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Dielectric Measurements of Polymer Electrolyte Based Composites as a Technique for Evaluation of Membrane Homogeneity

Serguei D. Mikhailenko[a,b], Fabricio Celso[b], Marco Antônio Siqueira Rodrigues[b], Serge Kaliaguine[a,*]

[a] Chemical Engineering Department, Laval University, Quebec, Canada
[b] Institute of Exact Sciences and Technology, Feevale University, Novo Hamburgo, Brazil

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ABSTRACT

Three series of composite proton exchange membranes containing SiO_2 as filler were prepared and studied by a.c. impedance spectroscopy. Cast membranes were based on SPEEK and Nafion polymers and one more series was obtained by Nafion impregnation via sol-gel technique. This reaction was carried out under equilibrium conditions at long diffusion time with pre-defined water and TEOS contents as a given ratio per -SO_3H group. The study of electro-physical properties of composite membranes showed that the dielectric permittivity, measured using a simple probing device in different locations of a composite film, may be used not only for structural and electro-physical characterization of the materials but also as a parameter allowing to estimate homogeneity and spatial uniformity of the membranes.

1. Introduction

Proton exchange membranes (PEM) were suggested for use and are already being used in a large number of industrial applications, such as electrolysers, electrochemical batteries, fuel cells, permselective separators in chlorine production and many others. The most common are perfluorosulfonic polymers, since they possess high protonic conductivity and chemical and mechanical stability required for long term efficient operation of the electrochemical devices. There are a number of commercially available perfluorosulfonic membranes, for instance Nafion®, Flemion®, Aciplex®, Dow®, as well as an abundant literature where their properties are closely reviewed [1,2]. At the same time, the high cost of perfluorinated polymers stimulated the development of non-fluorinated membranes, such as sulfonated poly(sulfone), poly(ether ether ketone), poly(phosphazene), poly(amide)s, poly(benzimidazole) and others [2–6].

However, despite intensive investigations all presently existing pure polymeric PEMs are still not free of limitations. The most significant problem is the inability to retain water at elevated temperatures, which results in a decrease in the membrane conductivity close to water boiling point [7] and the poor performances of many of them to act as a separator, for example in such important application as direct methanol fuel cells [8–10].

One of the strategies that can be used to develop a PEM with improved properties is formation of organic-inorganic composites, where an organic component provides structural flexibility and convenient processing, while inorganic compounds may offer a range of desirable dielectric, magnetic and conductance properties along with mechanical and thermal stability [11]. Besides, the composites possess a high concentration of organic-inorganic interfaces. These interfaces have defect structure [12] and provide free volume that can accommodate and retain significant amount of water which makes the composite membranes promising for electrochemical applications.

A method for producing silica/Nafion nano-composites using sol-gel reaction was proposed by K. Mauritz [8,9,13–15]. The process starts with soaking the polymer in a sol (colloidal suspension or solution in ethanol) of tetraethyl orthosilicate (TEOS). Gelation of the sol is accomplished through the low temperature hydrolysis, catalyzed in situ by pendant–SO_3H groups of Nafion, accompanied by condensation reactions initiated by water. The sol-gel reaction of TEOS is confined to the polar clusters of sulfonic acid functions which were regarded as nanometer reaction vessels [15].

Various composite membranes, both Nafion based and the ones having non-fluorinated matrix, have been prepared using similar procedure, where inorganic phases were silicon oxide [16], zirconium oxide [17], mixed silicon–titanium, silicon–aluminum

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* Corresponding author. Tel.: +1 418 656 2708.
E-mail address: Serge.Kaliaguine@gch.ulaval.ca (S. Kaliaguine).

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oxides [18] and others. The composite PEMs prepared using the approach employed in refs. [8,9,13–15] were tested in direct methanol and hydrogen/oxygen FCs [19–21]. The dispersion of the solid in the bulk of the polymer was found to have a positive effect of the PEMFC performance, reducing methanol crossover and enhancing power density of the device owing to higher operational temperature. Improvement of the performance and simplification of water management was also noted in [21,22] for Nafion based composites.

In contrast to perfluorinated membranes manufactured by extrusion, many PEMs based on non-fluorinated polymers are produced by casting from solutions. Powdered inorganic phases may be directly dispersed in the casting solutions of these polymers, which makes the formation of organic-inorganic composites more convenient. Silica, metal phosphates and sulfophenylphosphonates were used as inorganic components in sulfonated poly(etheretherketone) (SPEEK) based membranes [23]. Some nano-clays embedded in SPEEK based membranes were found beneficial for proton conductivity of PEMs also improving their methanol impermeability and performance in DMFC [24]. Another approach to composite preparation is formation of the inorganic phase directly in the casting solution via sol-gel method prior to the casting [10]. Despite multiple evidences of a positive effect of embedding of inorganic nano-phase into membrane matrix, this technique still did not achieve industrial scale production, and is used mainly in R/D laboratories where membrane sizes are limited.

Scaling up the composite PEM production raises the issue of homogeneity of the membranes, the problem stemming from the nature of these materials. Indeed, cast membranes are always facing a risk to undergo phase separation during drying (accelerated precipitation of inorganic phase) or even at the stage of mixing the powdered component with casting solution due to different density of two phases. As to composite PEMs manufactured using sol-gel method, the first stage of this technique implies diffusion of colloidal suspension of a precursor to acid sites of the polymer. This process is difficult to control and as it is shown in this work, can also result in irregular distribution of the second phase within polymer films.

A technique to monitor the uniformity of the composite membranes seems to be requisite for quality control of these materials. This technique must be non-destructive and allow rapid analysis in different locations of large films. Direct measurement of the electric conductivity in various spots of the membranes looks as a most natural approach to this problem due to the fact that this parameter is their most important functional characteristic. However, an accurate measurement of the proton conductivity even for small specimens of electrolyte membrane presents a non-trivial experimental challenge [25].

The major problem in these measuring operations is associated with the strong dependence of PEM conductivity on its hydration state. Numerous experimental schemes used to control the measurement conditions were reported in the literature and have been analysed in [25]. All of them are rather expensive and cumbersome techniques, requiring an expendable piece of membrane which is not suitable for rapid non-destructive screening of large composite films.

In this work we have studied dielectric properties of composite membranes where silica nano-particles were embedded in Nafion and SPEEK matrices. The target of this investigation was to demonstrate that the dielectric permittivity, measured using a simple probing device in different locations of a large composite film, may be used not only for structural and electrophysical characterization of the materials but also as a parameter allowing to estimate consistency and spatial uniformity of the membranes.

2. Experimental

2.1. Preparation of the composites

2.1.1. SiO_2/SPEEK membranes

SPEEK based composites were prepared by casting from solution of the polymer (degree of sulfonation DS = 55%) mixed with commercial silica (Sigma-Aldrich, $S_{BET} = 400 m^2/g$, particle size about 7 nm). A 10wt% solution of SPEEK in dimethylacetamide was mixed with appropriate amount of silica preliminary suspended in the same solvent under mechanical stirring. The mixture after outgassing under vacuum was cast on an aligned glass plate and dried at room temperature for 48 h and cured at 120 °C for another 48 h.

2.1.2. SiO_2/Nafion membranes

Two approaches were employed for preparation of composite membranes based on perfluorinated polymer: 1) re-cast of mixture of SiO_2 powder and liquid Nafion and 2) soaking of commercial Nafion films in alcohol/water solution of tetraethoxysilane (TEOS) followed by sol-gel reaction resulting in silica nano-particles formation.

2.1.2.1. Re-cast SiO_2/Nafion. According to the first method, an appropriate amount of 5 wt.% Nafion solution in light alcohols (EW 1100, Electrochem. Inc) was mixed with SiO_2 powder (commercial fumed silica, Sigma-Aldrich, $S_{BET} = 400 m^2/g$) in a beaker and mechanically stirred with a magnetic stirrer and, at the same time, ultrasonicated with a probe, immersed in a bath, placed on a stirring plate. When the mixture became viscous it was cast in a glass tray and dried for 24 hours. Then, the recast membranes wetted with deionised water were detached from the glass, dried and hot pressed in order to improve their mechanical properties. Pressing was carried out between two Teflon films at 150 °C and 10 - 30 atm for 15 min which usually resulted in stronger membranes.

2.1.2.2. SiO_2/Nafion membranes by sol-gel method. Nafion 117 membranes were cut into squares approximately 10 × 10 cm and transformed into the acid form by successive boiling in 1 M H_2SO_4 (1 h), in water (>1 h), in 3% H_2O_2 (1 h) and again in water (>1 h). Protonated membranes were dried at 110 °C under vacuum, weighed and kept in a dessicator. Experiments at low water content were carried out under a flow of dried Ar and the membrane sample was additionally dried prior to impregnation by heating under vacuum in the reaction vessel. Anhydrous alcohol and calculated amount of water were added to the vessel under Ar flow and the sample was left overnight under stirring for swelling. The necessary amount of TEOS ($Si(C_2H_5O)_4$) was then added and the impregnation solution was stirred for 24 h at room temperature. Upon removal from the solutions, the films were surface-blotted and finally dried in vacuum oven at 110 °C for 24 h to promote silicon oxide condensation.

2.2. Silica content estimation

The cast membranes based on SPEEK were dried in a dessicator and weighed. Silica content was directly calculated as ratio of the introduced silica to total weight of obtained composite. Measurement of silica content in modified Nafion membranes could not be performed reliably on dried materials because of fluctuation of sample weight depending on its pre-treatment due to its extraordinary hydrophilicity. Therefore, the weight of modified sample was compared with the weight of initial piece of film in either case equilibrated with the room environment for several hours. The weighing method is valid only if relative humidity (RH) is constant and therefore it could be used to fast control of silicone oxide content at high inorganic phase concentrations. For measurements of low loadings of SiO_2, atomic absorption spectroscopy was