

A PEI SIPN systems used as membranes for fuel cell

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The development of new membranes in order to replace Nafion[®], with greater thermal stability, chemical, electrochemical, and high conductivity is one of the key to reducing the manufacturing costs of PEMFC. Many studies were found in the literature with composites and nanocomposites based on Nafion[®], which do not eliminate the dependence of this polymer [1]. Several studies involve commercial polymers sulfonation [2] and others basic polymers, among them poliimidazol and polibenzimidazol [3]. From these basic polymers are formulated complexes with strong acids, particularly H₃PO₄, which act as a source of protons to membrane charge transport. New polymeric materials have been explored, such as interpenetrating polymer networks (IPN) [4]. The IPN systems allow controlling the free volume and dimensional mechanical stability. Second IUPAC definition, while an interpenetrating polymer network (IPN) is "A polymer comprising two or more networks which are at least partially interlaced on a molecular scale, but not covalently bonded to each other and cannot be separated unless chemical bonds are broken. (...)", a SIPN (Semi-IPN)" is a polymer comprising one or more polymer networks and one or more linear or branched polymers characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules".

In this work, the SIPN was formed by the reaction of diglycidyl ether of bisphenol A (DGEBA) with curing agent 4,4' diaminodiphenyl-sulphone (DDS) and the linear polymer polyethyleneimine (PEI), as described previously [5].

The membrane SIPN 47% PEI was immersed in H₃PO₄ 5, 10, 15, 20 and 30% (w/w) aqueous solution at room temperature during 24h, in order to obtain acid doped membranes (SIPN47-H₃PO₄). Membrane of same composition was sulfonated [6] (SIPN47-SO₃H) using different sulfonating ratios 1:4, 1:2, 1:1 and 2:1 and they are kept in a desiccator under vacuum. The samples were characterized by FTIR, TGA, DSC and Electrochemical Impedance Spectroscopy (EIS).

The TGA and DTG curves show an initial weight loss (5.2 %) at approximately 80-85°C, associated with adsorbed water elimination. Since the samples were dried prior to the analysis, the water eliminated was probably rapidly adsorbed during the sample handling due its highly hygroscopic behavior. The SIPN membranes exhibit water elimination in a broad temperature range, up to 200°C. This is a very promising characteristic of the studied system, since water retention above 100 °C is one of the limiting features of polymer membranes for fuel cells, which operating at

temperatures higher than 120 °C, avoid the catalyst poisoning by CO. SIPN samples degradation starts at approximately 280°C.

The DSC curves show only one Tg at 67°C, indicating the miscibility of the system. No other thermal event was observed, indicating that the system does not undergo phase changes at this temperature range.

The impedance study shows the dependence of the conductivity with the concentration of acid present in the sample. The conductivity was $8.29 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 80°C. On the other hand, sulfonated SIPN samples do not show increase in the conductivity with the sulfonating ratio increase. Table 1 and 2 lists the conductivity values between 20 and 80 °C, as well as $\log(A_0)$ and activation energy values for the SIPN47-H₃PO₄ and SIPN47-SO₃H membranes at different sulfonating ratios.

Table 1: Conductivity, $\log(A_0)$ and activation energy values obtained for SIPN47PEI-H₃PO₄ membranes.

Samples	Log (A ₀)	E _a (kJ.mol ⁻¹)	σ ($\Omega^{-1} \text{cm}^{-1}$, 20° C)	σ ($\Omega^{-1} \text{cm}^{-1}$, 80° C)
SIPN ₄₇ /5%H ₃ PO ₄	2.66	11.92	$(6.55 \pm 2.41) \times 10^{-4}$	$(5.21 \pm 1.31) \times 10^{-3}$
SIPN ₄₇ /10%H ₃ PO ₄	1.66	0.848	$(9.76 \pm 2.41) \times 10^{-4}$	$(1.17 \pm 2.19) \times 10^{-2}$
SIPN ₄₇ /15%H ₃ PO ₄	0.65	1.860	$(7.00 \pm 1.15) \times 10^{-3}$	$(1.29 \pm 1.83) \times 10^{-2}$
SIPN ₄₇ /20%H ₃ PO ₄	1.06	6.094	$(4.10 \pm 0.16) \times 10^{-2}$	$(8.29 \pm 1.28) \times 10^{-2}$
SIPN ₄₇ /30%H ₃ PO ₄	0.70	5.234	$(3.42 \pm 1.28) \times 10^{-2}$	$(7.5 \pm 0.29) \times 10^{-2}$

Table 2: Conductivity, $\log(A_0)$ and activation energy values obtained for SIPNPEI47-SO₃H membranes.

Samples	Log (A ₀)	E _a (kJ.mol ⁻¹)	σ ($\Omega^{-1} \text{cm}^{-1}$, 20° C)	σ ($\Omega^{-1} \text{cm}^{-1}$, 80° C)
SIPN ₄₇ /SO ₃ H-2:1	0.06	3.36	$(2.06 \pm 5.45) \times 10^{-4}$	$(3.57 \pm 3.96) \times 10^{-3}$
SIPN ₄₇ /SO ₃ H-1:1	3.56	17.23	$(1.09 \pm 0.251) \times 10^{-4}$	$(2.75 \pm 1.77) \times 10^{-2}$
SIPN ₄₇ /SO ₃ H-1:2	0.95	10.95	$(2.91 \pm 0.398) \times 10^{-3}$	$(4.11 \pm 2.84) \times 10^{-2}$
SIPN ₄₇ /SO ₃ H-1:4	0.67	10.40	$(6.14 \pm 3.62) \times 10^{-2}$	$(2.69 \pm 1.07) \times 10^{-2}$

The increase of conductivity with the temperature observed for the SIPN47PEI-H₃PO₄ membrane is a consequence of different factors, including: higher mobility of water molecules, higher acid dissociation and homogenization of the membranes nanostructure, which allows the proton transport among different hydrated nanodomains inside the membrane. The high thermal stability exhibited by the SIPN membranes, above 270°C, is sufficient for their application in PEMFC.

The membranes doped with H₃PO₄ at 20% shows higher values of conductivity ($0.08 \Omega^{-1} \text{cm}^{-1}$) than the best sulfonated sample ($10^{-3} \Omega^{-1} \text{cm}^{-1}$).

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