Membranes based on phosphotungstic acid and polybenzimidazole for fuel cell application

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Abstract

Composite membranes based on phosphotungstic acid (PWA) adsorbed on silica (SiO_2) and polybenzimidazole (PBI) have been prepared and their physico-chemical properties have been studied. The membranes with high tensile strength and thickness of less than 30 μm can be cast. They are chemically stable in boiling water and thermally stable in air up to 400°C. Proton conductivity is influenced by the temperature (range: 30–100°C), relative humidity and PWA loading in the membrane. Maximum conductivity of 3.0×10^{-3} S/cm is obtained at 100% relative humidity and 100°C with membrane containing 60 wt.% PWA/SiO_2 in PBI. Conductivity measurements performed at higher temperatures, in the range from 90°C to 150°C, give almost stable values of $1.4–1.5 \times 10^{-3}$ S/cm at 100% relative humidity. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Solid polymer electrolyte membranes play a vital role in polymer electrolyte membrane fuel cell (PEMFC) systems. It is a general opinion that these systems, which have already reached an advanced level of development, need further improvement of proton conductor component before their massive entry in the market. Two main factors still hinder the complete development of the technology: (a) the excessive cost of the electrolyte membrane and, (b) the activity decay of fuel cell due to anode poisoning by CO present in the reformate fuel stream.

The cost of the most frequently used membranes in the PEMFC systems, Nafion 117 (Du Pont) and Dow are about 750 US$/m^2 and 1700 US$/m^2, respectively [1]. This high cost of the membranes contributes to the increase of total PEMFC system cost, making it too expensive with respect to the common systems of current generation.

The CO poisoning of anode is correlated with the thermal and chemical characteristics of the electrolyte. Thermal stability of polymer electrolyte membrane determines the operation temperature of the fuel cell. In the actual PEMFC, operating at temperatures below 100°C, the anode containing platinum as catalyst, quickly loses electrochemical performance when hydrogen, containing traces of CO is fed to it. An increase of temperature beyond 130°C would be useful to improve the stability of catalyst toward CO poisoning. Normally, the CO contained in hydrogen (fuel) is formed during the reforming process of most commonly used fossil fuels. The reforming of fossil fuels is nowadays the only feasible process that gives low operational costs of the fuel cells, but this, unfortunately, produces CO as a by-product in the hydrogen stream. The complete elimination of CO from fuel requires very expensive purification methods and for this reason, they are seldom used. Normally, methods that eliminate CO at least partially are used, and after such purification, the hydrogen fuel contains some hundreds of ppm of CO. To decrease the CO poisoning of anode, two ways may be followed: either to increase the working temperature of the fuel cell, or to utilize anode catalysts that are resistant towards CO poisoning. The temperature effect is well known in heterogeneous catalysis, where an increase of operating temperature in the reactors containing platinum as catalyst beyond 130°C causes a decrease of CO poisoning effect. The utilization of the catalysts other than pure platinum, like Pt

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alloys with some other transition metals, has given limited success until now. These catalysts are declared to be resistant up to a level of 100 ppm CO in the hydrogen fuel. We have studied recently the use of heteropoly acids (HPA) as proton-conducting electrolytes in the low-temperature fuel cell. In these studies, the HPAs have been used both, in crystalline form [2], or as the concentrated aqueous solution [3,4]. We have demonstrated during the tests in fuel cell that the activity of platinum anode is preserved in the presence of small amount (33 ppm) of CO in hydrogen even at room temperature [5,6]. Since the work of fuel cell operating on liquid electrolyte at low temperature is difficult to control, we decided to prepare a composite membrane containing HPA. In such a membrane, HPA is anchored to a support that maintains, as much as possible, the characteristics of the pure electrolyte (i.e. its high proton conductivity and its ability to protect Pt catalyst from poisoning by CO) and that is stable at temperatures higher than 100°C. Preliminary conductivity tests performed on membranes prepared by introducing directly the HPAs into the polybenzimidazole (PBI) dispersion gave very poor proton conductivity. Similar results on conductivity of PBI films doped with phosphotungstic acid (PWA) solutions were also obtained by Xing and Savadogo [7]. They found that the samples of PBI membranes doped with PWA solutions of various concentrations at various immersion times and at various temperatures gave specific proton conductivity in the order of 10^{-6} S/cm. The low conductivity was explained in terms of low interaction between the PWA and polymer that does not allow the acid to remain fixed in the membrane. However, our samples prepared by the adsorption of the HPAs on silica followed by introduction into the PBI dispersion gave substantially higher ionic conductivity. For these reasons, we have focused our research activity on the development of proton-conducting membranes based on HPAs supported on silica utilizing PBI as thermally stable material. PBI is a completely amorphous polymer with a reported glass transition temperature (T_g) of 420°C [8]. Recent works on PBI evidenced the chemical and thermal stability of this material and its use as the membranes in fuel cell [9,10] and sensor applications [11]. The PBI membranes were also functionalised with acid groups to form proton-conductive materials [12,13]. In our case, the PBI should form the network in which to keep the HPA supported on silica.

The PWA is a very conductive material in the crystalline form with 29 water molecules [14] and as a concentrated aqueous solution [4]. Tests performed on fuel cell in our lab with this electrolyte gave power density higher than 0.7 W/cm^2 at room temperature and with H$_2$ and O$_2$ at atmospheric pressure [3]. In recent works, a similar material, the silicotungstic acid (SiWA), was used to modify the commercial Nafion 117 membrane and to prepare membrane starting from the 5% Nafion 1100 solution [15,16]. The authors found that the proton conductivity of the Nafion membranes modified with SiWA were higher compared to that of commercial Nafion 117. They do not report, however, the thermal stability of the membranes.

In this paper, we report the preparation procedures and the main characteristics of the membranes based on PWA, silica and PBI.

2. Experimental

Membranes containing 40, 50, 60, 68 wt.% of PWA/silica in the PBI have been prepared. In all cases, the starting material was 30 wt.% of PWA on silica (PWA30). It was established that with this amount, the PWA was uniformly dispersed on silica as evidenced by XRD and FTIR analysis reported in our previous paper [17].

Phosphotungstic acid (PWA), $H_3PW_{12}O_{40} \cdot nH_2O$ (water content 10.2 wt.% with purity > 99%), supplied by Fluka, was utilized without further purification. Tetraethylorthosilane (TEOS), supplied by Aldrich was used as the precursor for silica formation. Because the PWA was introduced in the alcoholic solution containing TEOS and it catalyzed the formation of silica, the adsorption of the acid occurred as soon as silica was formed. PBI, having melting point > 300°C was an Aldrich product. The PBI was dissolved in N,N-dimethylacetamide at 150°C, and then the powder of PWA/silica (PWA30) was added under continuous stirring. The paste formed was casted with certain thickness on a glass plate and dried at low temperature for 18 h. The sample was then rinsed in distilled water, immersed in a concentrated solution of HCl and rinsed again in distilled water. The membrane so prepared, remained in distilled water until it was used for further characterization.

The membrane samples were quantitatively analyzed on the content of carbon, nitrogen and hydrogen, using a CHNS Carlo Erba analyzer, in order to evaluate their nominal chemical composition.

The differential scanning calorimetry (DSC) measurements were performed on the dried samples, in the range of temperatures between 40°C and 570°C, in order to obtain the information on thermal stability of the composite membranes. Measurements were performed using a Netzsch STA 409 instrument in combination with a temperature programmer Netzsch 410 and data acquisition system 414 used with a personal computer. The samples were flushed with air at a flow rate of 50 ml/min and analyzed at scanning rate of 10°C/min.

Ionic conductivity measurements on the membrane samples were performed in a test station consisting essentially of three parts: a gas humidification zone (saturator), a through-flow cell containing the membrane sample and a universal bridge for the conductivity measurement. In this configuration, the inert gas flows through the saturator, kept at a pre-selected temperature and then passes through the conductivity cell with the membrane sample main-

tained at temperature higher than saturator. The temperatures of the humidifier and conductivity cell are preset at such values as to obtain the desired gas relative humidity in the cell compartment. Conductivity measurement was carried out in three different regimes:

(a) at different temperatures, in the range from 90°C to 150°C and at fixed relative humidity (40% or 100%),
(b) at fixed temperature of 100°C and relative humidity ranging from 20% to 80%, and
(c) at fixed relative humidity, 100%, and temperature ranging from 30°C to 100°C.

In order to avoid water boiling in the humidifier, when the temperature was set over 100°C, the pressure inside the gas circuit was fixed at 0.5 MPa. The universal bridge, GW LCR Meter Model LCR-815, operating at the frequency of 1 kHz and connected to two gold discs, each having area of 1.0 cm^2, between which the membrane sample was pressed, was used for the resistance measurements. Two discs of carbon cloth, covered with a thin layer of active carbon and PTFE, were inserted on both sides of the membrane in order to improve the contact between golden discs and membrane sample. The resistance of membranes was read at fixed temperature and relative humidity after it reached stable values.

3. Results and discussion

The composite membranes prepared with diverse thickness have tensile strength that is not substantially lower than the tensile strenght of membranes prepared from pure PBI. The chemical stability of the membranes in water was tested by introducing small piece of the material in a beaker containing water, boiling it for 30 min and then, after cooling to the room temperature, measuring the pH of the water. The neutral pH of the water confirmed that the PWA was not leached out during such treatment.

The elemental composition (C, N, H) of the composite membrane samples having different content of PWA30 and of pure PBI and PWA products are reported in Fig. 1.
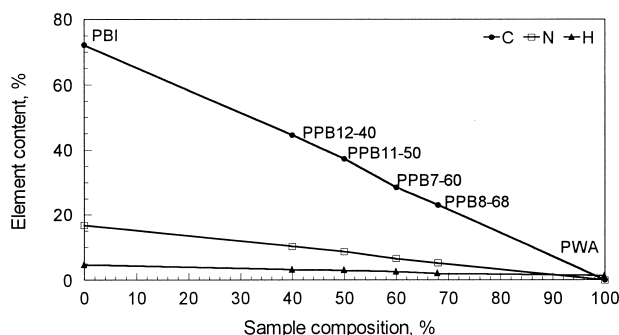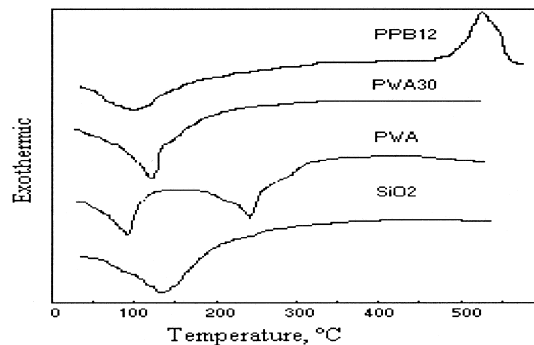

Fig. 2. DSC curves of the composite membrane containing 40 wt.% PWA (PPB12 sample), of the powder sample containing 30 wt.% of PWA on silica (PWA30 sample), of pure PWA and of pure silica.

A perfectly linear dependence of each element content on the PWA amount in the membrane is obtained. Moreover, an exact correspondence between the nominal and the real composition of membranes was obtained.

The DSC analyses were carried out on silica, PWA, PWA/silica (PWA30) and a representative sample of membrane containing 40% PWA30 in PBI. The DSC spectra of these samples are reported in Fig. 2. It can be observed that the second peak of water desorption from PWA is missing in the samples PWA30 and PPB12. This effect is due to the uniform and fine dispersion of HPA on silica as we have evidenced in a previous paper [17]. An exotherm starting at about 450°C in the PPB12 sample is due to the decomposition of the organic polymer (PBI). Judging on this, the composite material can be considered thermally stable up to 400°C.

Ionic conductivity measurements were performed on samples of composite membranes with different PWA30 content in PBI and on pure PBI. The values of specific proton conductivity as a function of the temperature at 100% of relative humidity are reported in Fig. 3. The specific conductivity of the samples increases with temperature. It also increases with the content of PWA in them, with exception of the sample containing 68% of PWA (PPB8-68) that has a lower conductivity with respect to the
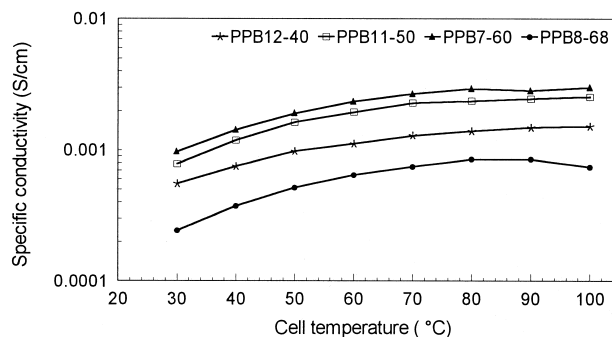

Fig. 1. Relative content of the C, N, and H elements in the membrane samples as the function of PWA loading.

Fig. 3. Proton conductivity of composite membrane samples with different PWA/SiO$_2$ loading in PBI as a function of temperature. Relative humidity: 100%.
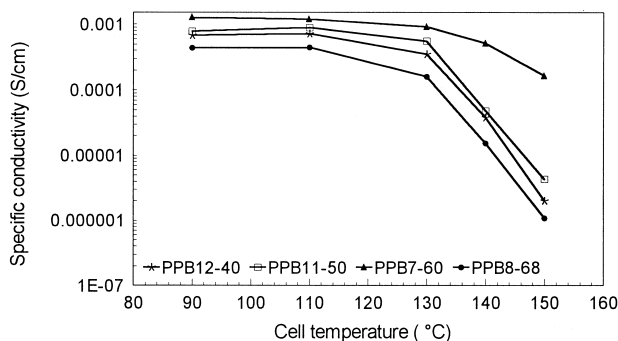
Fig. 4. Specific conductivity of composite membrane samples with different content of PWA as a function of temperature. Relative humidity: 40%.

Fig. 6. Specific conductivity as a function of relative humidity. Temperature: 100°C.

samples containing less PWA. Thus, one can conclude that the proton conductivity increases with PWA loading up to 60%, while it decreases at higher PWA loading. The sample PPB7-60 has the highest conductivity among the measured samples. It increases from 9.7×10^{-4} S/cm at 30°C to 3.0×10^{-3} S/cm at 100°C.

At higher temperatures in the range from 90°C to 150°C and at 40% of relative humidity (Fig. 4), the trend is different. Almost stable values of conductivity are registered for all samples in the temperature interval between 90°C and 110°C, then a continuous decrease of conductivity is observed at higher temperatures. The explanation for the decrease in composite membrane conductivity at temperatures above 110°C under these relative humidity conditions is the lowering of the amount of water in the membranes with the increase of temperature. In fact, the measurements carried out at 100% relative humidity (Fig. 5) on two membrane samples show more stable proton conductivity in the same temperature interval. The presence of water in the membrane is essential for proton conduction and the presence of silica is useful in creating the path for this. We believe that the commonly observed poor proton conductivity of the PBI membranes doped with PWA mentioned in Section 1 is due to the difficulty of the water to enter the hydrophobic PBI membrane. The presence of silica in the composite membrane creates
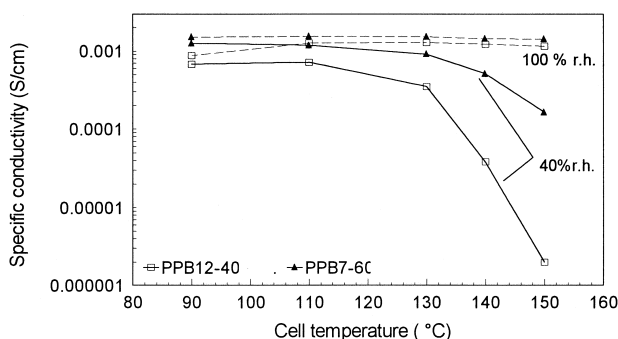
hydrophilic domains and helps the PWA to retain as much water as possible.

The specific conductivity as a function of the relative humidity at 100°C is given in Fig. 6. A continuous increase of specific conductivity was observed for all samples with the increase of relative humidity. Also in this case, the conductivity is highest for the composite membranes containing 60% of PWA30. At higher PWA30 content, the specific conductivity of composite membranes decreases.

4. Conclusions

Composite membranes based on PWA supported on silica embedded in a PBI structure have been successfully prepared.

The membranes are thermally stable up to 400°C.

The specific conductivity of composite membranes increases with relative humidity.

In the temperature interval between 30°C and 100°C and at 100% relative humidity, the specific conductivity of the composite membranes increases little. At 100°C and 100% relative humidity, a specific conductivity of 3×10^{-3} S/cm was measured.

The presence of silica in the composite membrane and the 100% relative humidity allow the membranes to maintain almost stable proton conductivity at temperatures up to 150°C. The proton conductivity measured at 150°C $(1.42 \times 10^{-3}$ S/cm) is still low for fuel cell application but in our opinion, it can be improved significantly in the future by modifying the preparation procedure and/or the final treatments.

Fig. 5. Specific conductivity of two composite membranes as a function of temperature for relative humidity of 40% and 100%.

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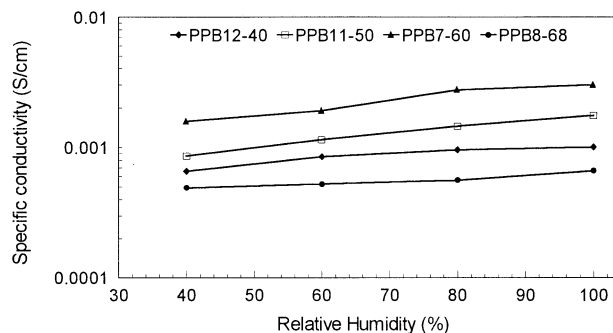[1] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47.

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