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Synthesis and testing of a composite membrane based on sulfonated polyphenylene oxide and silica compounds as proton exchange membrane for PEM fuel cells

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ABSTRACT

The present work is an attempt to improve the usseful properties of sulfonated polyphenylene oxide in order to obtain a proton exchange membrane (PEM) for proton exchange membrane fuel cells(PEMFC). Formation of siloxane compounds inside the polymer matrix through an in situ sol-gel process improves properties of the composite membrane: water retention, tensile strength and dimensional stability of the membrane. The presence of the silicone atoms inside the polymer matrix is highlited in the X-ray fluorescence spectra. Parameters related to water absorbtion and proton transport inside the membrane such as: water uptake, hydration number (λ), dimensional expansion by hydration, ion exchange capacity and sulfonation degree show an optimization of the composite membrane compared to the polymeric one. Furthermore, the tensile strength of the composite membranes is better than the polymeric one when both samples are fully hydrated.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are electrochemical devices that convert chemical energy of hydrogen/methanol to electricity through REDOX reactions. These could be used as power sources for a number of mobile and stationary applications. The polymer electrolyte membrane (PEM) is one of the main components of the PEMFC acting as electrolytic bridge, therefore it provides a conductive path for the ionic species (H_3O^+) and separates anode and cathode reaction chambers, preventing gaseous reactants mixing and electrons passing through membrane.

The membrane must fulfill several requirements in order to accomplish the operating functions and maintain the integrity and stability in the PEMFC aggressive operating environment [1]: i) chemical and electrochemical stability under acid and oxidizing environment; ii) dimensional stability to water-uptake (in the range from liquid water to water vapours) preserving meantime the mechanical strength and durability; iii)low gas permeability through the membrane; iv)high proton conductivity in the operating conditions [2,4]; v) low cost and easy to recycle. At the same time, it must provide highest ion conductivity/low resistance (the recommended value is 0.18 Ωxcm in the operating conditions [5]).

In general, the fuel cell performance is strongly dependent on the ion conductivity into the membrane. The most important factor governing the efficiency of the fuel cell is the concentration of proton donor moieties, such as sulfonic or phosphonic groups. Other important factors that affect the proton conductivity of almost all PEM (except the acid-base complexes – based on polybenzimidazoles and inorganic acids) are the degree of hydration and the ionic channels morphology [3]. Distribution of the ionic channels inside the amorphous polymer matrix results from the polymer microphase separation into hydrophilic and hydrophobic domains. It is very important to control the physical balance between the hydrophilic and hydrophobic domains, the first ones being responsible for water and methanol transport, while the second ones offer stability and mechanical strength against serious swelling. The rate of proton transport into polymer electrolyte membrane is directly influenced by the water content

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of the membrane. The hydration degree of electrolyte polymer is often described as the number of water molecules per fixed ionic (HSO_3^-) moieties (λ) [8], usually dependent of the ion exchange capacity (IEC).

Many polymers, polymer blends or hybrid organic-inorganic composite polymers were investigated as inexpensive alternative materials for trademark Nafion.

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) is an ordinary engineering plastic used in many industrial applications as presented or modified by bromination, carboxylation/methyl esterified carboxylation, sulfonation and acylation [9]. PPO posses many useful properties for this application (as PEM): high thermal, mechanical and chemical stability and film forming capacity. Sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) is a hydrophilic material [9] with high swelling capacity at higher sulfonation degree. Phase separation occurs in hydrated sPPO polymer. The conductive phase consists in hydrated ionic clusters dispersed in the insulator PPO matrix [10,11]. When the hydration degree increased up to percolation threshold, the ionic clusters join together in the ionic channels network. Water uptake usually increase material dimensions and decrease the mechanical resistance of the film. However, the membrane loss water quickly, in the normal atmospherique conditions and also when the fuel cells operate in dewatering conditions: temperature above 100 °C [7], higher current values, or inadequate water management.

In order to enhance the mechanical strength, dimensional stability under hydration/dehydration conditions and water retention capacity we prepared a hybrid organic-inorganic composite membrane with silica particles dispersed inside the sPPOmatrix. Composite membranes combine the stability of the inorganic particles with the flexibility and ionic behavior of the organic macromolecules [12] and at the same times showed an improved mechanical and thermal stability, and a better water retention [13,14]. The inorganic silica particles were made in situ by sol-gel method which provides a good dispersion insight the polymer matrix. Unlike the other similar synthesis [15–17], this simple method does not involve organic linker, therefore this membrane posses a simpler structure including only silica (SiO_2) and silicon $SiO(CH_2—\text{-CH2-}_2—H)_{\text{nReplace with: (SiOx(OC2H5)4-x)n}}$ particles, uniform distributed in the polymer matrix.

The present work investigates the influence of silica particles on membrane properties. The membranes composition was analyzed by FTIR and X-ray fluorescence spectroscopy. The ion exchange capacity (IEC) and sulfonation degree (SD) have been determined by titration along with the water uptake (WU) and aria expansion (Ea) by hydration. Both polymer and composite membranes were characterised in terms of thermal and mechanical behaviour. We notice the improving of swelling properties and the tensile strength of the composite membrane compared to the unmodified sPPO membrane.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) powder, from Aldrich (Tg = 211 °C, Tm = 268 °C) was used as received. Chloroform from Merck, purity >99%, was treated with appropriate amount of chlorosulfonic acid (1 ml/100 ml chloroform) right before use in order to destroy water and ethanol (stabilizer) which could interfere with the sulfonation reaction. Chlorosulfonic acid Sigma-Aldrich, 99% purity), 2-propanol (Merck) and *N,N*-dimethylformamide (DMF, Poch, 99,8%) were used as received. Tetraethyl ortosilicate (TEOS Aldrich, 99%) and hydrochloric acid from Merck acid, sodium chloride and sodium hydroxide (Chimopar) where used for titration analysis.

2.2. Synthesis of sulfonated polyphenylene oxide (sPPO) and composite membrane preparation

Sulfonation of the polymer was made with chlorosulfonic acid as the sulfonation agent [18,19,30] under continuous nitrogen flow. The 10/100 W/v ratio PPO in chloroform were introduced in a four necks reaction flask and stirred for about 2 h until a homogeneous solution was obtained. This time, the sulfonating reagent was prepared on the ice bath from a calculated amount of chlorosulfonic acid (for 50% theoretical sulfonation degree) and 100 ml chloroform. Then the solution was slowly dropped into the reaction flask under continuous stirring and continuous nitrogen flow at ambient temperature (around 25 °C). After the entire sulfonating reagent was added into the reaction mixture the stirring and the nitrogen flow where stopped and the reaction was left 24 h for completion. Finally the reaction was stopped by adding 25 ml of isopropanol inside the reaction flask. The sulfonated polymer was then precipitated by pouring the solution into the boiling water, extracted by filtration, washed with demineralised water and dried at 60 °C under vacuum.

Membrane preparation. The dried polymer was dissolved in DMF to obtain a solution of 40% W/v. The solution was homogenized under magnetic stirring and used to get the membrane by recasting from solution. Thus the homogeneous solution was laminated with a COATMASTER film preparatory device and the solvent was evaporated at normal pressure and room temperature. Membranes with thickness between 20 and 40 μm were obtained [19].

Preparation of composite membrane. The tetraethyl ortosilicate (TEOS) was used as precursor of silica nanoparticles for preparing the composite membranes. Previously it was prepared a sol from TEOS, water and hydrochloric acid (as catalyst) in the molar ratio TEOS: H2O: HCl = 1:4:0,1 [23,24]. The sol was then mixed with a solution of sPPO in DMF for 15 minuts on the ultrasonic bath. The homogeneous solution with the weight ratio TEOS/sPPO < 0.1 was poured onto the borosilicate glass plate of the COATMASTER device and a membrane film was laminated with a knife. The membrane was first dried at room temperature for 24 h and then the temperature of the plate was stepwise increased to 120 °C: one hour at 60 °C, 1 h at 90 °C, 1.5 h at 100 °C and 30 min at 120 °C. The neat polymer and the composite membrane were analyzed and compared.

2.3. Characterization of the membrane samples

FTIR analysis. The chemical structure of polymer and composite membranes was analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Infrared spectra of the film samples by PPO, sPPO and composite sPPO-silica were obtained with a spectrometer Bruker Vertex 70 using the attenuated total reflectance (ATR) method.

Energy Dispersive X-ray Fluorescence (EDXRF) spectroscopy. The presence of silicon in composite membranes was proved by fluorescence spectroscopy. X-ray fluorescence analyses were performed using a PW4025 MiniPal 2 (PANalytical, Netherlands) EDXRF spectrometer. Determinations were carried out in helium atmosphere, for 300 s, without any filter, at 20 kV and with automatically adjustment of the current intensity.

Determination of the ion exchange capacity (IEC) and sulfonation degree (SD) The IEC of the membranes (miliequivalents sulfonic acid groups/G polymer) was titrimetrically measured [19,20]. The membrane samples were first swollen in 0.1 M HCl solution for 24 h to bring all the sulfonic moieties to the acid form (-SO3H). Further the samples were rinsed with deionized water, wiped with filter paper and weighted. The samples were then dried at 50 °C, under vacuum until constant weight. The weight of the hydrated samples (m_h) and the weight of the dried sample (m_d) were used to

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