Chemical Modification of Perfluorosulfonated Membranes with Pyrrole for Fuel Cell Application: Preparation, Characterisation and Methanol Transport[×]

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Abstract

In situ chemical polymerisation of pyrrole in Nafion®-115 membranes produces a composite material that shows a decrease in methanol crossover compared with the non-modified material, and a good protonic conduction (area resistance of 0.65 Ω cm^2). Pyrrole is impregnated from an appropriate solvent, and the choice of oxidising agent (hydrogen peroxide, ammonium peroxodisulfate) provides two types of modified membrane. Membrane characterisation using infrared spectroscopy shows the presence of pyrrole oligomers and polymer, but the proton conductivity is lower than that of the Nafion®-115 membrane by only a factor 2–3. Methanol transport measurements in 2 mol dm^{-3} methanol with and without application of an electric field show ca. 30% lower crossover for the pyrrole-modified membranes. In single cell hydrogen – oxygen fuel cell tests, the pyrrole-modified Nafion® prepared using hydrogen peroxide oxidant gave higher open circuit voltage and current density, in particular at > 80 °C, than non-modified Nafion®-115.

Keywords: Fuel Cells, Hydro-Organic Media, Ion Exchange Membranes, Methanol Crossover, Pyrrole-Modified Nafion®

1 Introduction

The predicted exhausting of oil reserves is the drive for the search for new means of power production. In addition to natural renewable energy sources: wind, geothermal, hydraulic power etc., the enormous recent investment in research on fuel cells has led to much progress bringing commercialisation closer to reality. There are at the moment several categories of fuel cells operating at high or low temperature, including the Proton Exchange Membrane Fuel Cell (PEMFC) and the Direct Methanol Fuel Cell (DMFC).

The proton conducting membrane generally used in PEMFC is Nafion® (DuPont® USA) or other perfluorosulfonic acid material [1, 2], which demonstrate excellent chemical and mechanical properties as well as a high proton conductivity when hydrated. The application of Nafion® in DMFC [3] however is less satisfactory, the most important reason for which being the cross-over of methanol from the anode to the cathode side. This alcohol leakage poisons the reaction at the cathode and decreases the efficiency of the fuel cell [4–7]. Methanol crossover in Nafion® in the presence of a solvent is facilitated by the swelling of the polymer matrix that readily occurs due to the absence of a crosslinked structure. Several different approaches have been reported in the literature with the aim of reducing the methanol permeability of Nafion® [8–13] or of producing new membranes better adapted to DMFC operation than Nafion® [14–16]. Among the former is the composite Nafion®/polyvinyl alcohol membrane, which shows a low methanol cross-over but reduced DMFC performance compared to pristine Nafion® [8]. Chem-

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ical modification of ion exchange membranes by pyrrole or 1-methylpyrrole has also been described, with the objective either of improving the membrane selectivity [17] for application in electrodialysis or of decreasing the methanol crossover [18]. Although methanol permeability is indeed reduced, the native membrane electrical resistance is increased, and performance in PEMFC is reported to decrease [19]. Recently, and during the course of the present work, Easton et al. [20] described composite polypyrrole/Nafion® membranes showing a better performance in DMFC than Nafion®-115 under some experimental DMFC operation conditions.

Up to now, any modification of Nafion® with pyrrole has always been carried out in an aqueous medium [17, 18, 20–22]. However pyrrole is hydrophobic and weakly soluble in water, giving solutions of concentration $< 10^{-1}$ mol dm^{-3}. In the present study, we chose to use alternative solvents in particular N-methylformamide (NMF) in order to increase the pyrrole concentration in solution and to favour its penetration into the membrane. On the one hand, NMF has a high dielectric constant, so is a good solvent for pyrrole and, on the other, it efficiently swells the polymer matrix of Nafion® [23]. Membrane swelling with NMF allows penetration of pyrrole into the thickness of the membrane, while restricting its localisation mainly to the hydrophobic regions. In this way the hydrophilic sites are kept intact, and the perfluorosulfonic acid polymer chains inter-bound or "cross-linked" by polymerised pyrrole.

Rapid chemical polymerisation of pyrrole is well described in the literature [24–25], generally by oxidation with either cationic ($FeCl_3$) anionic [$(NH_4)_2S_2O_8$] or neutral (H_2O_2) species or by both acids and bases [26]. Possible membrane contamination by Fe^{3+} using the first of these reagents led us to avoid ferric chloride, and we consider here the use of hydrogen peroxide and ammonium peroxodisulfate as oxidants for the *in situ* polymerisation of pyrrole in Nafion®-115, and compare the resulting modified membranes in terms of their pyrrole content, the extent of polymerisation, permeability of methanol under static conditions and under the effect of an electric field. In the second part of this article, we describe the fuel cell evaluation of pyrrole-modified membranes and assess their stability with respect to free radical degradation using Fenton's reagent.

2 Experimental Section

2.1 Materials

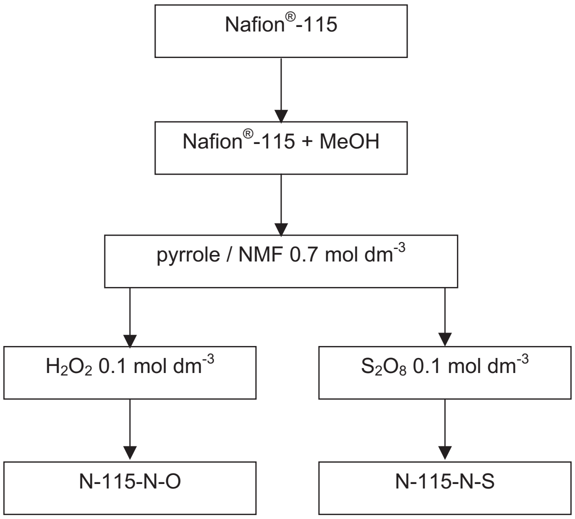
Methanol and NMF were Carlo Erba and Fluka products respectively, of purity > 99%, H_2O_2 (35 wt.%) from Aldrich, pyrrole (C_4NH_5, 97%) from Fluka and ammonium peroxodisulfate [$(NH_4)_2S_2O_8$] from Prolabo were all used as received. Water was deionised by reverse osmosis. Nafion®-115 was purchased from Fluka and submitted to the treatments described below.

2.2 Nafion® Preparation

Nafion® film was cut into pieces around 40 cm^2. Prior to any modification with pyrrole, all membranes were treated by boiling in 3% aqueous hydrogen peroxide (1 h) and rinsed with cold water. They were then soaked in HNO_3 (10 mol dm^{-3}, 30 min at room temperature) and were rinsed again, before heating in water (100 °C, 1 h). After this cleaning stage, membrane samples were first soaked and then heated in sulfuric acid (1 mol dm^{-3}, 1 h, 100 °C) to ensure acidification of any remaining non-protonated sites. Cleaned and washed Nafion® samples were stored in 0.5 mol dm^{-3} sulfuric acid and were immersed in water for 8 h at 80 °C, which has the effect both of removing any excess sulfuric acid and swelling the Nafion® membrane, before modification with pyrrole.

2.3 Nafion® Modification

Scheme 1 shows the various stages developed for modification of Nafion® by pyrrole impregnation/polymerisation. Each step was carried out at room temperature, for 24 h. Modified membranes were then washed and hydrated at 80 °C for 8 h. Nafion®–pyrrole membranes prepared using hydrogen peroxide and ammonium peroxodisulfate oxidants are denoted N115-N-O and N115-N-S respectively.



Scheme 1 Modification of Nafion® by *in situ* chemical polymerisation of pyrrole.

2.4 Membrane Characterisation

The membrane electrical resistance R_H was measured using the clip-cell method described previously [27], in an aqueous solution of 0.05 mol l^{-1} H_2SO_4 at 25 ± 0.1 °C. The surface electrical resistance R_S (Ω cm^2) is related to the specific conductivity σ (S cm^{-1}) through $\sigma = e / R_S$, where e (cm) is the membrane thickness.

The amount of polypyrrole in modified Nafion® membranes can be considered, in a first approximation, to be the weight difference between the wet membranes before and after pyrrole modification. More precise estimation of the amount of polypyrrole in the membrane was obtained by elemental microanalysis of carbon, sulfur, nitrogen and hydrogen (by combustion) with a Flash EA 1112 series from Thermo Finnigan. Nafion® is a perfluorosulfonated polymer, composed only of carbon, fluorine, oxygen and sulfur, and determination of S and N contents allows calculation of the amount of polypyrrole in the composite membrane system. Membrane water content was determined using a Mettler Toledo Halogen Moisture Analyser, HR73. The weight of a membrane sample (0.1 g), pre-conditioned as described above, is monitored with temperature up to 80 °C when the variation of weight with time is less than 1 mg per 140 s. The membrane thickness of membranes pre-conditioned as described above was determined with an Electronic Digital Micrometer (Codiam Scientific).

The infrared spectra given by the surface of membranes was recorded using a Nicolet NEXUS Golden Gate FT-IR-ATR instrument, and the acquired data analysed with OMNIC 6.2 software.

Methanol transfer studies were conducted using the polytrifluorochloroethylene laboratory cell (PTFCE) shown in Figure 1. The study was carried out at room temperature on modified and non-modified membrane samples of surface area 7 cm^2. Contents of both cell compartments were mechanically stirred by glass-stem stirrers [28]. The measurement of methanol flux was carried out in diffusion and in electro-osmosis modes, the latter using a current density of 10 mA cm^{-2}. The donor compartment was filled with methanol (2 mol dm^{-3}) in 0.05 mol dm^{-3} sulfuric acid solution.

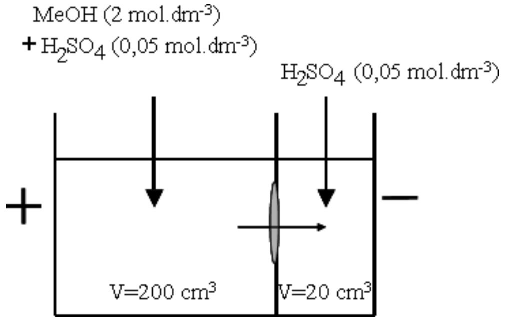


Fig. 1 Hittorf-type cell for determination of methanol transfer through Nafion®.

Methanol transferred through the membrane separator was analysed by Raman spectroscopy. Although not a commonly used method to quantify methanol, it allows rapid semi-quantitative determination of methanol concentration with a 6% estimated error, and with the advantage of avoiding the salt problem that occurs using gas chromatography.

Non-modified Nafion®-115, and N115-N-O and N115-N-S membranes were pre-conditioned by treating in dilute hydrochloric acid (0.1 mol dm^{-3}, 80 °C, 1 h) and water (80 °C, 1 h) They were then assembled with E-TEK electrodes (1 mg_{Pt} cm^{-2}, 0.6 $mg_{Nafion®}$ cm^{-2}). The membrane-electrode assemblies were prepared at room temperature, without application of pressure, and were mounted in a fuel cell of 4 cm^2 active area. The cell was fed with hydrogen and oxygen, the anode gas (only) being hydrated through a bubbler at 10 °C above the temperature of the fuel cell. Polarisation characteristics were recorded at 70, 80 and (for Nafion®-115 and N115-N-O), 90 °C after stabilisation of cell voltage at 0.5 A cm^2 at each temperature.

3 Results and discussion

3.1 Pyrrole-Modified Membranes: Composition and Conductivity

Non-modified Nafion® membrane has a specific resistance at 25 °C of 0.2 Ω cm^2, in good agreement with previous results on the protonated form of Nafion® membranes [29]. The presence of polypyrrole led to an increase of the electrical resistance by a factor 2 (using persulfate oxidant) or 3 (using hydrogen peroxide). This can easily be accounted for on the basis of a slight decrease in the number of charge carriers present as hydronium ions or other protonated water species. Chemical polymerisation leads to positively charged polypyrrole (3 pyrrole units/positive charge [25]), balanced in a bulk polymer by counter-ions supplied by the oxidising agent. For polymerisation with hydrogen peroxide, only the fixed negatively charged sites on Nafion® are available to balance positive charge. Using ammonium peroxodisulfate, the overall number of positively charged species is higher since SO_4^{2-} ions (by-product of the polymerisation reaction) are also present in the modified membrane. The overall number of protonated species is higher, which could account for the lower membrane resistance observed.

In Table 1, the ratio N/S obtained by elemental analysis expresses the number of pyrrole units per Nafion® ion exchange site. These ratios are quite different for modified membranes prepared using dilute hydrogen peroxide (N/S = 0.32) and ammonium peroxodisulfate (N/S = 0.087) i.e. N115-N-O contains 4 times more (poly)pyrrole than N115-N-S. This marked difference is probably a consequence of the negative charge on the persulfate anion, which effec-

Table 1 Characteristics of pyrrole-modified Nafion® membranes.

	Membrane				
	N115	**N115-N-O**		**N115-N-S**	
		Before FC test	After FC test	Before FC test	After FC test
Membrane resistance in H^+ / Ω cm^2	0.2	0.65	n.d.	0.4	n.d.
Δ*thickness* /%[a]		+5.8		+7.1	
Δ*m* /%[a]		3.0		3.4	
λ^b	16	17	19	22	19
Ratio /% N/S		31.6	11.4	8.7	3.6

a Δ*thickness*: Change in membrane thickness ; Δ*m*: Increase in membrane weight
b $\lambda = n(H_2O)/n(SO_3)$ with $n(H_2O)$ calculated from the difference between mass of wet and dry membranes, and $n(SO_3)$ calculated using values from elemental analysis

tively excludes it from penetrating into the thickness of the polymer, because of repulsion between fixed SO_3^- sites and peroxodisulfate $S_2O_8^{2-}$ [21]. Solvent exchange however, (and thus membrane swelling), does allow a certain quantity of persulfate to be trapped, leading to some *in situ* formation of polymer in the membrane. For N115-N-S, optical microscopy observations (not shown) indeed indicate that the polypyrrole is essentially on the surface of the membrane, with only a small quantity of polymer within its bulk. In general, with use of oxidants of ionic character, oxidation begins at the surface of the membrane, most accessible to the ions. In the present case, polymerised pyrrole at the two outer faces of the membrane limits diffusion and impedes the transfer of peroxodisulfate through Nafion® through a steric effect. The rate and extent of the polymerisation reaction are expected to depend on the rate of diffusion of the oxidant.

Using dilute aqueous hydrogen peroxide, less polypyrrole forms on the surfaces of Nafion®-115, and oxidant diffusion through the bulk is less impeded since no electrostatic repulsion acts. Oxidant hydrogen peroxide is therefore able to diffuse into the membrane bulk at the same time as the solvent. The polymerisation reaction is slow, being limited by diffusion of hydrogen peroxide through the membrane, and is probably catalysed by the protons at the acid sites of Nafion®. These slow reaction kinetics could lead to a partial release of the impregnated pyrrole from the membrane, owing to the concentration difference between the monomer in the membrane and in the surrounding solution.

In both cases, polypyrrole formation was accompanied by an increase of the membrane thickness Δt, of the membrane mass Δm, and the ratio N/S (%). The hydration number (λ, number of water molecules/sulfonate group) of the pyrrole modified membrane prepared using ammonium peroxodisulfate is higher ($\lambda = 22$) than that of pristine Nafion® ($\lambda = 16$), while that of N115-N-O prepared using hydrogen peroxide is similar to that of non-modified Nafion®. Hydrated sulfate groups in the former modified membrane increase the average number of water molecules/sulfonate site, and the higher degree of hydration of N115-N-S is also certainly a contributing factor to the lower membrane resistance in this case.

3.2 *Characterisation by ATR FTIR*

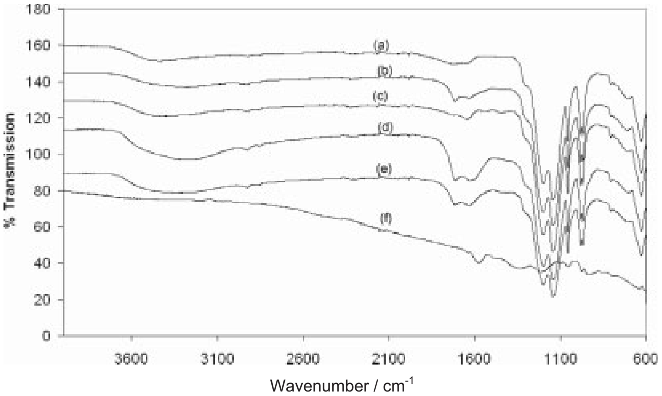


Fig. 2 ATR-FTIR spectra of Nafion® (a), N115-N-O as prepared (b) and after fuel cell operation (c), N115-N-S as prepared (d) and after fuel cell operation (e) and polypyrrole (f).

The ATR-FTIR spectra of bulk polypyrrole and pyrrole were recorded to provide reference data (Figures 2 and 3). The polypyrrole sample was prepared by oxidation with ammonium peroxodisulfate, and it is denoted PPy-S. Its ATR-FTIR spectrum shows the band characteristic of asymmetric C=C and symmetric C-C stretching vibrations of the pyrrole ring at ca. 1,560 cm^{-1}, although the exact position of the band is sensitive, *via* the degree of electron delocalisation, to polymer chain length, this band occurring in the pyrrole monomer at 1,710 cm^{-1}. The absorption at 1,490 cm^{-1} results from ring C-N stretching vibration, and the broad absorption between 1,250 and 1,400 cm^{-1} from C-H or C-N in-plane deformation modes. In the region 1,300–1,100 cm^{-1}, bands corresponding to the breathing vibration of the pyrrole ring are observed and C-H and N-H in plane deformation vibrations appear at 1,050 cm^{-1}, C-C out of plane ring deformations at 974 cm^{-1}, and bands arising from C-H out-of-plane deformation vibrations of the pyrrole ring at 939 and 800 cm^{-1}.

Analysis by FTIR-ATR is limited to the surface of membrane samples. The spectra given by membranes N115-N-S and N115-N-O are shown in Figure 2. Overall, the spectra are similar in band pattern but the intensity of absorption in the region 1,300–1,750 cm^{-1} is different, in particular that of doublet with maxima at 1,725 and 1,625 cm^{-1}. Comparison of the spectra of the modified membranes with that of bulk PPy-S shows a shift of +65 cm^{-1} (from 1,560 to 1,625 cm^{-1}) for the C=C / C-C stretching. In an IR spectroscopic study of various (poly)pyrrole oligomers, Tian and Zerbi [30] identified C=C / C-C in dipyrrole and polypyrrole at 1,618 cm^{-1} and 1,565 cm^{-1} respectively. This suggests that in the present case pyrrole oligomer is present on the membrane surface. The band C-N at 1,490 cm^{-1} for the bulk polymer is more difficult to distinguish in the spectra of N115-N-O and N115-N-S, being masked by the broad band centred at 1,625 cm^{-1}. Other peaks characteristic of PPy-S merge with the broad C-O-C absorption of Nafion® in the region at 1,350 to 1,100 cm^{-1}.

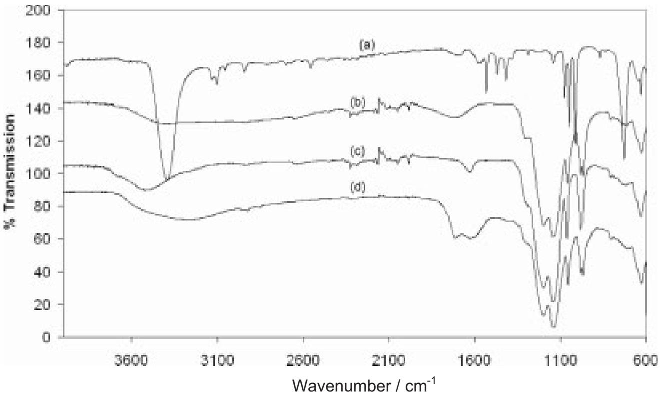


Fig. 3 ATR-FTIR spectra of pyrrole (a), Nafion® in protonated (b) and sodium ion form (c) compared with N115-N-S (d).

C-H and C-N at 1,050 cm^{-1} and the C-C deformation at 974 cm^{-1} appear at the same frequencies as the intense C-F absorption bands of Nafion® [22].

The band at 1,725 cm^{-1} which appears in the spectra of both pyrrole-modified membranes is almost absent in the spectrum of PPy-S and is weakly observed in that of Nafion®-115. Absorption at such a wavenumber could have various origins, including oxonium ions, known to be present in (non-modified) Nafion® after immersion in aqueous acid (proton transfer from sulfonic acid groups to water), pyrrole monomer trapped in the membrane (and not removed by washing), related to the presence of polypyrrole, or, less likely, from impurity species containing carbonyl groups [25].

In the ATR-FTIR spectrum of non-modified Nafion® (Figure 3), a weak and broad absorption of maximum around 1,730 cm^{-1} is seen, which could indeed involve HOH deformation in oxonium ions. To further verify this assignment, 3 pieces of Nafion®-117 were soaked (30 h), in a solution of H_2SO_4 (9 mol dm^{-3}), in sodium hydroxide (1 mol dm^{-3}) and in NaCl (2 mol dm^{-3}) respectively. After rinsing in distilled water and drying, ATR-FTIR spectra were recorded. The peak at 1,730 cm^{-1} is clearly visible in the spectrum of the acid form membrane (N117-H), while for sodium hydroxide-treated (N117-NaOH) and sodium chloride treated (N117-NaCl) membranes, the band at 1,730 cm^{-1} is replaced by one at 1,650 cm^{-1}, corresponding to the deformation of water. Pyrrole-modified Nafion®-115 gives both bands in FTIR, probably due to the presence of both water and oxonium ions. However, in comparison with the spectrum of N117-H, absorption in the 1,730 cm^{-1} region by the pyrrole-modified membranes is significantly more intense, suggesting the occurrence of another phenomenon which amplifies the intensity.

The spectrum of pyrrole monomer obtained by ATR-FTIR has a weak absorption at 1,710 cm^{-1} and a more intense band at 3,400 cm^{-1} corresponding to N-H stretching vibrations. The possibility should also be considered that Nafion® was able to concentrate monomeric pyrrole, especially with NMF as swelling agent. As described above, mixture of oligomer and polypyrrole forms on the surface when the membrane is oxidised, which could form an impermeable layer that traps non-polymeric pyrrole in the membrane or linked with the formed polymers, which then becomes no longer accessible to the oxidant.

The spectra of the pyrrole-modified membranes indeed show a broad band around 3,300 cm^{-1} which is compatible with the presence of pyrrole monomer. It may thus be concluded that the absorption band at 1,730 cm^{-1} in the pyrrole-modified Nafion® membranes is a composite band, resulting on the one hand from acid form Nafion® and, the other from the composite membrane-entrapped pyrrole. The surfaces of both types of modified membrane correspond to a mixture of monomer, oligomer and, for hydrogen peroxide prepared N115-N-O, polymer species. The presence of polypyrrole is confirmed only for N115-N-O from the presence of bands at 1,560 cm^{-1} characteristic of C=C / C-C of polypyrrole and C-N at 1,490 cm^{-1} more clearly visible after fuel cell operation of the membrane (see below). For N115-N-S, only the presence of monomer and oligomer were detectable.

3.3 Transport of Methanol in Pyrrole-Modified Membranes

The permeability of methanol through pyrrole-modified and pristine Nafion®-115 membranes was measured using a Hittorf-type cell (see experimental section). Semi-quantitative analysis (to within 6% error) of the amount of methanol transferred through the membrane was made using Raman spectroscopy using dioxane for internal calibration curve allowing quantification of methanol. Measurements were made in both diffusion and electro-osmotic modes, and the results shown in Figure 4 are the average of 3 separate experiments. The permeability to methanol of N115-N-O is > 30% lower than that of Nafion®-115, both in diffusion and electro-osmosis, whereas for N115-N-S, the permeability of methanol in diffusion is lower than for Nafion®-115, but not in electro-transport, where the flux is similar to that of Nafion®.

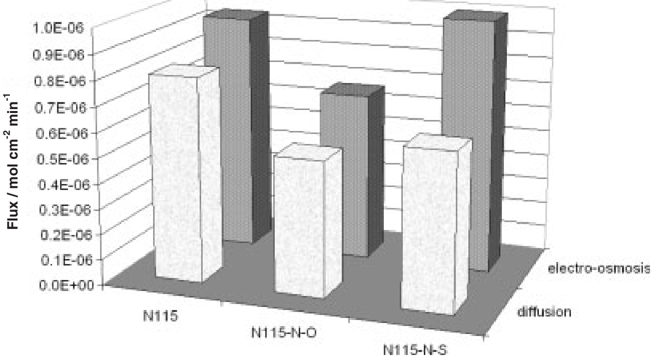


Fig. 4 Methanol flux through pyrrole-modified and non-modified Nafion® in diffusion and electro-osmosis modes.

As described above, modification of Nafion®-115 using peroxodisulfate leads to modification essentially on the surface. In simple diffusion, permeation of methanol through the membrane is impeded because of the polypyrrole barrier on the surface. However, with application of current density at 10 mA cm^{-2} methanol is able to migrate to the receiver compartment, indicating that the effect of a simple polypyrrole barrier is inadequate under the effect of the electric field, with the result that the electro-osmotic flux of N115-N-S is similar to N115. In contrast, for N115-N-O lower methanol crossover was measured than for Nafion®-115 both in the absence and presence of an electric field, and it may be concluded that the presence of polypyrrole both on the surface and within the membrane represent an effective partial barrier to diffusion and electroosmotic transport of methanol. Lower methanol flux across the pyrrole-modified Nafion® is important in the context of the application of pyrrole-modified membrane in a direct methanol fuel cell. Membrane resistance measurements indicate that proton access to the bulk is not drastically affected by surface enrichment in polypyrrole.

3.4 Fuel Cell Application of Modified Membranes

Pyrrole-modified Nafion® has been evaluated as a composite membrane applicable as an electrolyte in a hydrogen-oxygen fuel cell to assess the impact of polypyrrole on the system. Polarisation curves were recorded at 70, 80 and 90 °C, for each membrane and the results are shown in Figure 5 and Table 2. At 80 °C, membrane N115-N-O gave better performance than Nafion®-115. This improvement is still more marked at 90 °C, showing that the temperature increase has less effect on the conductivity of pyrrole-modified membrane, due to the role played by polypyrrole in enhancing membrane hydration, particularly at 90 °C. These results confirm the potential of such membranes as fuel cell electrolytes. A further difference between modified and non-modified systems is that the open circuit voltage for the cell with pyrrole-modified membrane is higher than that of the cell with pristine Nafion®-115 (inset in Figure 5), which might suggest a lower gas permeability for the composite membrane.

For N115-N-S, the membrane dehydrated during tests at 80 °C, and it punctured at 90 °C. Qualitatively, it was noted that the membrane N115-N-S had discoloured after fuel cell operation, and characterisation (ATR-FTIR, microanalysis, water content) of both pyrrole-modified membranes was performed after operation in the fuel cell.

From results presented in Table 1, N115-N-O appears to be more hydrated after fuel cell use (λ is higher). However, since the water content is expressed as the ratio of the quantity of water to the initial mass of the membrane, and since some polypyrrole elution is observed, the water content is in fact almost the same as that of the starting material. The loss of polypyrrole is shown by the decrease in the ratio N/S after operation in the fuel cell, and ATR spectra confirmed this partial loss of polypyrrole, a decrease of intensity of bands at 1,725 cm^{-1} and 1,645 cm^{-1} being observed. However since the ratio of the 2 bands is similar in N115-N-S and N115-N-S-FC, it may be concluded that the same quantity of monomer as oligomer is lost. In contrast, the spectrum of N115-N-O-FC showed a modified intensity ratio of these 2 peaks compared to N115-N-O, with additional bands at 1,550 and 1,480 cm^{-1} corresponding to the vibrations C-C / C=C and C-N respectively, and which probably indicates preferential loss of monomer and retention of polypyrrole in this membrane.

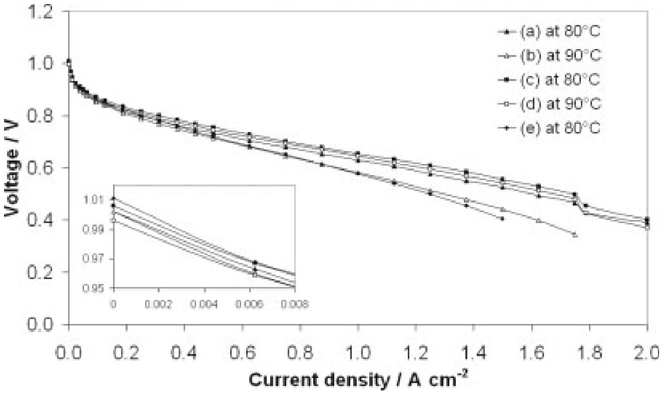


Fig. 5 Polarisation characteristics of Nafion®-115 (a, b) and of polypyrrole modified membranes using H_2O_2 (c, d) and $S_2O_8^{2-}$ (e) oxidants at 80 and 90 °C respectively, except for (e) at 80 °C.

Table 2 Cell voltage (V) at 0.5 A cm^{-2} for pyrrole-modified and pristine Nafion® membranes.

Temperature / °C	Cell voltage / V at 0.5 A cm^{-2} with		
	N115	N115-N-O	N115-N-S
70	0.74	0.75	0.74
80	0.73	0.75	0.72
90	0.71	0.74	–

The cathode reaction produces water with transfer of 4 electrons. Hydrogen peroxide or its radicals can however be generated by a 2-electron transfer reaction [16], and these species can give rise to a process of degradation of both polypyrrole and the Nafion® membrane itself. Our observation of a change in colour of (poly)pyrrole-Nafion®-115 membranes after fuel cell evaluation led us to assess the extent of polymer modification *ex situ* using the Fenton reaction.

3.5 Stability of Modified Membranes in Fenton's Reagent

Fenton's test using warm hydrogen peroxide is now a recognised means of accelerating the ageing of polyelectrolyte membranes, although the relation between such *ex situ* ageing and membrane-electrode assembly lifetime in a fuel cell still requires clarification. In the present case, such accelerated ageing allowed us to follow membrane degradation with time *ex situ* and to assess the possible stability of polypyrrole in PEMFC.

The solution used is composed of 3 wt.-% hydrogen peroxide and 1 ppm Fe^{2+} held at a temperature of 68 °C. Qualitatively, it was observed that (poly)pyrrole-modified membranes rapidly became lighter in colour after immersion in this medium, and membranes recovered at given times were analysed for their nitrogen and sulfur content.

Figure 6 shows the change in N/S ratio with time. The decrease in N/S ratio indicates loss of pyrrole from the composite membrane: for both modified membranes, the amount of polypyrrole decreases quickly during the first ten minutes

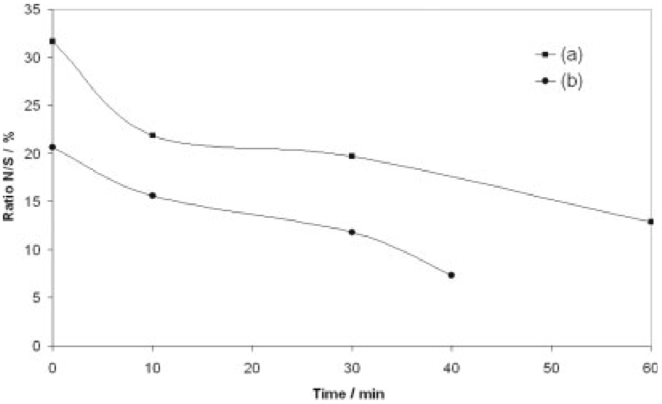


Fig. 6 Degradation of N115-N-O (a) and N115-N-S (b). Change in ratio (N/S) with time of immersion in Fenton's reagent.

and then continues more slowly. The ratio (N/S) for N115-N-S was higher than could have been expected from the analytical data following fuel cell testing of these membranes (cf. Table 1), and we conclude that the difference probably arises from the presence of ammonium peroxodisulfate in this sample. Even considering both contributions to nitrogen and sulfur contents, the total amount is lower than the N115-N-O membrane.

As a control, membranes were also aged in water at 68 °C for a period of 10 hours, and again at 100 °C for N115-N-O. The results of micro-analysis confirm that N115-N-O is stable to hydrolysis (ratio N/S unchanged), whereas N115-N-S was unstable in water for long periods, since it partially discoloured at the border and the ratio N/S dropped from 8.7 to 6.1%.

Changes to the polypyrrole component were also followed using infrared spectroscopy. ATR-IR of N115-N-O (typical of both types of modified membrane) taken after immersion in Fenton reagent for periods up to 1 h are reported in Figure 7. From changes in intensity of characteristic absorptions, the spectra indicate that oligomer and some polymer are converted to monomers during the first 10 minutes (increase in intensity of bands at 1,725 and 3,400 cm^{-1}), most probably by attack by hydrogen peroxide. The free pyrrole species is then removed from the membrane to solution. Its exact nature was not further analysed, but the loss of free pyrrole can explain the long-term degradation of membrane.

To date, no direct study of the stability of polypyrrole in a fuel cell environment has been undertaken [20], although previous reports of the electrochemical generation of polypyrrole in a polyelectrolyte matrix have indicated the possible presence of side electrochemical reactions at high potentials giving radicals that produce nucleophilic attack and partial degradation of polypyrrole chains [31]. The results described here highlight the apparent dual role of hydrogen peroxide or peroxide radicals, an efficient initiator for pyrrole polymerisation on the one hand, but also responsible for *in situ* depolymerisation and polymer degradation. Analytical data after fuel cell operation (ratio N/S) and Fenton's test provide indirect evidence for a degradation process initiated by free radicals under fuel cell test conditions.

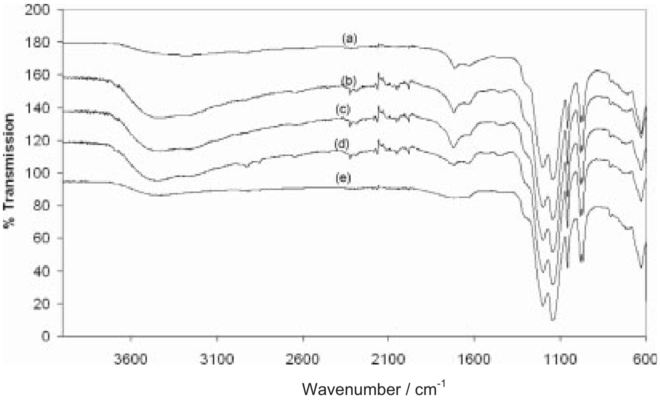


Fig. 7 ATR-FTIR spectra of N115-N-O at t = 0 (a), 10 min (b), 30 min (c) and 60 min in Fenton's reagent (d) compared with the non-modified membrane (e).

4 Conclusion

The objective of limiting permeability of methanol through Nafion® can be achieved by polymerisation of pyrrole using aqueous hydrogen peroxide. By operating in solvents of high dielectric constant, polymerisation probably occurs at the boundary of hydrophilic and hydrophobic domains of Nafion®. Chemical polymerisation routes lead to generation of more oligomer than polymer on the surface of the modified membranes, possibly due to the concentration of oxidant used, too low to adequately oxidise all the pyrrole concentrated inside the membrane. Characterisation of N/S ratio in the modified membranes, water uptake and permeability measurements showed that the nature of the oxidant has an impact on membranes properties, and in which the polymerised pyrrole penetrates the membrane thickness to a greater or lesser extent. Most promising results were obtained when hydrogen peroxide is used to induce polymerisation, since the permeability of methanol was reduced by more than 30%. In addition, this membrane had a better performance when incorporated in a membrane electrode assembly of a PEM fuel cell operating on H_2/O_2 than that of pristine Nafion®-115, and this despite the partial loss of polypyrrole by the radical attack during fuel cell operation. Future work aims to increase the mass of polypyrrole in polyelectrolyte membranes, to evaluate their performance in DMFC and to attempt to devise means of limiting by-products of the electrochemical reaction.

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