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Nafion-Mesoporous Silica as Electrolyte for Ethanol Fuel Cells

Z. Ahmed[a], B. R. de Matos[b], D. Z. de Florio[a], S. Licoccia[c], E. Traversa[c], V. Esposito[c], E. I. Santiago[b] and F. C. Fonseca[b]

[a] Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas,Universidade Federal do ABC, Santo André, São Paulo 09090-400, Brazil
[b] CCCH - IPEN/CNEN, Cid. Universitária, São Paulo 05508-000, Brazil
[c] Dipartimento di Scienze e Tecnologie Chimiche Università di Roma Tor Vergata, Rome 00133, Italy

In this work, mesoporous silica with medium surface area was prepared. The synthesized mesoporous silica was characterized by BET, SEM and TEM demonstrating the formation of an organized pore structure of the silica. Nafion-SiO2 composite membrane with 5% of the filler was characterized by thermogravimetry and ac impedance spectroscopy. The composite membranes exhibited higher proton conductivity than the reference Nafion membrane, due to the increasing of the water retention of the system. Direct ethanol fuel cell polarization curves of the composite were also conducted at 80°C and 130 °C, confirming the enhancement in ethanol fuel cells performance, due to a reduced ethanol cross over, as well as to enhanced proton conductivity of the composite membrane.

Introduction

Direct alcohol fuel cell is a device that uses alcohol directly as a fuel without any further modification. Ethanol is an attractive alternative to methanol because it is less toxic when compared to methanol, renewable and relatively cheap (1). On the other hand, as in the case of methanol, the ethanol crossover through the polymer electrolyte membrane reduces the efficiency of the fuel cells. So many composite materials were then studied to overcome this problem.

Previous works were conducted to enhance the water retention of Nafion and related membranes by incorporating transition metal oxide particles (2-9), such as SiO_2, TiO_2 and ZrO_2, obtaining promising results. Antonucci et al. (10) studied a silica composite membrane for direct methanol fuel cell application and they attributed the enhanced performance of the composite membrane to the hygroscopic properties of silica. Watanabe et al. (11) investigated silica and titania impregnated Nafion composite membranes. They reported that the silica particles were superior to titania particles in terms of water-retention qualities within the Nafion membrane and attributed this effect to the higher water sorption properties of silica. Nishiyama et al (12) studied the possibility of the use of mesoporous materials for fuel cells application. The authors reported that the ordered structure of pores seems to contribute to the high proton conductivity of the system.

In this work, a mesoporous silica with medium surface area was synthesized, characterized, and used as a filler for Nafion. Nafion-silica composites were evaluated as electrolyte in Direct Ethanol Fuel Cell (DEFC) at 80^oC and 130^oC, with the aim to reduce the ethanol crossover and to increase the water retention of the polymer at high temperature. We expect also that the organized porous structure of the mesoporous silica is suitable for the transport of protons in the polymer matrix.

Experimental

Tetraethoxysilane (TEOS) was used as the silica source and nonionic amphiphilic block copolymers as the structure-directing agents (SDA). A 5 % Nafion solution was used to prepare membrane by casting. All other chemicals (Aldrich) were reagent grade and were used as received.

Mesoporous Silica Synthesis

Mesoporous silica (MPS), with medium specific area, was prepared by using triblock copolymers with the trade name Pluronic (BASF Corp., USA) as a surfactant. In our work Pluronic F127 (Mw=12600, EO99PO69EO99) types were used. Pluronic F127 (1 g) was dissolved in 40 mL of 0.5 M HCl at room temperature, then TEOS (4 g) was added drop wise at 40°C. The resulting slurry was stirred at 40 °C for 6 h. The product was then aged over night at 100°C. The solution was then filtered, washed with water and ethanol, and then dried at 100°C for 1 h. The sample was then calcined at 600 °C for 7 h (2 K/min).

Membranes Preparation

Nafion solution (5% (w/w), DuPont) was first evaporated at 80 °C then redissolved in 10 mL of DMSO. A dispersion of silica in DMSO was prepared separately and then added to the Nafion solution. The mixture was kept under stirring for 24 h, dropped in a Teflon mold, and dried in oven at 150 °C for 4 h. The obtained film was then pilled off and was post-treated in 7 mol L^{-1} HNO_3, 3% (w/w) H_2O_2 and 0.5 M H_2SO_4 to purify the membrane. A membrane with a thickness of about 110 μm was obtained. As a comparison, a re-cast Nafion membrane with a thickness of 100 μm was prepared by the same procedure described above.

Electrodes Preparation

Anode and cathode were prepared in house, using a Pt and Nafion loadings of 1 mg cm^{-2} and 30 wt%, respectively. PtSn(3:1)/C (20%, BASF) and Pt/C (20%, BASF) were used as catalyst for the anode and cathode, respectively.

Measurements

Thermogravimetry (TG) analysis was conducted in the temperature range of 30-500 °C with rate of 5°C/min. SEM imaging was acquired using FE-SEM, LEO mod. Supra 35, the electron beam energy being in the range 2 to 20 keV.

Conductivity measurements were carried out on membranes with 8 mm in diameter, sandwiched between gas diffusion layers, which were pressed on the membrane faces by means of porous stainless steel discs. The membrane conductivity was determined as a function of temperature (from 80 to 100 °C) and relative humidity (RH from 15 to 100 %) by impedance spectroscopy in the frequency range 10 Hz–1MHz at a signal amplitude of 100 mV.

Nafion-mesoporous SiO_2 and Nafion recast membranes were evaluated in a 5 cm^2 single fuel cells fed with ethanol solution (2 mol L^{-1}, either 2 mL min^{-1} or 4 mL min^{-1}) in the anode and pure oxygen in the cathode with cell temperature and oxygen humidifier heated at 80°C and 130°C. The anode temperature was kept at room temperature and atmospheric pressure (1 atm). The absolute oxygen pressure was 3 atm.

Results and Discussion

The N_2 adsorption-desorption profiles of the synthesized MPS exhibit type IV-like isotherms, typical of ordered mesoporous materials, as shown in Figure 1. The surface area was analyzed by the BET (Brunauer, Emmett and Teller) method. The BET surface area of the silica samples after the removal of the templates was 428 m^2g^{-1}.

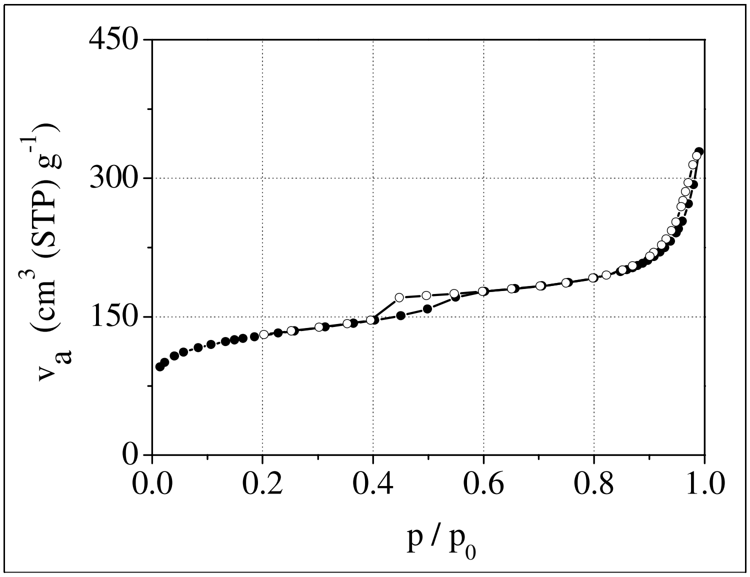
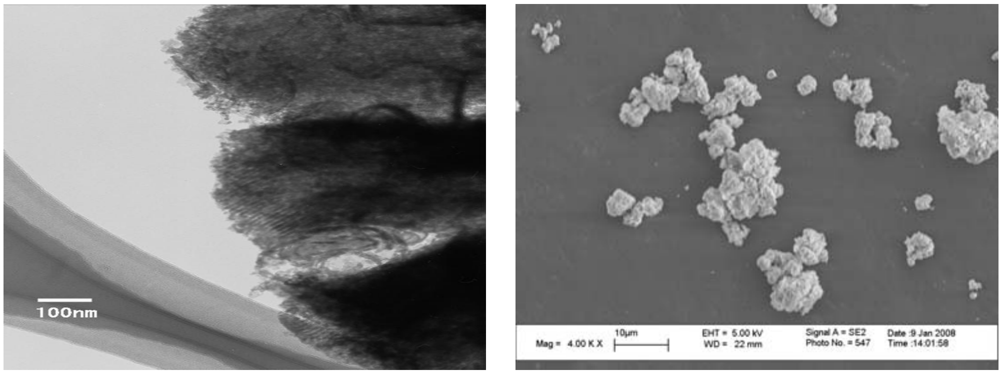


Figure 1. Nitrogen adsorption-desorption isotherms for MPS.

The pore organization was confirmed by TEM images (Figure 2 a). The pore organization deriving from surfactant removal could be clearly observed.

Figure 2 (b) shows the SEM micrographs of the synthesized mesoporous silica particles having average size of about 2 μm.



(a) (b)

Figure 2. TEM (a) and SEM (b) images of the MPS sample.

Figure 3 shows the thermogravimetry curve of the composite membrane. The TG of a pure Nafion membrane is reported for the sake of comparison. The TG curves of the doped membrane do not show any notable changes on the decomposition temperature of the composite, which can be attributed to the small amount of the filler.

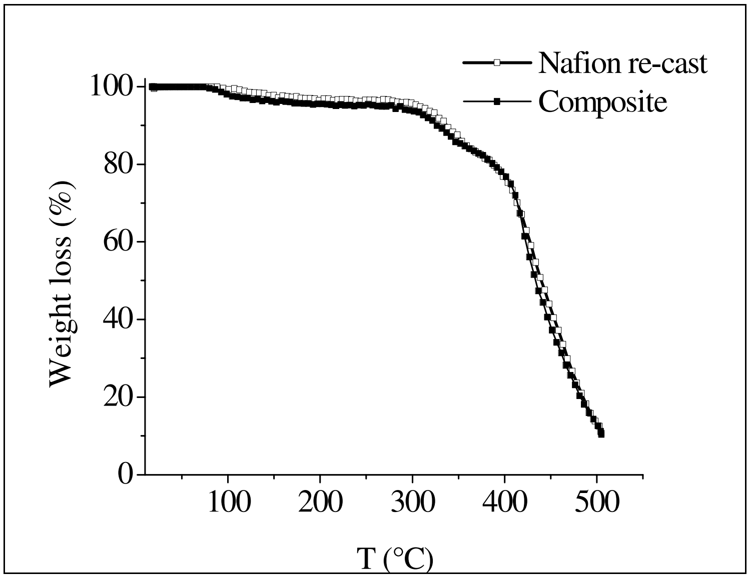


Figure 3. TG of Nafion wt.5%/MPS and reference Nafion recast membrane.

The membrane conductivity was determined as a function of temperature (from 80 to 100°C) and relative humidity (RH from 15 to 100%) by impedance spectroscopy in the frequency range 10 Hz–1MHz at a signal amplitude of 100 mV.

Figures 4 and 5 show the electrical conductivity of the composite and the recast membrane at 80 and 100°C, respectively, at different RH. The conductivity value of the composite is slightly higher than the pure polymer, especially at low relative humidity. Such finding is a support of the fact that the mesoporous silica fillers increase the water retention of the system, so a better conductivity is obtained.

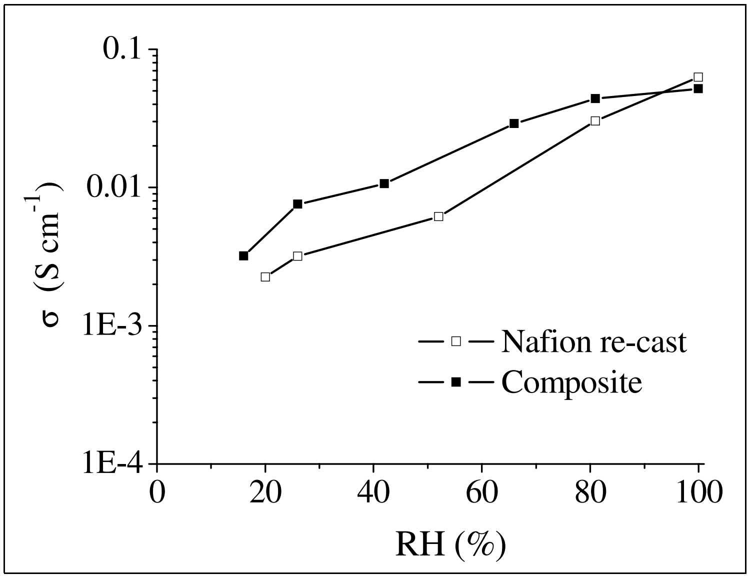


Figure 4. Conductivity as a function of RH determined for the composite Nafion/MPS 5 wt.% and Nafion recast membrane at 80°C.

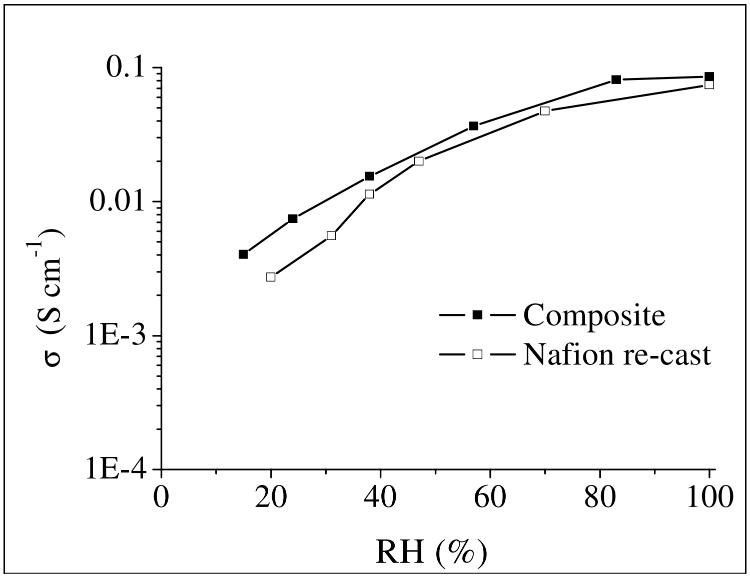


Figure 5. Conductivity as a function of RH for the composite Nafion/MPS 5 wt.% and Nafion re-cast membranes at 100 °C.

In order to evaluate the influence of physico-chemical properties of the inorganic filler on the electrochemical behavior, composite recast Nafion membranes containing 5 wt.% MPS powder was prepared and tested in a single DEFC device. The polarization curves was recorded at 80°C and at 130°C for the MEAs composed with the composite Nafion ~~membranes~~ and pure recast Nafion membrane as electrolyte. The fuel cell experiments were conducted by using two different ethanol flows (2 mol L^{-1}, 2 mL min^{-1} and 4 mL min^{-1}).

Figure 6 shows the polarization curves of the composite and the pure re-cast membrane at 80 °C fed with ethanol (2.0 mol L^{-1}, 2 mL min^{-1}). In these conditions the performance of the recast membrane is better than the composite, as a result of the effect of the filler on the proton conductivity at this temperature. Increasing the ethanol feed (4 mL min^{-1}), the performance of the recast membrane decreases (Figure 7) (the OCV decrease from 0.71 V to 0.67 V) and the composite polarization curve is still unchanged (OCV about 0.64 V), which confirms the effect of the filler on the ethanol crossover reduction.

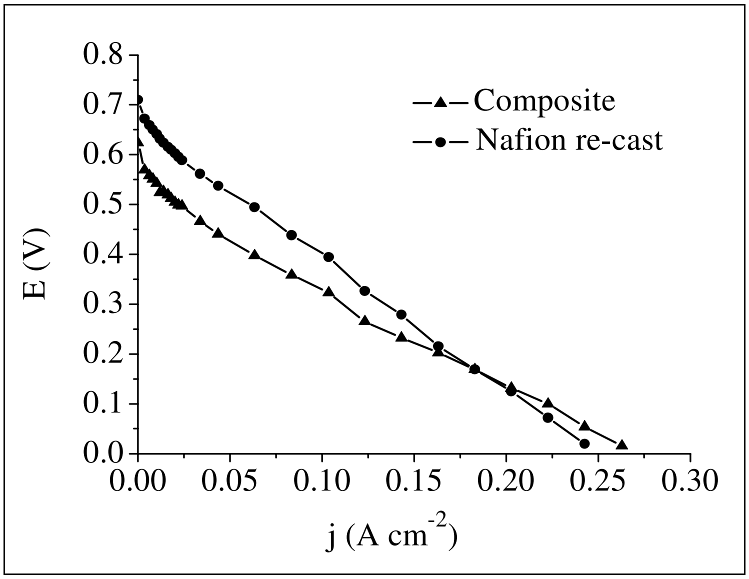


Figure 6. Polarization curves for DEFC: 80°C (■) cast Nafion, (▲) Nafion-MPS (5 wt%), Anode (PtSn/C 3:1) fed with ethanol (2.0 mol L^{-1}, 2 mL min^{-1}) at 25°C and atmospheric pressure. Oxygen pressure = 3 atm.

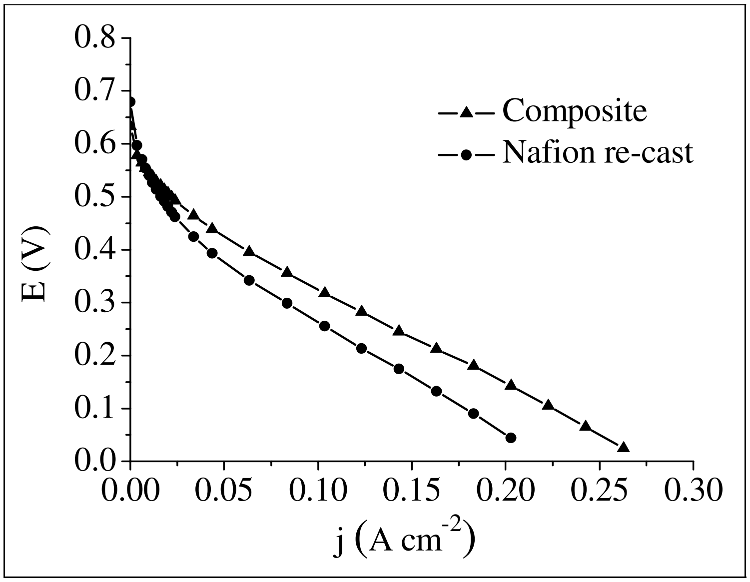


Figure 7. Polarization curves for DEFC: 80°C (■) cast Nafion, (▲) Nafion-MPS (5 wt%), Anode (PtSn/C 3:1) fed with ethanol (2.0 mol L^{-1}, 4 mL min^{-1}) at 25°C and atmospheric pressure. Oxygen pressure = 3 atm.

At higher temperature (130 °C) the DEFC performance of the composite is better than the recast membrane for both ethanol feed (2 mL min^{-1} and 4 mL min^{-1}). Using 2 mL min^{-1} ethanol feed (figure 8) the composite shows a maximum power density similar to the recast membrane (~37 mW cm^{-2}), otherwise, using 4 mL min^{-1} ethanol feed (figure 9) the composite shows higher maximum power density (about 43 mW cm^{-2}) and higher OCV (0.743V).

The variation in performance can be mainly attributed to the presence of the filler with high specific area. A powder with a large specific surface area is characterized by a large number of adsorbing sites. Accordingly, a significant number of water molecules will be coordinated by the OH groups present on the surface of MPS particles, promoting the proton transport through the membrane at high temperatures. On the other hand the MPS filler acts as a barrier decreasing the ethanol cross-over.

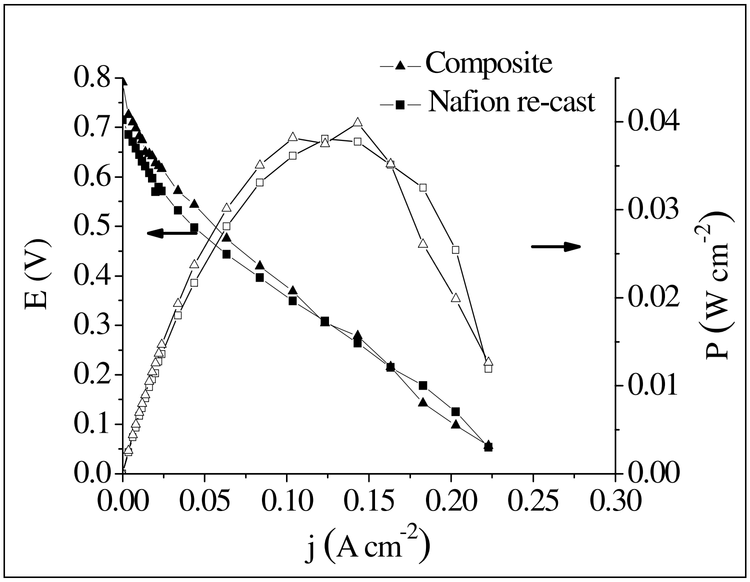


Figure 8. Polarization (solid symbols) and power density (open symbols) curves for DEFC: 130°C (■) cast Nafion, (▲) Nafion-MPS (5 wt%). Anode fed with ethanol (2.0 mol L^{-1}, 2 mL min^{-1}) at 25°C and atmospheric pressure. Oxygen pressure = 3 atm.

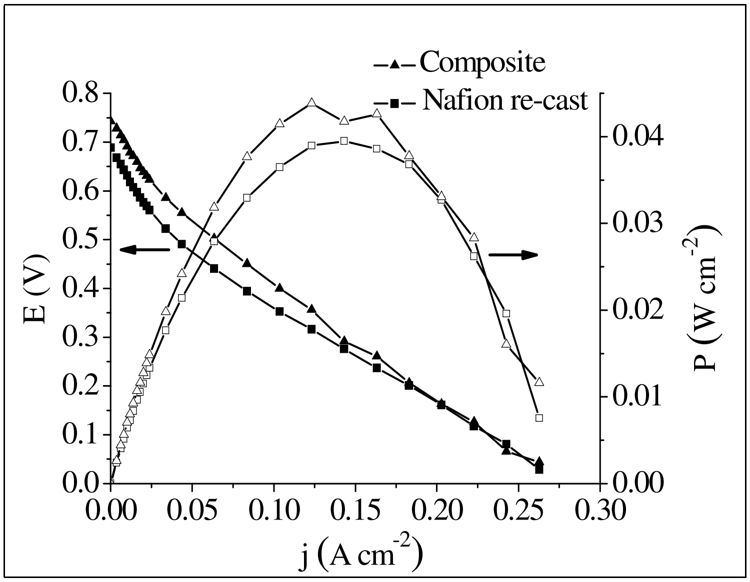


Figure 9. Polarization (solid symbols) and power density (open symbols) curves for DEFC: 130°C (■) cast Nafion, (▲) Nafion-MPS (5 wt%). Anode fed with ethanol (2.0 mol L^{-1}, 4 mL min^{-1}) at 25°C and atmospheric pressure. Oxygen pressure = 3 atm.

Conclusion

The addition of mesoporous silica to Nafion electrolytes was found to enhance the proton conductivity especially at low relative humidity, as a result of the effect of the filler on the water retention of the system. The crossover seems to be reduced using

MPS as a filler. The DEFC using composite Nafion/MPS as electrolyte shows better performance than pure Nafion membrane in terms of OCV and power density especially at high temperature.

Acknowledgments

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