickness value than MN4, in this case the result could be explained considering that MN1 exhibited a better proton conductivity which reduces membrane ability to reject V ions. On the other hand, although the MN4 membrane presents a considerable value of charge density, the results of this test indicate that membrane structure plays a more important role on its performance.

The observed trend in Figure 5 is that composite membranes prepared, excepting MN5, show lower vanadium permeability than the commercial Nafion® membrane due to a combination effect of chemical composition (Nafion® 117 content), internal morphology and film thickness, so it is not possible to state how each effect contributes to the behavior observed, the vanadium permeation values of the composite membranes reported in this work were lower than the membranes reported by Fu *et al*. (2016).

It is important to point out that the vanadium permeation through the membrane implies mixed potential at the VRFB, reducing the performance due to ions crossover. It was stablished that the most important aspects that influence the performance of the membrane are the proton conductivity and the V(IV) permeability. In order to evaluate the performance of the membranes the ion selectivity, which relates both parameters, was calculated. Table 2 shows that the V(IV) permeability value of MN2 and MN6 is too low, however, the proton conductivity value is too low. On the other hand, MN3 and MN4 showed an intermediate V(IV) permeability value, however, the proton conductivity value of MN3 membrane is higher than the other composite membranes. Ion selectivity

value of MN2, MN3 and MN6 composite membranes are competitive with the value of the membranes reported by Fu *et al*. (2016).

Conclusions

In this article the preparation of composite membranes with different chemical compositions and thickness is reported. Membranes were prepared by phase inversion method and were compared with the commercial Nafion® membrane to determine feasibility of these new membranes as possible option to VRFC application. The composite membranes were prepared incorporating Nafion® 117 (at 2%, 3% and 4% w/w) as component to provide proton conductivity and also to reduce the cost of membrane by decreasing the quantity of this high-cost polymer in membrane. During polymer solution preparation it was found necessary to heat the solution to get a homogeneous solution, as well during the membrane casting-step it was very important proceed at temperature of 60 °C to avoid defects during polymeric film distribution due to viscosity changes of polymeric solution.

It was possible to implement a reproducible method for composite membranes preparation, in terms of thicknesses. The membranes produced are thinner and more selective to the vanadium crossover than the commercial Nafion® membrane. SEM micrographs reveal differences on composites membranes surfaces showing a pore-like pattern, this is an evidence of different phase inversion mechanism, even when the same synthesis conditions were kept, suggesting an important effect of the chemical composition of polymeric solution on preparation method.

Commercial Nafion® membrane resulted with the highest proton conductivity, determined by EIS technique, in comparison to the composite Nafion® 117 membranes prepared. From composite membranes, MN1 and MN3 exhibited the highest proton conductivity, with values one order of magnitud lower than commercial membrane; however synthetized composite membranes showed lower vanadium permeability and an expected lower processing cost. In order to evaluate the membranes, ion selectivity relates both parameters: proton conductivity and V(IV) permeability, in that case MN2, MN3 and MN6 exhibited a remarkable ion selectivity value, becoming in potential candidates for their usage in VRFB application.

Finally results suggest that for VRFB application the prepared composite Nafion® 117 membranes could reduce the power density but it could increase the useful lifetime of the device.

Acknowledgements

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