Open Research Online

Synthesis and characterisation of polyaniline (PAni) membranes for fuel cell

Franco D.R. Amado[*1,2], **Satheesh Krishnamurthy**[2]

[1]PROCIMM, State University of Santa Cruz, Rodovia Jorge Amado, km 16, Ilhéus - Bahia - Brasil
[2]Materials Engineering, Department of Engineering and Innovation, The Open University,
Milton Keynes, MK7 6AA, United Kingdom

[*]Corresponding author. Tel: (+44) 1908654636; E-mail: fdramado@uesc.br

ABSTRACT

Over the past decade or so, alternative energy plays a pivotal role in addressing challenges posed by nature. Polymer electrolyte membrane fuel cell is one of the promising alternative energy and there has been significant research and technological investments done in this field. The key information and future prospective of the field is energy conversion and storage, both of which are essential in order to meet the challenges of global warming and the limited fossil fuel supply. However, polymer membrane in particular plays a crucial role in advancing this technology further. The utilization of conducting polymers in manufacturing membranes combining their electrochemical properties along with mechanical properties is of primary importance to enhance the efficiency of this system. In the present study blends of high impact polystyrene (HIPS) and polyaniline (PAni) were obtained with the aim of producing membranes for fuel cell. HIPS and PAni were dissolved in tetrachloroethylene, a common solvent for both materials. After dissolution, PAni was dispersed in an HIPS polymeric matrix. The membranes were molded on to glass plates using a laminator to keep thickness constant, and the solvent evaporated slowly for 24 h under room temperature. The amount of polyaniline used was 10 and 20 % weight. The electronic and structural properties were carried out using X-ray photoelectron spectroscopy (XPS), Thermogravimetric Analysis (TGA) Raman spectroscopy, Scanning electronic microscopic (SEM). The analysis indicate that PAni incorporation and its dispersion into the polymeric matrix modifies the membranes properties and show improvement in efficiency. Copyright © 2016 VBRI Press.

Keywords: HIPS; fuel cell; membranes; polyaniline; properties.

Introduction

Over the past two decades, alternative energy plays a pivotal role in addressing challenges posed by the conventional energy. Polymer electrolyte membrane fuel cell is one of the promising alternate energy. There has been significant investment happening in this area of technology both commercialization and fundamental understanding of the technology. One of the key elements to the structure of the fuel cells is the polymer membrane which plays a crucial role in advancing this technology further. In Brazil through Ministry of Mines and Energy was created the National energy plan and has a target to be reached until 2030 to implement the hydrogen-based fuel cells [1].

Novel materials hold the key to fundamental advances in energy conversion and storage, both of which are essential in order to meet the challenges of global warming and the limited fossil fuel supply. Transportation represents a significant portion of world energy consumption and contributes considerably to atmospheric pollution. Hence, the development of an appropriate energy conversion system is an important issue from both commercialization and environmental points of view. It is widely accepted that proton exchange membrane fuel cell as an efficient chemical energy converter will play major role in the sustainable growth of transportation sector. Tremendous

efforts in the past decade across the globe to develop materials for PEM fuel cells. Among them, membrane is one of the key challenge to tailor the properties that is cost effective and energy efficient with better transport properties [2, 3].

The advantage of present field is that fuel cells offer several advantages over conventional technologies obtaining energy, reduction in the pollutants emission and high efficiency. As one important type of fuel cell is alkaline membrane fuel cell (AMFC), together with proton exchange membrane fuel cell (PEMFC) [2]. The hydrogen fuel cells or direct injection of methanol have shown great versatility. For the feasibility of using fuel cells, materials with specific characteristics should be studied for hydrogen purification processes, the proton conduction and membrane-electrode interface [1].

A number of ionic conducting membranes have been tried in the past membranes but with little success. It is has been widely accepted that Nafion is the widely used ion exchange membrane in fuel cell industry, But these membranes are expensive and has its own limitations in terms of porosity and gas diffusion. [4, 5]

The polymer studied in this work was the high impact polystyrene (HIPS), a thermoplastic with melting temperature of 240 °C, and possess excellent chemical resistance [5, 6]. Polyaniline (PAni) and other conducting polymers are used in the membranes production because

they present ion exchange characteristics. However, conducting polymers do not present good mechanical properties, so blends with high impact polystyrene have been used to obtain adequate mechanical properties [**7, 8**].

In this context, the purpose of this study is synthesis and characterization of membranes of HIPS and polyaniline (PAni) doped with camphorsulfonic acid (CSA) to use in a fuel cell, because the conducting polymers have good electrical properties, easy and low cost intention. Several works is using fuel cell to storage energy and membranes with conducting polymers [**9, 10, 11**]. This field is very import to the future because limited fossil fuel supply [**12-17**].

Experimental

Materials

The chemicals were all reagent grades and were used without further purification. High Impact Polystyrene (Innova) and aniline (Nuclear) were used to produce the membranes; camphorsulfonic acid (CSA) (Aldrich) was used to dope emeraldine base polyaniline. Ammonium peroxidissulfate $(NH_4)S_2O_8$ (Synth) was used in the PAni synthesis.

Polyaniline synthesis

Aniline was polymerized according a standard method described elsewhere [**4**]. Doped polyaniline was first filtered and then treated with 1.0 M NH_4OH to obtain PAni in emeraldine base (EB) form. Subsequently, polyaniline was doped with 1.5 M camphorsulfonic acid (CSA), stirring the solution for 24 hours.

Membrane preparation

HIPS and PAni were dissolved in 20 mL of tetrachloroethylene. After dissolution, PAni was dispersed in an HIPS polymeric matrix for 30 minutes. This dispersion was performed at 1,000 rpm in a mixer (Fisaton). The membranes were molded on to glass plates using a laminator to keep thickness constant, and the solvent evaporated slowly for 24 hours under room temperature. The membranes were referred to as MCS10 and MCS20.

Membrane characterization

The synthesized MCS membrane was characterized by Raman Spectroscopy, X-ray photoelectron Spectroscopy, and morphology using Scanning electronic microscopy.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a load-locked Kratos XSAM 800 apparatus equipped with a dual anode X-ray source using an Mg Ka (1253.6 eV) excitation source. All spectra were calibrated using the C1s photoelectron component peak of amorphous carbon (284.8 eV) present in the sample and data analysis was performed with Casa XPS software using a Shirley background subtraction.

Thermogravimetric analysis (TGA)

The membranes were analyzed using a TA Instruments Thermogravimetric Analyser model TGA 2050 in the temperature range from 25 to 1000 °C, with a N_2 atmosphere. The heating rate was 20 °C/min for all samples.

Raman spectroscopy

All samples were analyzed using Jobin Yvon Labram HR laser Raman microprobe equipped with 3 lasers (514nm Ar ion, 632nm HeNe and a 785nm diode). The spectra were recorded in the spectral range of 400-4000 cm^{-1}.

Morphology

Scanning electron micrographs of membrane surfaces were taken by a Zeiss Supra 55VP microscope after sputtering the samples with gold.

Results and Discussion

X-ray photoelectron spectroscopy (XPS)

Fig. 1 shows the XPS comparison of MCS20 and MCS10 membranes respectively. In **Fig. 1A** elemental analysis comparison were performed between MCS10 and MCS20 membranes; oxygen, nitrogen, carbon and sulfur. **Fig. 1B** shows the peak around 532 eV. There is a change in line shape and line width of the two different samples, the higher intensity and change in lines shape is due to dopant group of SO_3 from polyaniline. The peak intensity of MCS20 membrane is greater since it has a higher concentration of polyaniline in the membrane.
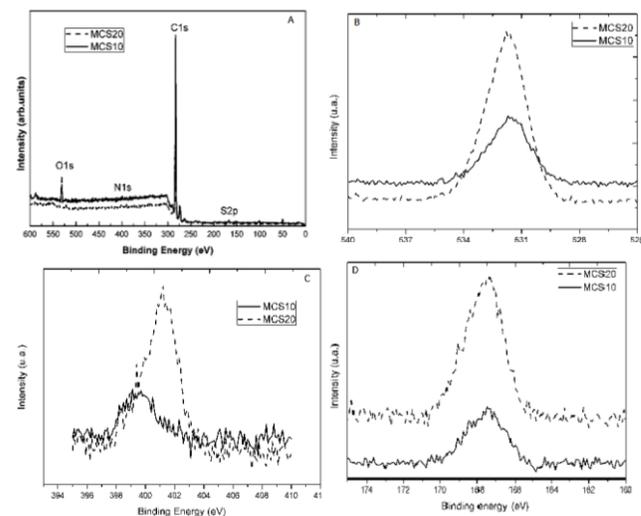

Fig. 1. Spectra XPS of MCS20 and MCS10 membranes (A) Surrey, (B) Oxigen range, (C) Nitrogen range and (D) Sulfur range.

Fig. 1C shows difference in nitrogen stoichiometry of the two different samples. The peak at 401 eV is the nitrogen bonded to carbon, and the difference between the intensities of the nitrogen peaks are also evident, because of the presence of main chain of polyaniline, and the greater the amount of this conductive polymer, resulted in largest peak

intensity. **Fig. 1D** shows peaks at 168 eV, similar variation in the Sulphur content the differences between the sulfur peaks are related to the different stoichiometry and hence the differential properties.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of MCS10 and MCS20 membranes compared to HIPS sample without polyaniline is presented in **Fig. 2**. The thermogram shows that pure HIPS present a first thermal event that begins at around 320 °C, due to the decomposition of the polymeric chain. The thermal behavior of MCS10 and MCS20 membranes is similar to HIPS, but the degradation begins at around 250 °C, due to the mixture with polyaniline. Polymer main chain degradation starts around 300ºC and displays a process of continuous degradation until 1000 ºC.
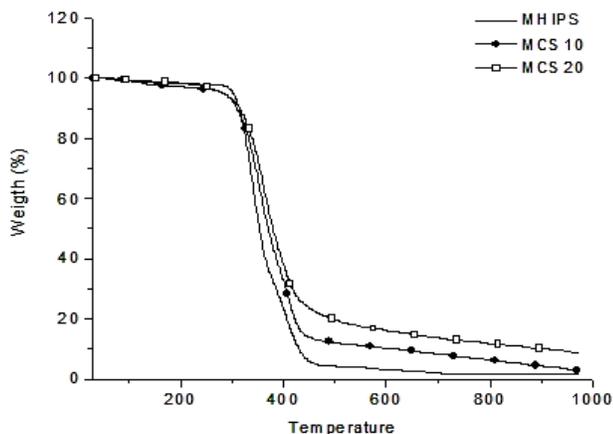
Fig. 2. Thermogravimetric analysis of MCS10 and MCS20 membranes and HIPS sample.

It should be highlighted that when the amount of polyaniline increases, the residue at 1000 °C does too, probably due to aromatic rings with stable bonds in the main chain of polymer that are not decomposed at high temperatures in N_2 atmosphere.

Raman spectroscopy

To make sure the incorporation of Pani into the polymeric matrix, MCS20 and MCS10 membrane were analyzed and **Fig. 3** shows this difference. The polyaniline spectrum is similar to the one described in the literature [6]. Peaks at 1168 cm^{-1} are related to C-H bonds of quinoid rings. The peak at 1339 cm^{-1} is associated to formation of the polarons C-N^{+} group. The peaks at 1506 and 1580 cm^{-1} correspond to stretching of C=N and C=C respectively. The peak at 1034 cm^{-1} shows S=O groups associated to the sulfonic acid used as dopant. In the HIPS spectrum, a peak was observed at 1000 cm^{-1} corresponds to the stretching of aromatic ring [6].

Scaning eletronic microscopy

For the application in fuel cell is important that the membranes have, besides thermal, chemical and mechanical strength, structural homogeneity. This way, the membrane

should present a constant thickness and that the blend should have a homogeneous distribution between HIPS and PAni.
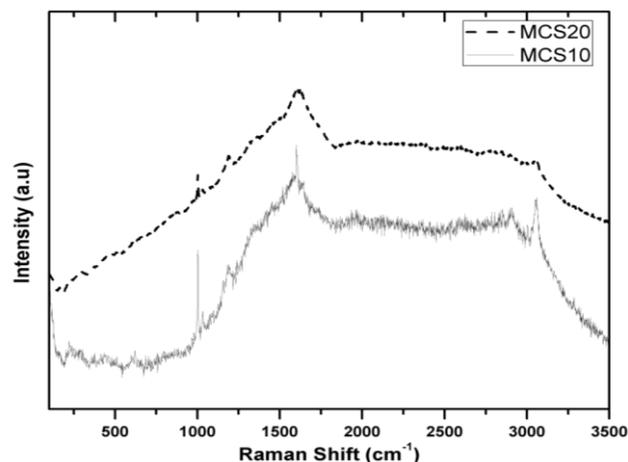

Fig. 3. Raman spectrocopy of MCS20 and MCS10 membranes.

Fig. 4 show that the polyaniline inserted into the polymeric matrix modifies the membranes surface morphology [4]. The difference between the MCS10 and the MCS20 membrane is noticeable. The greater of the polyaniline amount, greater is agglomerates numbers. The agglomerates possibly correspond to the presence of PAni in the membranes, indicating that a good dispersion of PAni in HIPS was not achieved. This fact has negative influence in the mechanical properties and in the diffusion efficiency.
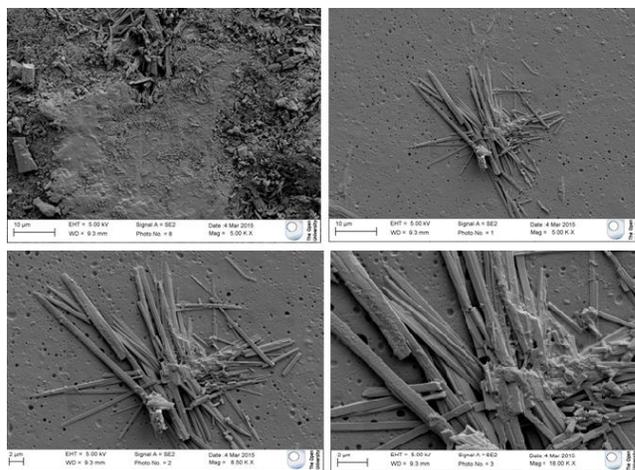

Fig. 4. Micrographs of MCS10 (A and B) and MCS20 (C and D) membranes.

Conclusion

The analysis indicates that the incorporation of Pani and its dispersion into polymeric matrix modifies the membrane properties and shows improvement in efficiency. The Raman spectroscopy has shown characteristic bands of PAni in the spectra of the membranes, especially the peak at 1034 cm^{-1} regarding the group S=O. The difference between the MCS10 and the MCS20 membrane is noticeable, because is possible to observe the difference in agglomerates amount. The thermogravimetric analysis
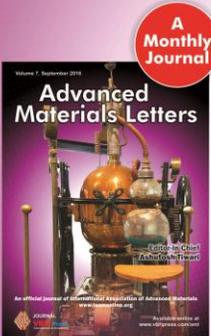
showed that the membrane presented thermal stability until 250 °C. The future prospective is utilization of these membranes in fuel cell is being tremendous efforts in the past decade across the globe develop materials for PEM fuel cells. Among them, membrane is one of the key challenges to tailor the properties, that is cost effective and efficiency.

References

1. Gomes, A.C.O.; Uieda, B.; Tamashiro, A.A.; Ruvolo Filho, A.C.; Pessan, L.A; Paranhos, C.M; *Polimeros*, **2014**, 24*(4)*, 464.
    DOI: 101590/0104-1428.1131
2. Liu, L.; Tong, C.; He, Y.; Zhao, Y.; Lu, C; *J.Membr.Sci.*, **2015**, *487*, 99.
    DOI: 10.1016/j.memsci.2015.03.077
3. Genies, C.; Mercier, R.; Silion, B.; Cornet, N.; Gebel, G.; Pineri, M; *Polym.*, **2011**, *42*, 359.
    DOI: 10.1016/S0032-3861(00)00384-0
4. Amado, F. D.R.; Rodrigues, M.A.S.; Bertuol, D.A.; Bernardes, A.M.; Ferreira, J.Z.; Ferreira, C.A.; *J.Membr.Sci.*, **2009**, *330*, 227.
    DOI: 10.1016/j.memsci.2008.12.065
5. Amado, F. D.R.; Gondran, E.; Rodrigues, M.A.S.; Ferreira, J.Z.; Ferreira, C.A; *J.Membr.Sci.*, **2004**, *234*, 139.
    DOI: 10.1016/j.memsci.2004.01.017
6. Amado, F. D.R.; Rodrigues, M.A.S.; Morisso, F.D.P.; Bernardes, A.M.; Ferreira, J.Z.; Ferreira, C.A; *J.Colloid Interf.Sci.*, **2008**, *320*, 52.
    DOI: 10.1016/j.jcis.2007.11.054
7. De Paoli M.A., Conductive polymer blends and composites, in Handbook of Organic Conductive Molecules and Polymers: vol 2. Conductive Polymers: Synthesis and Electrical Properties. John Wiley & Sons Ltda, **1997**.
8. Gazotti, W.A.; Nogueira, A.F.; Girotto, E.M.; Gallazzi, M.C.;De Paoli, M.A.; *Synth. Met.*, **2000,** *108*, 151.
    DOI: 10.1016/S0379-6779(99)00272-6
9. Boudghene Stambouli, A.; Traversa, E; *Renew. & Sust. Energy. Rev.*, **2002**, *6*, 433.
    DOI: 10.1016/S1364-0321(02)00014-X
10. Liu, B.; Zhang, Y; *J. Univ. Sci. Techn. Beijing, Mineral, Metal. Mat.*, **2008,** 15*(1)*, 84.
    DOI: 10.1016/S1005-8850(08)60017-1
11. Theodosiou, G.; Stylos, N.; Koroneos, C; *J. Cleaner Prod.*, **2015,** *106*, 576.
    DOI: 10.1016/j.jclepro.2014.05.096
12. Tomczyk, P; *J. Pow. Sources*, **2006,***160*, 858.
    DOI: 10.1016/j.jpowsour.2006.04.071
13. Nagarale, R.K.; Gohil, G.S.; Shahi, V.K; *J. Memb. Sci.*, **2006,** *280*, 389.
    DOI: 10.1016/S0379-6779(99)00272-6
14. Moreno, N. G.;. Gervasio, D.; García, A.G.; Robles, J.F.P; *J. Pow. Sources*, **2015**, *300*, 229.
    DOI: 10.1016/j.jpowsour.2015.09.070
15. Mohameda, H.O.; Obaida, M.; Khalilc, K.A.; Barakat, N.A.M; *Inter. J. Hydrog. Energy*, **2016**, 41(*7*), *4*251.
    DOI: 10.1016/j.ijhydene.2016.01.022
16. Zakaria, Z.; Kamarudin, S.K.; . Timmiati, S.N; *Applied Energy.*, **2016,** *163*, 334.
    DOI: 10.1016/j.apenergy.2015.10.124
17. Xin Lia, Marco Drachea, Uwe Gohsb, Sabine Beuermann *J. Memb. Sci.* **2015**, *495*, 20.
    DOI: 10.1016/j.memsci.2015.07.056