

Electrochemical Studies of Poly(styrene-co-acrylic acid) PEM Membranes Synthesized by two Different Methods

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ABSTRACT

The synthesis of two alternatives to Nafion random copolymers was carried out by radical copolymerization. Poly(styrene-co-acrylic acid) (PSAA) in a 94:6 styrene-acrylic acid molar relation, partially cross-linked with trimethylol propane trimethacrylate (TMPTMA) was synthesized by mass polymerization. The PSAA obtained was sulfonated (PSAAS-m) with sulphuric acid, considering the 100 % molar substitution of styrene benzene rings. Separately, same random PSAA was synthesized by solution polymerization, but cross-linked with Divinylbenzene (DVB) and sulfonated (PSAAS-s) with acetyl sulphate at a 20 % molar substitution with respect to benzene rings. Copolymers, including non sulfonated blanks, were dissolved in THF and used to coat a platinum (Pt) electrode by "deep coating" and studied electrochemically by the voltamperometric cycle technique in H₂SO₄ 0.5 M. Both non-sulfonated PSAA copolymers showed only a baseline signal, indicating no proton conductivity through them. Similarly was observed for the PSAAS-s copolymer, suggesting no proton conductivity as well. On the other hand, the copolymer synthesized in mass and highly sulfonated (PSAAS-m) showed the corresponding signals of Pt reduction, as observed in the experiment carried out for the Pt electrode without any coating.

Keywords: sulfonated PSAA, fuel cells, Pt electrode.



1. Introduction

Fuel cells (FC) have the potential to become an important energy conversion technology. It is believed that FC are the next generation of solution for stationary energy supply systems, portable electronics and motor vehicles. With hydrogen as fuel, this technology is environmentally friendly, since power generation involves the reaction of hydrogen oxidation and oxygen reduction. Such reaction has water as the only one byproduct [1].

Among the different family types of FC's, one of the most important is the Proton exchange membrane fuel cells (also named as "polymer electrolyte membrane"-PEM). The PEMFC are the most attractive candidates for applications in the automotive and portable electronics industry [2], [3], due to their advantages as reduced corrosion, mechanical simplicity, quick implementation, high efficiency, modularity and versatility.

The heart of a PEMFC is the polymeric membrane, which in turn must have some specific capabilities such as high proton conductivity, a suitable barrier to fuel mixture and reactant gases, as well as being chemically and mechanically stable in the demanding environment of the FC.

Commercial membranes of PEMFC are basically made of poly(perfluorosulfonic acid) (PFSA) and the most popular is the Nafion from DuPont. Nowadays some other makers have developed similar materials, as Flemion made from Asahi Glass or Aciplex from Asahi Chemical; all of them are highly expensive [4]. An alternative to this kind of membranes, are the hydrocarbonated copolymers. This materials are cheaper, commercially available comonomers, and their structure allow the introduction of polar sites, like hanging groups, with the intention of increasing the water absorption an ionic conductivity [5].

Electrolytic polymers and copolymers has been developed to replace PFSA membranes, as the poly(styrene-acrylic acid) (PSAA) sulfonated to enhance ion conductivity, and crosslinked with divinyl benzene (DVB) or trimethylol propane trimethacrylate (TMPTMA) [6], [7], [8].

In this work, two different random PSAA copolymers were synthesized and both cross-linked. One of them was synthesized via mass polimerization, sulfonated with sulfuric acid at 100 % molar substitution with respect to benzene rings and crosslinked with TMPTMA and the other was synthesized in solution, crosslinked with DVB and sulfonated with acetyl sulfonate at a 20 % molar substitution with respect to benzene rings. Electrochemical studies were carried out for both for inter-comparison.

2. Experimental

2.1 synthesis and sulfonation of mass copolymer (PSAAS-m)

The synthesis was carried out in a glass reactor with mechanical stirring at 250 rpm, 100 °C and inert atmosphere of nitrogen during 2 hours. The molar ratio was 94:6 of styrene-acrylic acid. The amount of BPO (benzoyl peroxide) initiator was of 0.05 % molar and 0.01 % molar of the crosslinking agent TMPTMA. Acetone was added to finish the reaction and 5 minutes after methanol was added to precipitate the copolymer. The material was finally vacuum dried at 40 °C.

The sulfonation procedure was carried out in the same glass reactor. 6 g of copolymer were dissolved in dicloromethane (DCM) at 40 °C and then the sulfonant agent (sulfuric acid 98 %) was added in a molar ratio of 100 % with respect to benzene rings. Atmosphere, time and stirring conditions were the same used during the copolymerization reaction.



2.2 Synthesis and sulfonation of solution copolymer (PSAAS-s)

This copolymer was synthesized using the same molar ratio of styrene-acrylic (94:6). The reaction was carried out via polymerization in solution of diethylbenzene, BPO 0.045 % molar as initiator and DVB (divinyl benzene) as crosslinking agent in a 0.25 % molar concentration. The reaction was carried out in a reactor at 200 rpm and 90 °C during 2 hours in a nitrogen atmosphere. Methanol was added to finish the reaction after the 2 hours of polymerization time. The copolymer was dissolved in THF and precipitated again in methanol and finally dried at 65-70 °C under vacuum during 48 h.

The sulfonation process was carried out by using acetyl sulphate in a 20 % molar ratio of the theoretical benzene rings in the copolymer. This reaction was carried out in the same reactor at 200 rpm dissolving the copolymer in DCM during 40 minutes at 40 °C and then adding the sulfonation agent during a reaction time of 30 minutes.

2.3 FTIR characterization

Infrared spectroscopy was used to verify that synthesized copolymers contained the comonomers and sulfonic species in its chemical structure. A Nicolet 6700 spectrophotometer was used to analyze films, with 25 scans and a resolution of 4 cm⁻¹.

2.4 Electrochemical studies

With the general idea of investigating the capacity for proton conductivity of the materials, the unsulfonated and sulfonated materials were analyzed. A H₂SO₄ 0.5 M electrolytic cell was used for measurements through the voltamperometric cyclic technique in the potentiostat at 100 mV/s. The copolymers were dissolved in THF and used to coat a Pt electrode by the “deep coating” technique. The uncoated Pt electrode was also analyzed in the same conditions. Figure 1 shows images of the Pt electrode before and after coating with PSAAS-m.

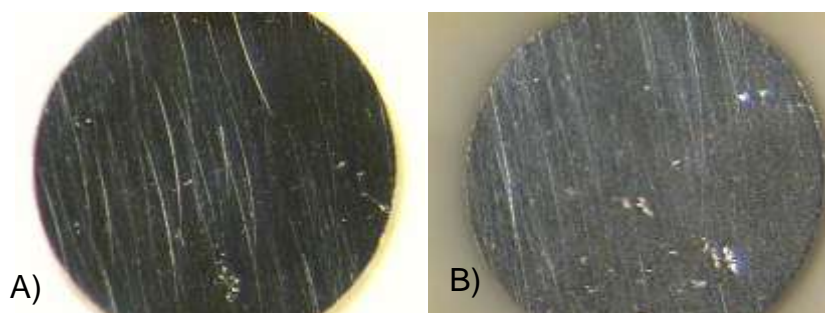


Figure 1. 40x image of Pt electrode: A) coated whit PSAAS-m; B) uncoated.



3. Results and discussion

The copolymers synthesized were analyzed by FTIR to corroborate their composition. Figures 2 and 3 show the corresponding spectra for the materials PSAA-s, PSAAS-s, PSAA-m and PSAAS-m. The characteristic C-H bands from benzene rings of styrene at $3000\text{--}3100\text{ cm}^{-1}$ are clear to see for both figures, as well as the characteristic aromatic overtone absorptions at the region of $1800\text{--}1900\text{ cm}^{-1}$. There is also a series of signals in 2925 cm^{-1} corresponding to the asymmetric and in 2852 cm^{-1} the symmetric elongation of CH_2 signals corresponding to the presence of the vinyl part of styrene and to the acrylic acid. The latter is also seen in the 1740 cm^{-1} carbonyl signal. Spectra identify the copolymer of styrene/acrylic acid.

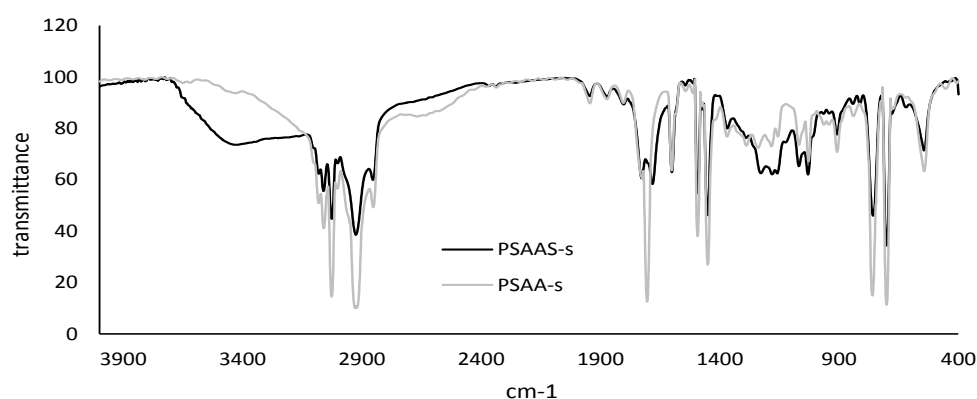


Figure 2. FTIR of PSAA-s and PSAAS-s

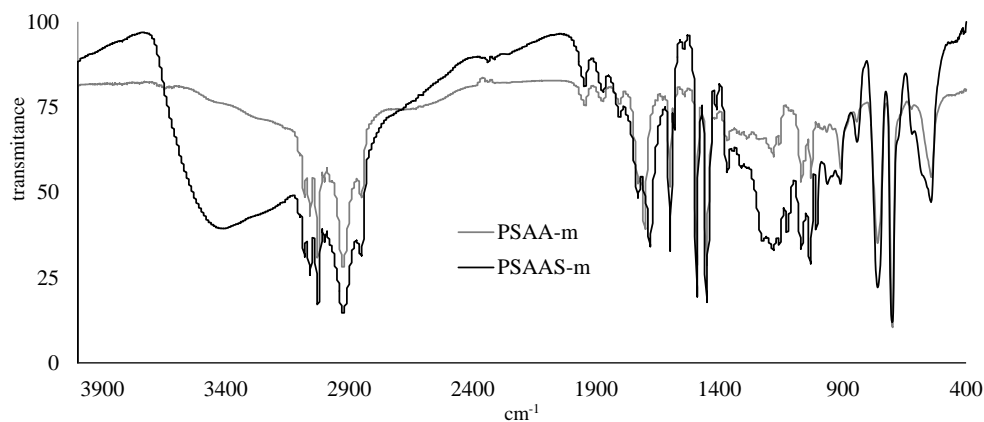


Figure 3. FTIR of PSAA-m and PSAAS-m

The main difference between the sulfonated and unsulfonated copolymers is a broad band in the region of $3100\text{--}3400\text{ cm}^{-1}$, indicating the presence of the OH groups, which in turn confirms the incorporation of



the sulfonic groups (SO_3H). The absorptions between $1290\text{--}1390\text{ cm}^{-1}$ corresponding to the SO_2 group indicate sulfonation of the copolymers as well.

Figure 4 shows the corresponding voltamperogram for the uncoated Pt electrode. A typical sequence of Pt oxidation/reduction trace in a sulfuric acid media is seen; oxidation from $0\text{--}700\text{ mV}$ and reduction from $300\text{ to }-450\text{ mV}$. Small signals at the region of $-400\text{ to }-700\text{ mV}$ correspond to hydrogen adsorption [9].

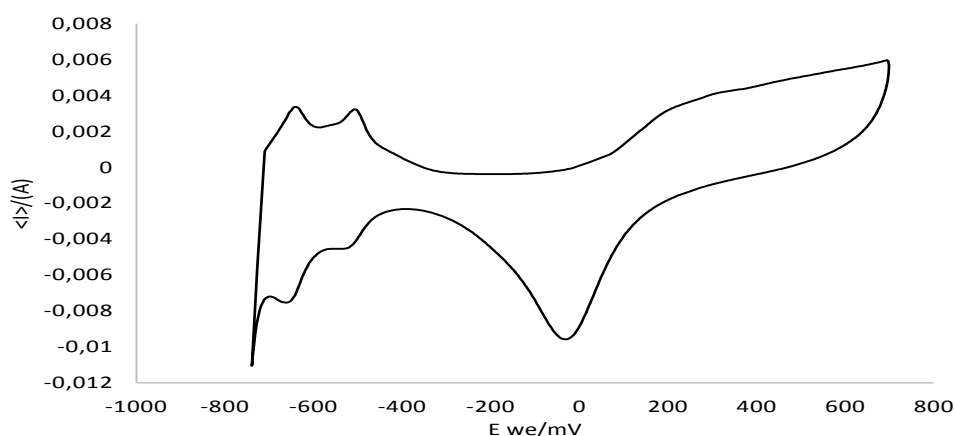


Figure 4. Voltamperogram of uncoated Pt electrode.

Figure 5 shows the same voltamperograms for the Pt electrode coated with the copolymer synthesized by mass copolymerization, before (PSAA-m) and after (PSAAS-m) sulfonation; the uncoated electrode trace is placed for comparison. It is very clear to see that unsulfonated material does not allow protons from the electrolytic cell go through for the redox reaction of the Pt electrode to take place. However, for the case of sulfonated copolymer (PSAAS-m), a very similar trace to the uncoated electrode is seen, indicating the ability of the material for proton transportation to reach the electrode [10].

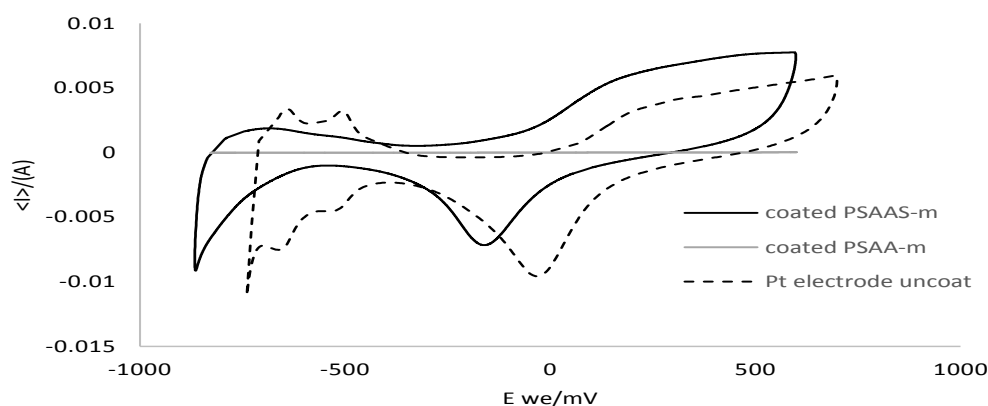


Figure 5. Voltamperograms of uncoated Pt electrode and coated with PSAA-m and PSAAS-m.



On the other hand, the results obtained for the copolymer synthesized by solution copolymerization are shown in Figure 6. The voltamperogram corresponding to the uncoated electrode is placed for comparison and the sulfonated copolymer (PSAAS-s) does not show any redox reaction for the Pt in the electrode. There seems to be a series of side reactions occurring during the copolymerization reaction in the solvent media, which in turn alter the sulfonation reaction and reduce its proton conductivity [11]. It has to be considered as well, that sulfonation was taken only to 20 % of theoretical benzene rings, while for mass copolymer it was taken to 100 %, and obviously the amount of sulfonic groups needed for proton conduction is considerable reduced in the copolymer structure.

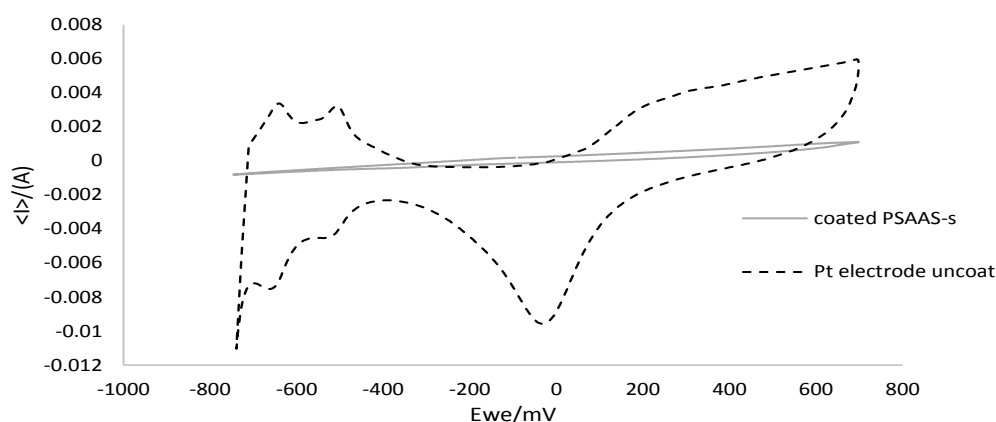


Figure 6. Voltamperograms of uncoated Pt electrode and coated with PSAAS-m.

4. Conclusions

Two styrene/acrylic acid copolymers were prepared by mass and solution copolymerizations reactions and then sulfonated for giving proton conductivity characteristics. Voltamperometric measurements with a Pt electrode coated with copolymers indicate that the material prepared by mass reaction has proton conductivity enough to allow redox reactions in the Pt electrode, while solution copolymer does not have enough proton conduction. The latter as a result of possible secondary reactions during copolymerization and to the low level of sulfonation in the material.

Acknowledgements

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