

Short communication

An NMR spectroscopic study of water and methanol transport properties in DMFC composite membranes: Influence on the electrochemical behaviour

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Abstract

Water and methanol transport properties through bare recast Nafion and composite Nafion membranes containing ceramic fillers characterised by different acid–base behaviour were investigated by nuclear magnetic resonance (NMR) spectroscopy. The water self-diffusion coefficients were determined for the different membranes in the temperature range from 25 to 150 °C; the methanol self-diffusion coefficients were recorded for the most performing composite membrane (Nafion–SiO₂) and compared to the bare Nafion membrane. Water and methanol transport characteristics of these membranes were correlated to the electrochemical behaviour in direct methanol fuel cells. NMR and electrochemical polarization data indicate that both electrical properties and transport mechanism are influenced by the surface properties of the inorganic fillers; there is a clear evidence that acidic fillers such as silica promote the proton transport in the membrane with respect to basic alumina.

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1. Introduction

Direct methanol fuel cells (DMFCs) are a promising clean energy source for transportation, portable and small-scale stationary power generation [1–3]. The DMFC and PEMFC technology is based on perfluorinated membranes (i.e. Nafion) as electrolytes, operating at a temperature around 80 °C [4,5]. This limit of temperature results from the difficulty in maintaining a suitable amount of water in the membranes as required to have good proton conductivity at temperatures above 100 °C at suitable pressures. Polymer electrolyte membranes capable of operation above 120–130 °C can take advantage from the increase of methanol reaction kinetics and oxygen reduction in a DMFC as well as from the enhancement of carbon monoxide (CO) tolerance and improvement of heat removal in a PEMFC [6–8].

The addition of an inorganic filler into a polymeric matrix may improve both physical and chemical characteristics of a membrane, influencing the mechanical and hydration properties in particular at high temperatures, consequently enhancing fuel cell performance and stability. In particular, composite membranes show less water dehydration constraints than bare Nafion on account of the presence of high surface area hygroscopic ceramic oxides inside the polymer matrix [9–16]. Furthermore, these fillers can enhance water retention properties of the membranes under low humidity conditions [9,10,13]. A reduction in methanol cross-over may be expected from the increased physical tortuosity factor due to the presence of the filler particles inside the composite membrane [10,17].

Actually, membrane conductivity and methanol cross-over have significant influence on the performance of high temperature H₂ and direct methanol fuel cells. Conductivity and cross-over properties are related to the self-diffusion coefficient of water and methanol in the membrane [18–23]. In the present paper, the transport properties of some composite membranes

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have been investigated by pulsed field gradient nuclear magnetic resonance (PFG-NMR) measurements and compared to those of bare recast Nafion membranes. Since the surface acid–base properties of the inorganic filler play an important role for the water uptake [24,25], we have investigated two composite membranes, containing an acidic (SiO_2) and a basic (Al_2O_3) ceramic oxide. Water and methanol transport characteristics of these membranes were correlated to the electrochemical behaviour in direct methanol fuel cells.

2. Experimental

Acidic silica (SiO_2) and basic alumina (Al_2O_3) ceramic oxide fillers have been purchased from Cabot and Aldrich, respectively. The physico-chemical properties of these fillers were previously investigated [25]. The SiO_2 mean particle size was 7 nm; whereas, it was 5.4 nm for the basic alumina [25]. The membranes were prepared by using a recast procedure described in Ref. [10]. The maximum temperature reached during the membrane preparation was 160 °C. Membrane and electrode (M&E) assemblies were prepared following a procedure previously described [26]. Fuel cell experiments were carried out in a 5 cm² single cell (GlobeTech, Inc.). A 2 M aqueous solution of methanol and oxygen were preheated at 85 °C and fed to the cell. The catalyst employed for methanol oxidation was a 60% Pt–Ru (1:1)/Vulcan XC (E-TEK), whereas a 30% Pt/Vulcan XC (E-TEK) was used for oxygen reduction. The platinum loading for all the electrodes was 2 mg cm⁻².

PFGSE (pulsed field gradient spin-echo) ¹H NMR experiments were performed in the temperature range from ambient temperature up to 150 °C in order to determine the self-diffusion coefficients of (i) water, (ii) 4 M methanol solution in deuterated water (D_2O) and (iii) pure methanol. The membranes were firstly swelled in the solvent at room temperature; thereafter, they were removed from the bath, the surface was dried with a paper tissue and the samples were loaded in a sample holder, where they were allowed to equilibrate under constant relative humidity (30%) for 48 h at 20 °C. The sample holder was then sealed and the self-diffusion study was carried out using PFGSE (pulsed field gradient spin-echo) ¹H NMR technique to probe the water and methanol diffusivities (D). This method has been shown to provide valuable information on both dynamic and structural aspects of self-assembling systems [21]. The most common form of this experiment is based on a pulse sequence consisting of a 90° radio frequency (rf) pulse at $t=0$ followed by a 180° rf pulse at $t=\tau$; this results in a spin-echo at $t=2\tau$. In addition to rf pulses, a pulsed magnetic field gradient is inserted on each side of the 180° rf pulse, causing the attenuation of echo intensities.

In the case of free Gaussian diffusion the theoretical expression of echo attenuation, R , is given by the well-known Stejskal–Tanner equation [27]:

$$R = \frac{I(g)}{I(0)} = \exp \left[-(\gamma\delta g)^2 D \left(\Delta - \frac{\delta}{3} \right) \right]$$

where $I(g)$ and $I(0)$ are the signal intensities at $t=2\tau$ in the presence of gradient pulses of strength g and in the absence of

any gradient pulses, respectively. The time between 90° and 180° rf pulses is τ , γ is the magnetogyric ratio, δ is the duration of the gradient pulses, Δ is the time between the leading edges of the gradient pulses (time of the diffusion) and D is the self-diffusion coefficient.

All experiments reported in this study were carried out under conditions of $\tau=0.020$ s.

The diffusion studies were performed on a home-built NMR spectrometer operating at 16 MHz for protons. The 90° rf pulse length was 9 μs , Δ and g were held constant to 0.020 s and 0.50 T m⁻¹, respectively. It is found that the diffusion coefficients are independent from Δ values for this system. The length of the gradient field pulse, δ , was changed in the interval 0.001–0.006 s while the gradient strength g was calibrated using a reference sample of pure tri-distilled water, with a known self-diffusion coefficient. The echo amplitude was measured accumulating 16 scans. The temperature was controlled by air-flow regulation with a stability of 0.2 °C.

3. Results and discussion

The electrochemical behaviour of composite and bare Nafion membranes was analysed by polarization experiments. Both the composite membranes were able to operate up to 145 °C, whereas the cell equipped with the bare recast Nafion membrane reached the maximum operating temperature of 120 °C. Fig. 1 shows the variation of the open circuit potential (OCP) as a function of temperature for the various membranes. The OCP is an important parameter in a DMFC in order to assess the methanol permeability of a membrane. The DMFCs based on SiO_2 –Nafion membrane and bare Nafion showed similar behaviour in the temperature range from 90 to 120 °C, whereas the cell equipped with Al_2O_3 -based membrane evidenced a lower value of OCP. Also the current density at 0.4 V (Fig. 2) was significantly lower for the basic Al_2O_3 –Nafion membrane compared to the bare Nafion and the acidic SiO_2 based membrane up to 120 °C. Above this temperature, the performance of bare recast Nafion dropped below the performance of the Al_2O_3 -membrane. The SiO_2 composite membrane was still quite more performing than Al_2O_3 -membrane up to 145 °C.

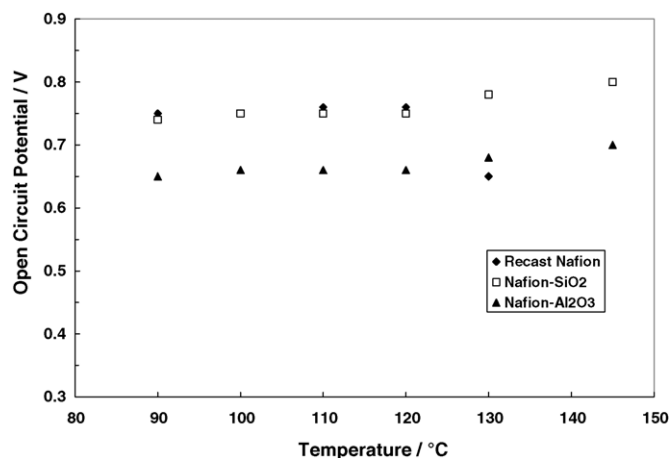


Fig. 1. Variation of the open circuit potential (OCP) as a function of temperature for DMFCs equipped with the composite and bare Nafion membranes.

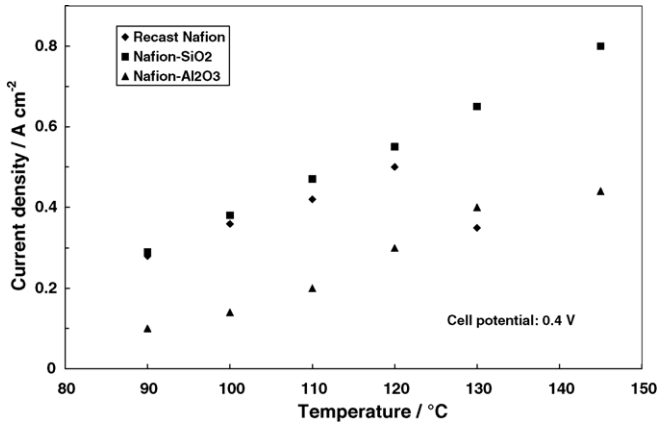


Fig. 2. Variation of current density at a cell potential of 0.4 V as a function of temperature for DMFCs equipped with the composite and bare Nafion membranes.

The average particle size of SiO₂ and basic Al₂O₃ is quite similar, i.e. 7 nm versus 5.4 nm. Accordingly, the different OCP values for these membranes could not be attributed to a change in the diffusion path (tortuosity effect). More properly, this may result from the different surface properties. Possibly, basic functional groups give rise to an acid–base reaction with Nafion sulfonic groups, thus decreasing proton activity close to the cathode–electrolyte interface [25]. This may contribute to decrease the reaction rate for oxygen reduction increasing the irreversibility of the electrochemical process [28], that is reflected by lower OCP values for the basic alumina membrane.

Fig. 3 shows the Arrhenius plot of the water (proton) self-diffusion coefficients for the two composite membranes and bare recast Nafion. The self-diffusion coefficients are for the basic Al₂O₃-based membrane lower than bare Nafion and Nafion–SiO₂ composite membranes in the whole temperature range, indicating a significant blocking effect played by the surface basic functional groups on the proton transport. The silica-based membrane shows proton diffusivities comparable to bare Nafion. The acidic functional groups do not strongly interact with hydronium ions as it occurs for the basic surface sites in the case of alumina. The water self-diffusion coefficient of bare Nafion is larger than the Al₂O₃-based membrane at high temperatures, although this latter is superior in the electrochem-

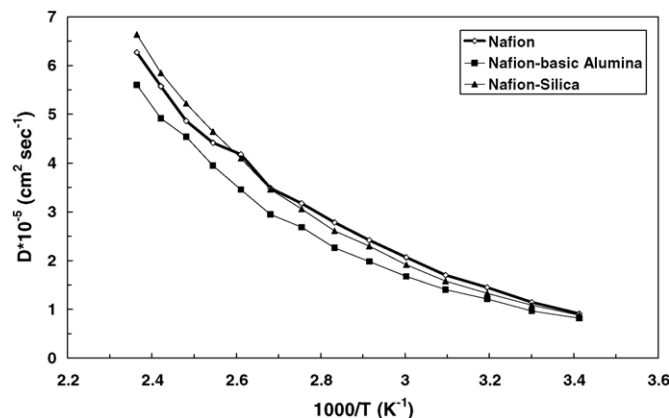


Fig. 3. Arrhenius plot of the water self-diffusion coefficients in bare recast Nafion and recast Nafion–ceramic filler composite membranes.

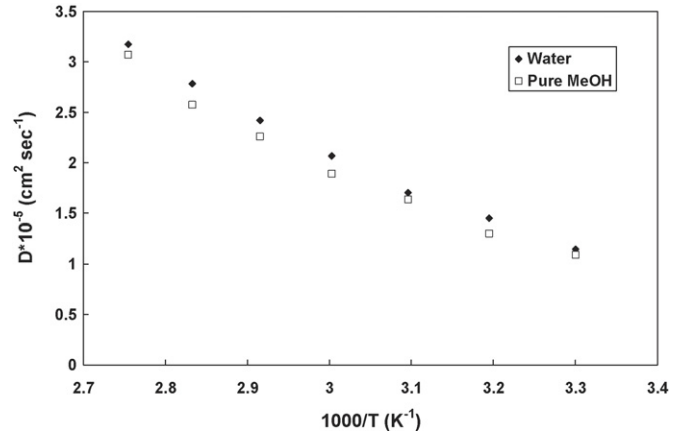


Fig. 4. Comparison of the water self-diffusion coefficients with the pure methanol self-diffusion coefficients in bare recast Nafion membrane.

ical performance at 145 °C. However, the physical environment may be not exactly the same in these two experiments (NMR, *I*–*V* polarization), especially in terms of water vapour pressure. In NMR experiments, the sample holder is closed and it does not allow the system equilibration with the external pressure, thus water retention is favoured. On the other hand, the composite SiO₂–Nafion membrane is more performing than the Al₂O₃-based membrane (Fig. 2) at high temperatures [24].

The favourable properties of the Nafion–SiO₂ membrane in terms of diffusion coefficients indicate interesting perspectives for application of this composite polymer electrolyte in direct methanol fuel cells. Accordingly, our attention has been focused on the methanol transport properties through this membrane and the bare recast Nafion.

A comparison of the water and methanol self-diffusion coefficients in the bare recast Nafion and SiO₂–Nafion membranes is shown in Figs. 4 and 5, respectively. It is observed that in the bare Nafion the mobility of water is higher than the pure methanol; whereas, it was found an opposite behaviour for the composite SiO₂–Nafion membrane where the methanol has higher diffusivity than the water. This evidence indicates the existence of a promoting effect of silica particles in enhancing the methanol

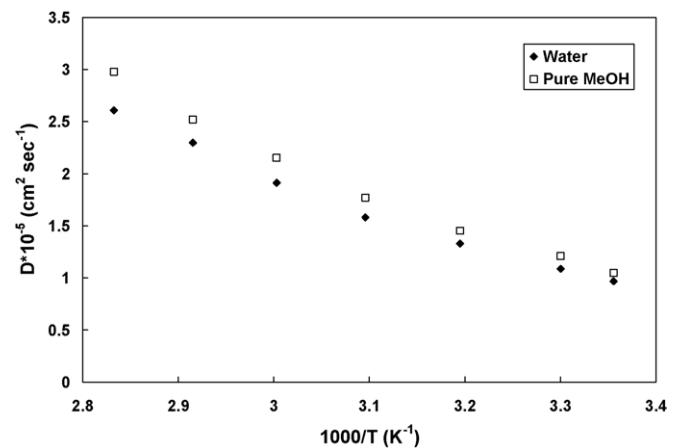


Fig. 5. Comparison of the water self-diffusion coefficients with the pure methanol self-diffusion coefficients in recast Nafion–SiO₂ filler composite membranes.

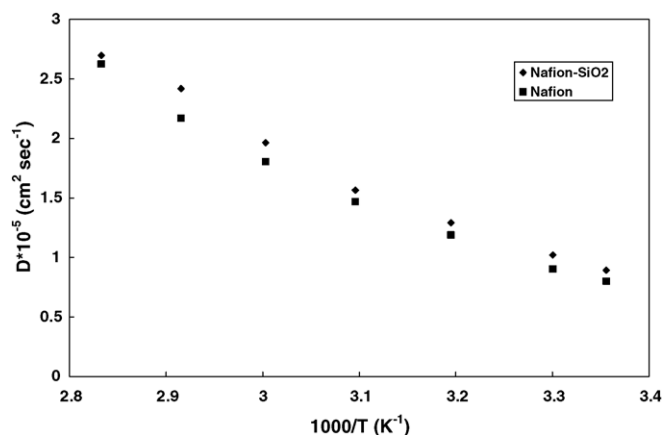


Fig. 6. Arrhenius plot of the methanol self-diffusion coefficients in bare recast Nafion and recast Nafion–SiO₂ filler composite membranes; CH₃OH–D₂O solution with 4 M methanol concentration.

self-diffusion coefficient. In the presence of a solution of methanol in water, a competition between methanol molecules and water coordinated protons for the adsorption on the silica surface may arise at pH values close to the zero point of charge of the filler, due to the lower dielectric constant of methanol with respect to water. In fact, silica shows low uptake characteristics for the adsorption of hydroxyl and hydronium ions at low pH values [29] which are typical of the Nafion–water environment. Under such conditions a labile adsorption of methanol on the filler surface is probably favoured. Generally, methanol fuel cells operate with a methanol concentration in the anode feed up to 2 M; yet, in order to increase the signal to noise ratios, a 4 M solution was selected in the present case. The methanol diffusion coefficient is generally higher in the Nafion silica membrane than in the bare Nafion in 4 M methanol solution (Fig. 6). Accordingly, one would hypothesise a larger methanol cross-over in the silica composite electrolyte with respect to bare Nafion membrane. This is in contrast with previous published data on methanol cross-over for composite SiO₂-containing membranes [10]. Effectively, membrane transport properties are governed by the mutual diffusion coefficients and there is a great possibility that membrane tortuosity is changed by the embedded silica filler. Possibly, at high temperatures the increase in methanol diffusion coefficients, observed for the composite SiO₂ membrane versus bare recast Nafion, produces a less significant influence than the physical barrier effect by the inorganic filler. This may explain the observed data of methanol cross-over for SiO₂-based membranes under real operating conditions.

4. Conclusions

A preliminary NMR investigation of the transport properties of water and methanol in composite inorganic filler-polymer membranes has been carried out. From this analysis and from the electrochemical polarization behaviour, it appears that the transport mechanism is influenced by the surface properties of the inorganic fillers; in fact, an acidic silica filler appears to promote proton transport in the membrane with respect to basic

alumina. The silica particles inside the membrane could be a potential physical barrier for methanol cross-over but they may also interact with methanol molecules enhancing the CH₃OH self-diffusion coefficient. A compensation between these two effects probably occurs under real operating conditions since low methanol cross-over values have been experimentally observed for composite membranes.

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