

Electrochemical evaluation of membranes of poly-[styrene-co-acrylic acid] for use in PMFC

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ABSTRACT

Nanotechnology allows to create and implement materials, structures and systems by mounting and manipulating in atomic and molecular scale. New effects observed on the nanometer scale are explored in this study for the development of membranes for application in fuel cells (PMFC). It has been observed that the incorporation of metal nanoparticles of gold, silver, among others, in polymeric matrices increases the thermal stability of the membranes. This is desirable since the catalytic activity of the catalysts employed in cells is associated with operating temperature. In this study we report the preparation and electrochemical characterization of polymeric membrane of poly-(styrene-co-acrylic acid) *sulfonated* (poly-(StS-co-AA)) for application in PMFC. Poly-(styrene-co-acrylic acid) (poly-(St-co-AA)) was prepared in the ratio 92:8, followed by sulfonation with H₂SO₄. Electrodes of Pt/poly-(StS-co-AA) were prepared by casting from a polymer solution deposited on its surface. The polymer films were characterized by cyclic voltammetry and electrochemical impedance spectroscopy in acidic and neutral environment. Cyclic voltammograms were recorded in 0.5 mol.dm⁻³ KCl solutions and was observed the presence of redox processes attributed to the H⁺ ions. The microstructural characterization was performed by atomic force microscopy

Keywords: Electrochemistry; membranes; fuel cells



1. Introduction

Many researchers are studying alternative technologies for the production of energy efficient and low cost, due to a future crisis in the energy sector. By a search for ways of generating clean and sustainable energy, the study and production of fuel cells is very promising, with several models developed and described in literature [1-8].

Fuel cells are electrochemical devices that consume hydrogen and oxygen to produce electricity [2,6]. Also called continuous battery operation, they produce direct current by electrochemical cold combustion of a gaseous fuel, usually hydrogen, being viable for stationary power generation [9]. Cells with low operating temperature, using a polymer membrane as the electrolyte, also called PEMFC (Proton Exchange Membran Fuel Cell), are promising as an alternative to research and development of techniques derived from clean technology with low emissions, high chemical, efficiency electric conversion, robustness, easy to drive and shutdown [9,10].

In a fuel cell system type PEMFC, supplied with hydrogen and oxygen are conducted two partial electrochemical reactions in two electrodes separated by a polymer electrolyte, forming water as a product of the overall reaction and generating electric and thermal power with high efficiency [3].

The development of membranes produced with nano polymeric materials for application in fuel cells, is increasingly being investigated for the generation of clean energy is a challenge to be pursued [5, 11, 12]. By having a low operating temperature, it is possible to emit zero NO_x as the use of these cells.

Aiming at technological interest is possible to combine the electrical conductivity of conducting polymers with the mechanical properties of conventional polymers [13]. The use of polystyrene (PS) is due to the fact that it is one of the most known thermoplastic in the plastics industry and the sulfonating process has been used for efficiency and versatility for obtaining polymers seen introducing polar substituents capable of increasing the hydrophilicity and conductivity of the membrane [4, 14, 16]. Therefore, this work describes the preparation and characterization of conducting membranes poly [styrene-co-acrylic



acid] sulfonated for use in fuel cells as alternative energy source. The Figure 1 illustrates a fragment of chain poly-(StS-co-AA).

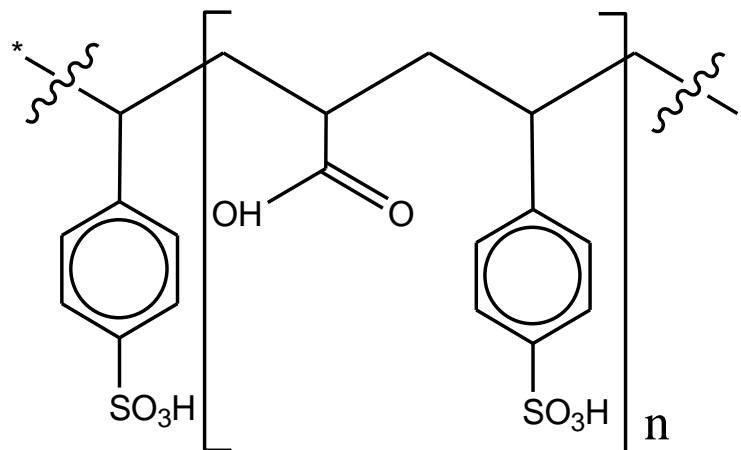


Fig 1. Schematic representation of poly-(StS-co-AA).

2. Experimental

Reagents and solvents were purchased from various commercial sources and used without further purification. The only exception was the Styrene (Sigma-Aldrich) that was previously purified by adding 10 ml of 2 mol.dm⁻³ solution of NaOH in 100 mL of monomer under stirring. This procedure was repeated until the styrene became transparent. After, the styrene was washed with distilled water until pH 7.0. Then, the monomer was dried with CaSO₄ under stirring for 3 hours and filtered. The procedure was repeated three times. Finally, the styrene was distilled under reduced pressure and protected from light.

The poly-(St-co-AA) was prepared by radical chain copolymerization in bulk, using benzoyl peroxide as initiator and 98:2 molar ratio of styrene and acrylic acid, respectively, as described previously [17]. The reaction medium was precipitated in methanol, washed with distilled water and dried under reduced pressure for 24 h. The poly-(St-co-AA) was sulfonated using H₂SO₄ as sulfonating agent and purified as previously described [17].

Polymer films surface were characterized by atomic force microscopy employing a Scanning Probe Microscope - SHIMADZU, model SPM-9700. The vibrational spectra of the films were recorded with a FT-IR - Shimadzu, model IRAffinity-1

Modified electrodes were prepared by casting, depositing 10μl of a copolymer solution (10mg/mL) in THF on the surface of a Pt disk electrode and allowed to dry at room temperature for 24 h to complete evaporation of the solvent. Previously, the electrode was mechanically polished followed by electropolishing in H₂SO₄ 0.5 mol.dm⁻³ using cyclic voltammetry technique. All electrochemical experiments were performed with a potentiostat / galvanostat - Biologic, model SP-200, using a typical three-electrode cell. All measurements



carried out on inert argon atmosphere. A commercial Pt disc electrode (0.018 cm^2) was used as working electrode; Saturated Calomel Electrode (SCE) as reference electrode; a Pt wire as auxiliary electrode. All data were acquired and treated with EC-Lab® software V10.23.

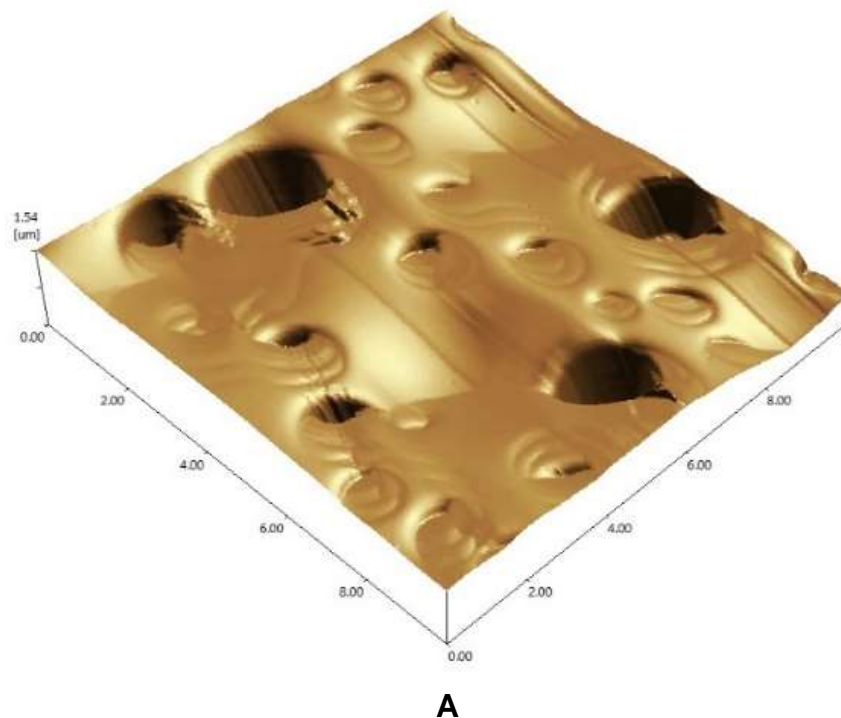
To evaluate the electrochemical properties of modified electrodes were used aqueous solutions of KCl 0.1 mol.dm^{-3} and H_2SO_4 0.5 mol.dm^{-3} as electrolytic medium. The modified electrodes were kept in KCl solution and the E_{oc} was monitored until achieve the equilibrium between Pt || film || solution interfaces

3. Results and discussion

The yields for the synthesized poly-(St-co-AA) and poly-(StS-co-AA) were 40.5% and 80.0%, respectively. Comparing the vibrational spectra FTIR between poly-(St-co-AA) and poly-(StS-co-AA), was observed the maintenance of the main vibratio

nal modes relative to styrene and acrylic acid after the sulfonation reaction. However, the sulfonated copolymer shows a stretching which ν in $3500\text{-}3100 \text{ cm}^{-1}$ corresponding to $-\text{SO}_3\text{H}$ groups in the polymer matrix.

The atomic force microscopy images of poly-(St-co-AA) and poly-(StS-co-AA) films showed marked morphological differences, as can be seen in Figure 2.



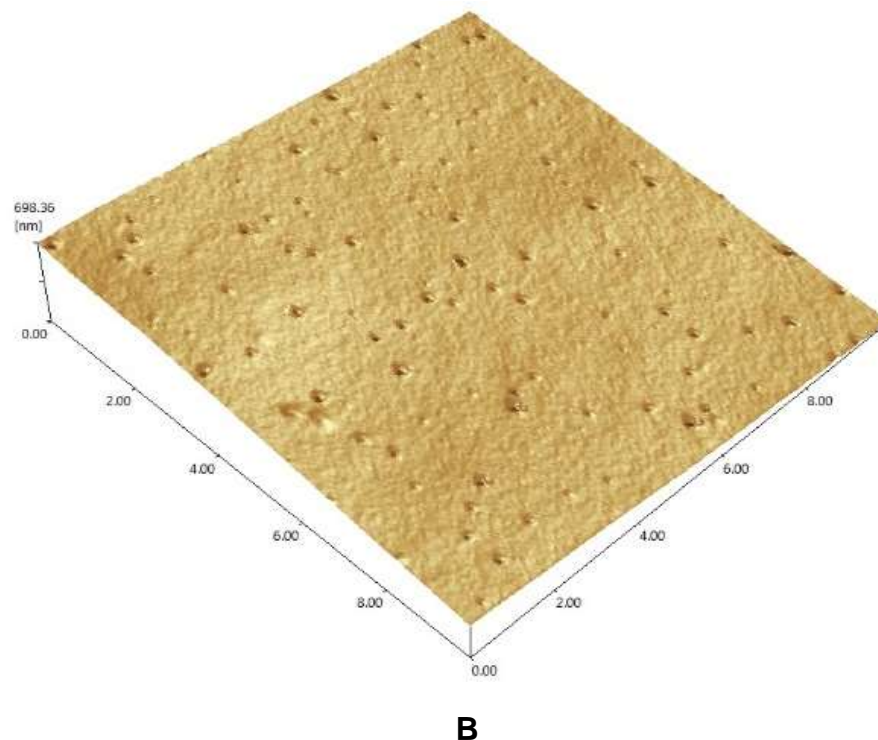


Fig 2. Pictures of films of poly-(St-co-AA) (A) and poly-(StS-co-AA) (B) from Atomic Force Microcopy.

The sulfonated copolymer (Fig. 2B) shows a much more regular and uniform surface, without the presence of "craters", when compared to non-sulfonated copolymer (Fig. 2A). A possibly explanation about it is the presence of sulfone groups increases the hydrophilicity of the material, reducing the rate of evaporation of the solvent. This leads to the formation of a layer more homogeneous and uniform than in the case of poly-(St-co-AA).

A Pt electrode coated with poly-(St-co-AA) was maintained in KCl 0.1 mol.dm⁻³ and the E_{oc} vs time monitored until to achieve the equilibrium in the Pt || Film || Solution interface. Then, the voltammetric profile was recorded in the range of 1.0 V to -1.0 V vs. SCE at a scan rate of 50 mV.s⁻¹. No redox process could be observed in this range, even after 24 h of immersion. This is an indicative of the film stability in solution.

The ionic permeability through the film was measured by transferring the electrode into a K₃[Fe(CN)₆] 0.05 mol.dm⁻³ + KCl 0.1 mol.dm⁻³ solution. Differences between the E_{pa} and E_{pc} values and the respective I_{pa}



and I_{pc} are observed in the voltammetric profiles recorded at different immersion times and presented in Figure 3.

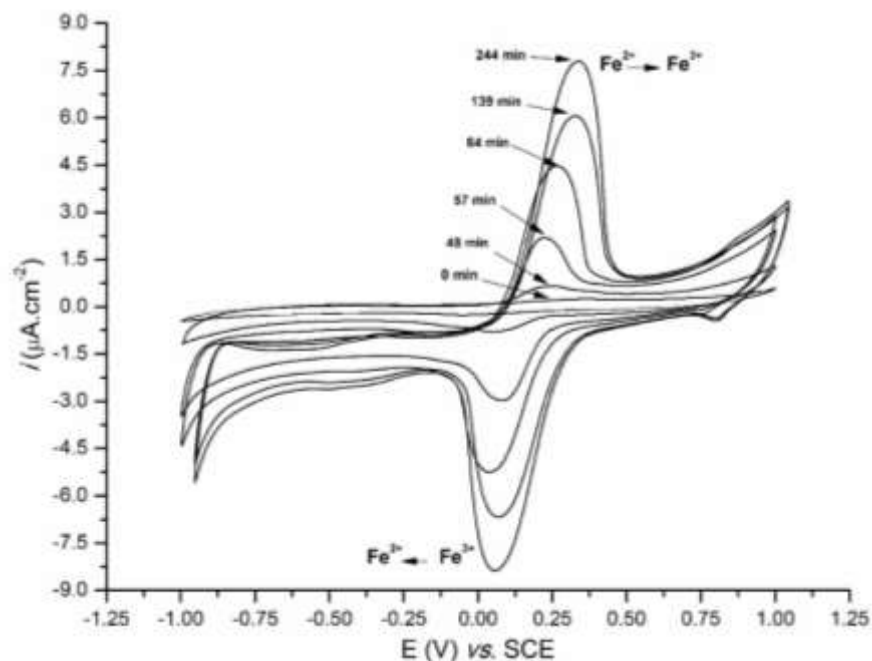


Fig 3. Cyclic voltammograms of $K_3[Fe(CN)_6]$ 0.05 mol.dm⁻³ KCl 0.1 mol.dm⁻³ of Pt electrode modified by poly-{ST-co-AA}. Reference: SCE. Scan rate 50 mV.s⁻¹.

The current of cathodic and anodic peak increases with the immersion time, but more sharply in the first hour. The $E^{1/2}$ remains constant and independent of immersion time. The ΔE_p is 280 mV, well above the value observed for the voltammetric profile for the $K_3[Fe(CN)_6]$ recorded on a Pt electrode unmodified.

In part, this should be associated to the uncompensated film resistance. Additionally, one may take into account, possible concentration gradients near to the Film || Electrode interface, where the concentration of



electroactive species is greater. Such differences in the chemical environment can influence the diffusion processes of the oxidized and reduced species within the polymer matrix.

A study of the scan rate dependence was performed in the range of 25 to 500 $\text{mV}\cdot\text{s}^{-1}$ and the obtained cyclic voltammograms are shown in the Figure 4.

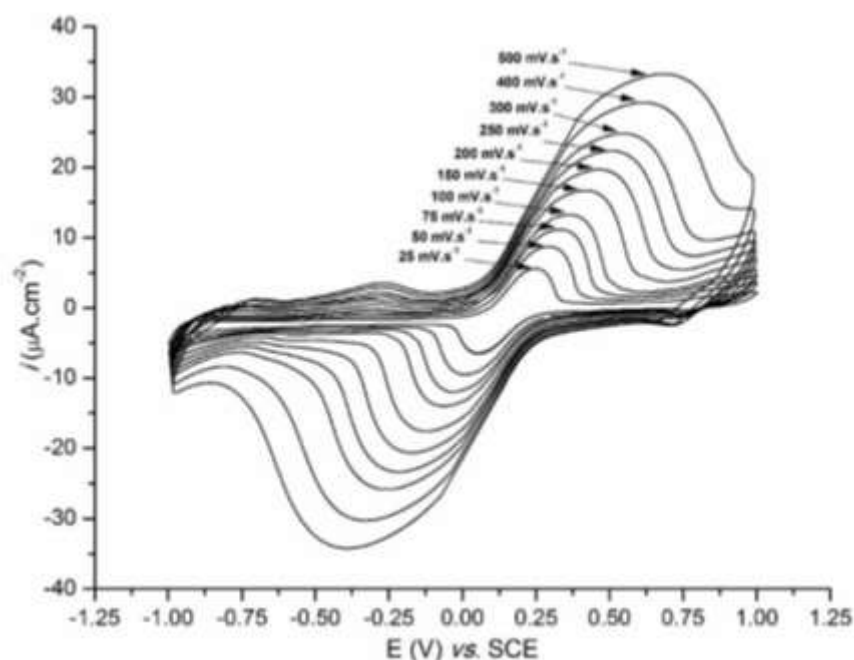


Fig 4. Cyclic voltammograms of $\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.05 $\text{mol}\cdot\text{dm}^{-3}$ KCl 0.1 $\text{mol}\cdot\text{dm}^{-3}$ of Pt electrode modified by poly-{ST-co-AA} recorded at different scan rates. Reference: SCE.

The plot of I_{pa} and I_{pc} vs. the square root of the scan rate is linear and with intercepts at zero, ie, follows Randles-Sevcik equation, as can be seen in Figure 5. This is typical for a limited diffusion system. In addition,



the $E^{1/2}$ is constant and independent of the scan rate. However, ΔE_p increases with increasing scanning speed [18].

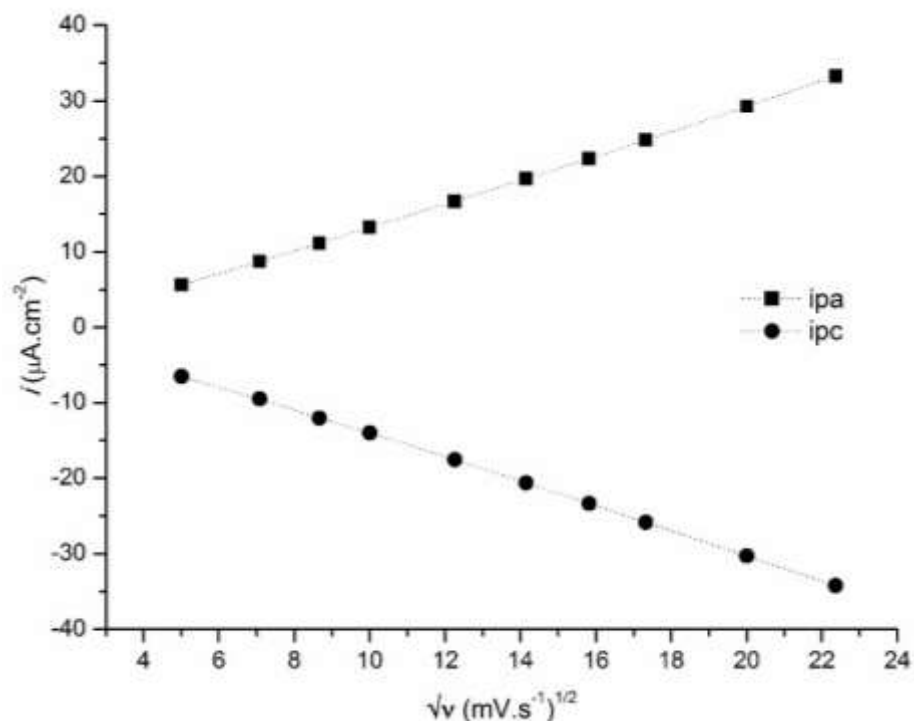


Fig 5. Plot of current of anodic and cathodic peak as a function of the square root of the scan rate corresponding to the cyclic voltammograms shown in Figure 4.

In order to evaluate the protonic permeability, cyclic voltammograms of electrodes modified by poly-(St-co-AA) and poly-(StS-co-AA) were recorded in H_2SO_4 0.5 mol.dm^{-3} solution and compared to a voltammetric



profile of unmodified Pt electrode. Figure 6 corresponds to CV of the three electrodes and clearly show five distinct regions.

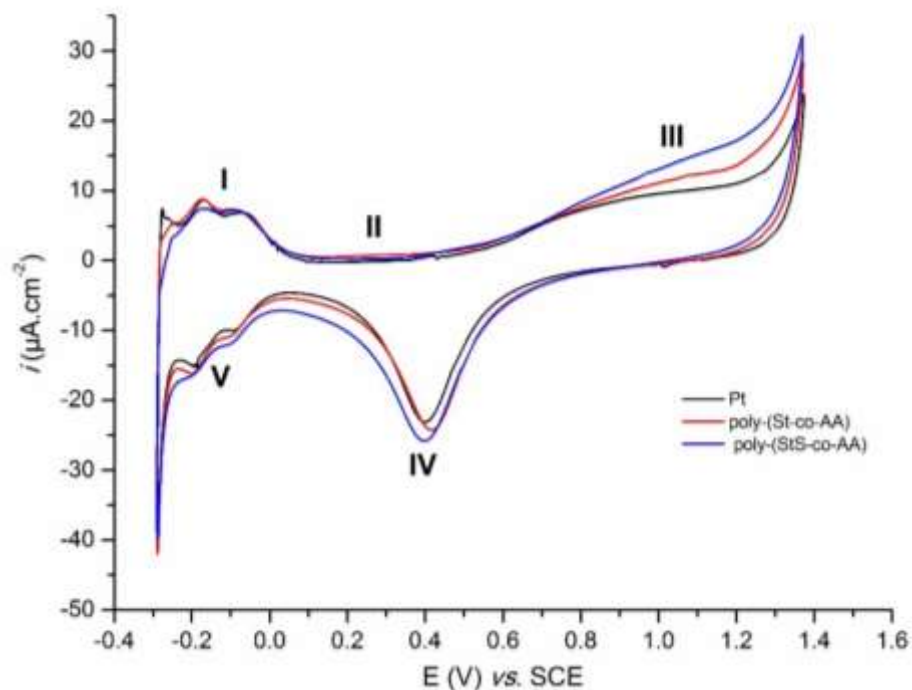


Fig 6. Cyclic voltammograms of (—) Pt, (—) poly-(ST-co-AA) and (—) poly-(STS-co-AA) electrodes in H_2SO_4 0.5 mol.dm⁻³. Scan rate 50 mV.s⁻¹.

The regions I and V corresponding to oxidation and redeposition of atomic hydrogen; Region IV is attributed to the formation of surface oxide on platinum. Region II corresponds to the double charge layer and the region III corresponds to adsorption of OH⁻ and its respective oxidation [18]. By comparing the three curves, it turns out that the regions II, III and IV does not show substantial differences. In addition, differences in regions I and V are very subtle, indicating that the active sites of platinum were not blocked. The relationship between the charges involved in redox processes attributed to oxidation and reduction of atomic hydrogen (I and V) are preserved in the three electrodes and are close to unity, even after more than 50 scan cycles. This shows that both copolymers are permeable to H⁺ ions and stable in acid medium, which is



desirable to membranes for use in fuel cells. These results are in agreement with images of atomic force microscopy, showing an excellent surface coating of the electrodes.

In order to demonstrate that the presence of sulfone group enhance proton conductivity, there was a cyclic voltammogram of an electrode modified by poly-(StS-co-AA) in KCl 0.1 mol.dm⁻³.

The modified electrode by poly-(St-co-AA) shows no redox process in KCl solution in the range between -1.0 V and 1.0 V vs. SCE. By other hand, the redox processes for the modified electrode with poly-(StS-co-AA) can be seen in the Figure 7.

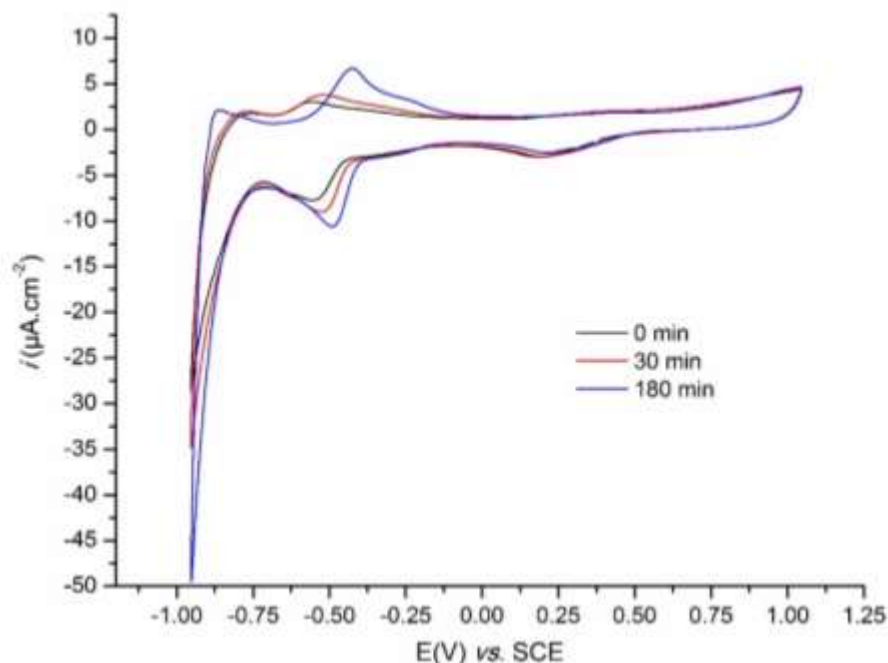


Fig 7. Cyclic voltammograms for a film of poly-(StS-co-AA) in KCl 0.1 mol.dm⁻³ in different immersion times. (—) 0 min., (—) 30 min. and (—) 180 min. Scan rate 50 mV.s⁻¹.

Shortly after KCl immersion, the voltammetric profile showed a redox process with $E^{1/2}$ in -0.55 V and $\Delta E_p = 0.3$ mV, which is much lower than expected by the Nernst equation for a reversible redox process. In this case, the shape of the voltammetric sine wave is characteristic of monolayer adsorption processes. It is reasonable to assume that these processes result from the ionization of protons from the -SO₃H groups. After 30 minutes of dipping, the $E^{1/2}$ shifts to the more positive potential region, close to -0.52 V and presenting $\Delta E_p = 8$ mV. Finally, after 180 min of immersion the $E^{1/2}$ stabilizes at -0.46 V and $\Delta E_p = 66$ mV. This change in the voltammetric profile can be explained by the slow ionization of the -SO₃H groups.

To confirm this hypothesis, the modified electrode was transferred to a basic solution of NaOH. After 30 minutes of immersion, the electrode was rinsed in distilled water and a new cyclic voltammogram was



recorded in KCl. One could note the suppression of the voltammetric waves observed in the Figure 8, regenerating a characteristic voltammetric profile of an electrode modified by poly-(St-co-AA).

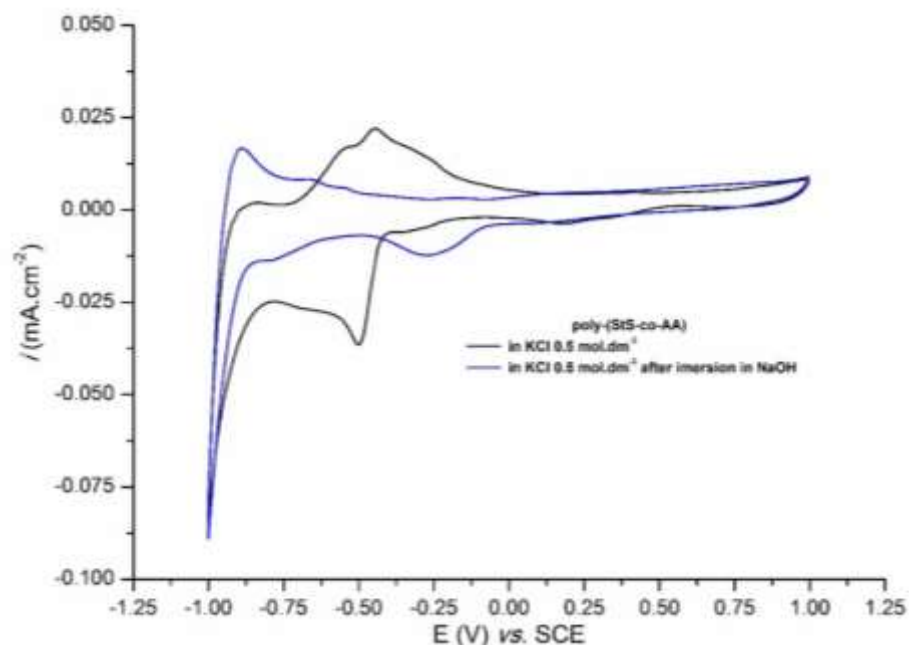


Fig 8. Cyclic voltammograms for a film of poly-(StS-co-AA) in KCl 0.1 mol.dm⁻³ (—) and in KCl 0.1 mol.dm⁻³ after immersion in NaOH (—). Scan rate 50 mV.s⁻¹.

The impedance diagrams of an electrode modified by poly-(StS-co-AA) in KCl 0.1 mol.dm⁻³ recorded in the potential E = 0.0 V vs. E_{oc}, E = -1.0 V and 1.0 V vs. SCE can be observed in Figure 9.



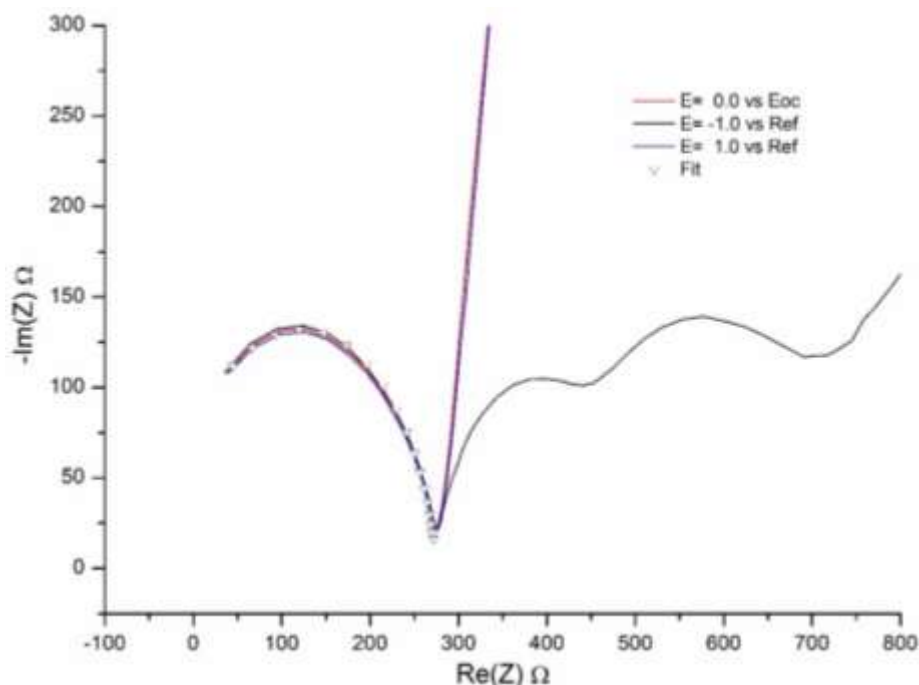


Fig 9. Nyquist Plot for a film of poly-(STS-co-AA) in KCl 0.1 mol.dm⁻³ at different potentials: 0.0 V vs. E_{oc} (—); -1.0 V vs. SCE (—); 1.0 V vs. SCE (—) and fit (Δ).

In all Nyquist impedance occurs the presence of capacitive arc in the region of high frequencies, that can be adjusted to the equivalent circuit showed in Figure 10. The circuit consists of a resistor R_1 in series with a resistor R_2 which is in parallel with a constant phase element Q_2 .

The impedance of Q_2 is obtained by equation: $Z(Q_2) = Q_2^{-1} i \omega^{-a}$, where Q_2 is a factor of proportionality, and "a" expresses the phase shift. When the value of "a" assumes values between 0.8 and 1, the element of



constant phase Q_2 corresponds a capacitance distortion due to surface roughness or a distribution/accumulation of charge carriers.

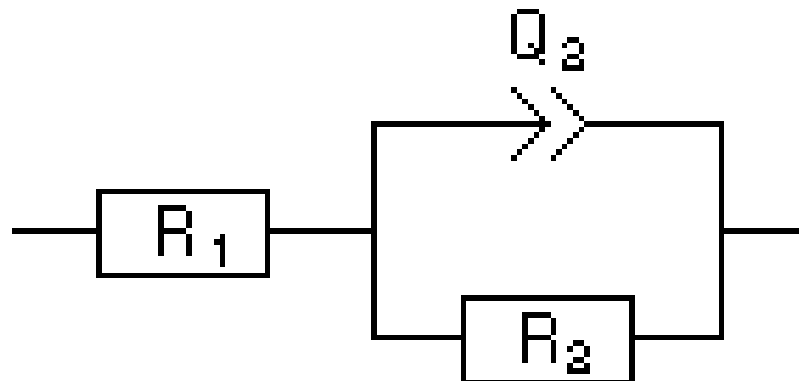


Fig 10. Schematic representation of the proposed equivalent circuit.

The values of the elements of circuit of Figure 10, obtained from the mathematical fit, are: $R_1 = -32.09$ Ohm; $R_2 = 307.00$ Ohm; $Q_2 = 2.33 \text{ nF.s}^{(a-1)}$, where $a = 0.90$.

Finally, the two capacitive arcs shows in the low frequency region can be attributed to the electrochemical diffusional process that occurs between the Pt||Film and Film||Solution interfaces.

4. Summary and perspectives

In this work we show that poly-(StS-co-AA) is an electroactive polymeric material and can be used like permeable membrane fuel cell due the considerable protonic conductivity.

Acknowledgements

This work was supported by grants from the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Universidade do Extremo Sul Catarinense UNESC). The authors would also like to thank CNPq and UNESC for their fellowship support.



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