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Nafion–TiO₂ hybrid membranes for medium temperature polymer electrolyte fuel cells (PEFCs)$^{☆}$

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Abstract

A nanocomposite re-cast Nafion hybrid membrane containing titanium oxide calcined at $T = 400\,°C$ as an inorganic filler was developed in order to work at medium temperature in polymer electrolyte fuel cells (PEFCs) maintaining a suitable membrane hydration under fuel cell operative critical conditions. Nanometre TiO_2 powder was synthesized via a sol–gel procedure by a rapid hydrolysis of $Ti(OiPr)_4$. The membrane was prepared by mixing a Nafion–dimethylacetammide (DMAc) dispersion with a 3 wt% of TiO_2 powder and casting the mixture by Doctor Blade technique. The resulting film was characterised in terms of water uptake and ion exchange capacity (IEC). The membrane was tested in a single cell from 80 to $130\,°C$ in humidified H_2/air. The obtained results were compared with the commercial Nafion115 and a home-made recast Nafion membrane. Power density values of 0.514 and $0.256\,W\,cm^{-2}$ at 0.56 V were obtained at 110 and $130\,°C$, respectively, for the composite Nafion–Titania membrane. Preliminary tests carried out using steam reforming (SR) synthetic fuel at about $110\,°C$ have highlighted the benefit of the inorganic filler introduction when PEFC operates at medium temperature and with processed hydrogen.
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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are being developed for automotive and stationary power applications. PEFCs operate either on direct hydrogen (DH-PEFC) or processed hydrogen (PH-PEFC) at a temperature between 60 and $80\,°C$. The material that is generally used as the polymeric electrolyte is Nafion®, which has a high-proton conductivity due to the presence of water molecules in its structure. An increase of the cell temperature produces enhanced CO tolerance in PH-PEFC, faster reaction kinetics and reduced heat-exchanger requirement. The main problem for PEFC operation above $100\,°C$ is the loss of proton conductivity of the perfluorosulphonic electrolyte due to the lower-water content with a consequent decrease of the cell performance. For all these reasons, great interest has been focused on the development of alternative membranes able to work above $100\,°C$. Several approaches have been used to overcome this problem, such as the use of thermally resistant polymers or the introduction of a hygroscope and/or proton conductor material as a filler in the polymeric perfluorosulphonic matrix. In the latter case, the inclusion of inorganic fillers improves the mechanical properties, the membrane water management and also contributes to inhibiting the direct permeation of reaction gases by increasing the transport pathway tortuousness [1].

Modified Nafion® membranes containing inorganic fillers such as SiO_2, TiO_2, ZrO_2 [2–7] and other compounds char-

acterised by water retention capacity or by proton conduction as hetero-poly-acids (PWA, PMoA, SiWA) or layered zirconium phosphate [8–13] are valid materials to use as polymer electrolytes in a medium temperature PEFC.

Several methods exist to disperse the inorganic solid into the cast solution. They are based on a simple dispersion by mixing the components, in situ formation of the inorganic powder in a preformed-membrane or in situ sol–gel reactions [14].

Titanium oxide is a good candidate as a hydrophilic filler for the polymer membranes because it allows a suitable hydration of the membrane under fuel cell operative conditions to be maintained and the mechanical properties to be improved.

In the present study, a composite membrane containing a 3% (w/w) of a synthesized nanometre TiO_2 powder, calcined at $T = 400\,^\circ C$, was developed through a simple dispersion of the inorganic compound in a Nafion solution. Compared to the commercial Nafion membrane, the obtained results have shown, upon introduction of the inorganic filler, improvements in water uptake, ion exchange capacity (IEC), conductivity and electrochemical performance of membranes in the temperature range of 80–130 °C.

2. Experimental

2.1. Membrane and membrane electrode assembly (MEA) preparation

Pure TiO_2 powder was synthesized by the sol–gel method starting with a $Ti(OiPr)_4$ and calcined a $T = 400\,^\circ C$ for 2 h. A detailed procedure for powder preparation is described elsewhere [5–7].

A 5% (w/w) Ion Power Nafion® solution was selected to manufacture the film. The original solution was dried at $T = 50\,^\circ C$ until obtaining a dry residue, successively diluted in dimethylacetammide (DMAc) as a solvent (10%, w/w, solution). An appropriate amount of TiO_2 powder (3%, w/w) was added and dispersed in an ultrasonic bath. A re-concentration of the solution was carried out until reaching a suitable viscosity. After the casting, the membrane was dried on a hot plate at $T = 80\,^\circ C$, then thermally treated at $T = 155\,^\circ C$. A chemical treatment in 7 M HNO_3, 5% (w/w) H_2O_2, 1 M H_2SO_4 was carried out to purify the membrane. A membrane (labelled NT1) with a thickness of 100 μm was obtained.

As a comparison, a re-cast Nafion membrane (N16) with a thickness of 70 nm was prepared with the same procedure described above.

The home-made NT1, N16 and commercial N115 membranes were hot-pressed between two electrodes to form the membrane-electrode assembly. The electrodes preparation procedure based on a spraying technique is described elsewhere [15]. Anodes and cathodes with the same Pt loading (0.5 mg cm⁻²) in the catalyst layer and low-PTFE content in the diffusion layer were prepared. A 30% Pt/Vulcan

(E-TEK Inc.) was used as an electro-catalyst for both electrodes.

2.2. Characterisations

The morphology of the TiO_2 powder was observed using field emission scanning electron microscopy (FE-SEM). The powder was characterised using X-ray diffraction (XRD) analysis.

The ion exchange capacity of the membranes was determined through an acid–base titration with an automatic titrator Metrohm (mod. 751GPD Titrino). The dry membrane was immersed in 1 M NaCl solution and this solution was titred with a 0.01 M NaOH solution to neutralize exchanged H^+. Plotting the pH variation and the added titrant volume, the titrant volume at the equivalent point was determined. The IEC is calculated using the following formula:

$$IEC = \frac{V \times M}{m_{dry}}, \tag{1}$$

where IEC is the ion exchange capacity expressed in meq g⁻¹; V, the added titrant volume at the equivalent point expressed in mL; M, the molar concentration of the titrant; m_{dry} is the dry mass of the sample expressed in g.

The water uptake (w.u.%) measurement gives us information on the water retention of the membrane and it is calculated by the difference in weight between wet and dry samples. The wet weight (m_{wet}) was determined after immersion of the sample in water at room temperature for 24 h while, for the dry weight (m_{dry}), the sample was kept in an oven at 80 °C under vacuum for 2 h. The percentage of absorbed water is given as follows:

$$w.u.\% = \left[\frac{m_{wet} - m_{dry}}{m_{dry}}\right] \times 1000, \tag{2}$$

where m_{wet} is the wet mass of the sample expressed in g and m_{dry} is the dry mass of the sample expressed in g.

The proton conductivity of the membranes was measured in the longitudinal direction with a four-electrodes method, by using a commercial conductivity cell (Bekktech). A 2 cm × 3 cm sample was assembled in the cell, in contact with two platinum electrodes placed at a fixed position. Through the proton current imposition, a voltage drop between the two fixed electrodes was measured and the resistance, R, derived. The membrane conductivity as a function of the temperature (from 80 to 130 °C) at different relative humidity percentages (RH %) was determined according to the following equation:

$$\sigma = \frac{L}{R \times W \times T}, \tag{3}$$

where $L = 0.425$ cm (the fixed distance between the two Pt electrodes); R, resistance in Ω; W, width of the sample expressed in cm and T is the thickness of the membrane expressed in cm. Fuel Cell tests were carried out on a 5 cm²

and a 16 cm^2 single cell using a Fuel Cell Technologies Test Station. MEAs with home-made electrodes were used for the 5 cm^2 single cell tests in the temperature range between 80 and 130 °C in H$_2$/air with humidified gases (100% RH) at 3.0 abs. bar. The gas fluxes were fixed at 1.5 times and 2 times the stoichiometric value at a current density of 1.0 A cm^{-2} for fuel and oxidant, respectively. In the 16 cm^2 single cell tests, the membranes were studied with commercial E-TEK electrodes. Polarisation curves were obtained in the temperature range between 70 and 110 °C at 3.5/4.0 abs. bar for H$_2$ or steam reforming (SR) synthetic fuel/air, respectively. The gas flux for the fuel was fixed at 2.5 times the stoichiometric value at a current density of 1 A cm^{-2}.

3. Results and discussion

The xero–gel obtained by sol–gel synthesis was calcined at 400 °C for 2 h. At this temperature, the thermogravimetric (TG) analysis shows the end of the weight loss, while the differential thermal analysis (DTA) shows an exothermic peak that can be attributed to the combustion of organic residues [5].

Fig. 1 shows the XRD pattern of the TiO$_2$ powder heated to 400 °C. Crystalline TiO$_2$ was present in the anatase phase (JCPDS No. 71–1166); moreover, other phases are not visible.

The SEM micrograph (Fig. 2) of the pure TiO$_2$ sample shows that the powder was made of spherical particles with a grain size between 5 and 20 nm.
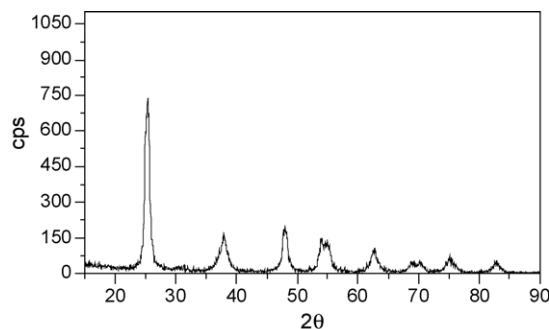

Fig. 1. XRD pattern for the synthesized TiO$_2$ powder after calcination at 400 °C.

Table 1
Chemical–physical results

Membrane	Thickness (μm)	Water uptake (%)	IEC (meq g^{-1})
N115	125	27	0.91
N16	70	20	0.89
NT1	100	29	0.93

Table 1 reports the chemical–physical characteristics of the NT1 membrane, containing 3 wt% of TiO$_2$ powder, in comparison with those of the commercial membrane (N115) with a similar thickness and of a Nafion re-cast membrane (N16) prepared with the same Nafion/DMAc solution of NT1, taken as a reference.

The water uptake measured for the commercial membrane is lower than that declared by the producer DuPont
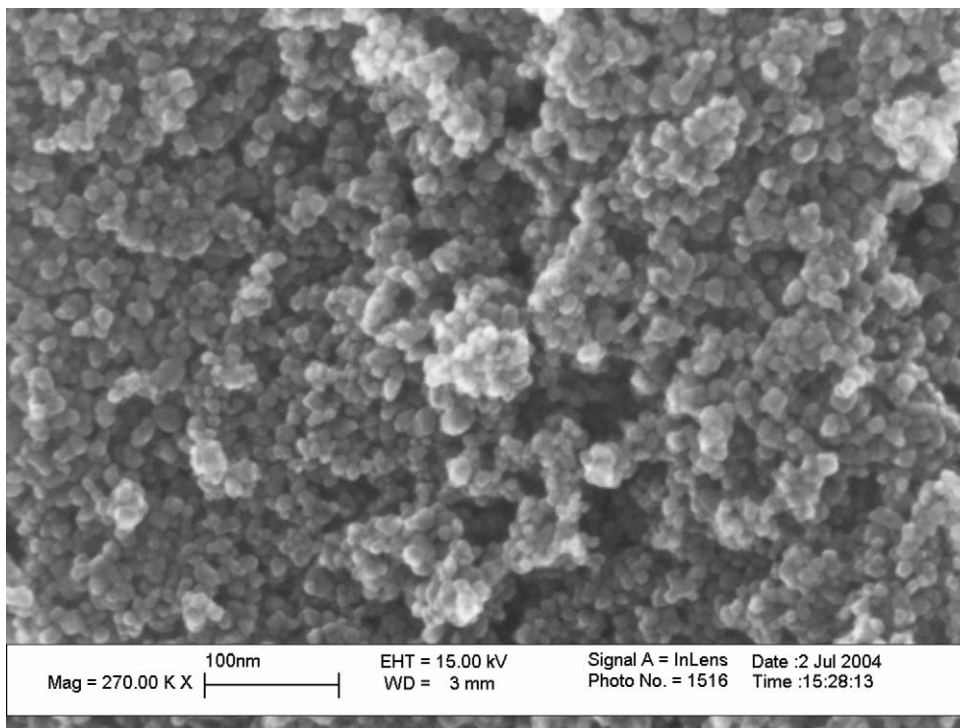

Fig. 2. SEM micrograph for the synthesized TiO$_2$ powder after calcination at 400 °C.

(38%). This difference is due to the different experimental conditions, in which the wet weight of the samples was determined. The room temperature used in this work, instead of 80 °C, does not permit a full hydration of the membranes. In any case, if we compare the results obtained in the same experimental conditions, the water uptake and IEC values for the composite membrane are slightly higher with respect to those of the commercial membrane and significantly higher than those of the Nafion recast. This can be attributed to the presence of the inorganic powder that is both hygroscope and a soft proton conductor.

This behaviour was confirmed by the proton conductivity data. Fig. 3a and b shows the conductivity of the tested membranes, measured at two different values of relative humidity (RH), 100 and 85% RH, respectively, and simulating the cell-operative conditions in the temperature range from 80 to 130 °C. In general, the conductivity slightly increased with increasing the temperature. The Nafion recast membrane showed the lowest-ionic conductivity ranging from 0.12 to 0.14 S cm^{-1}, while the NT1 composite membrane showed the highest values in the range 0.15–0.18 S cm^{-1}.

The Nafion–TiO$_2$ membrane was tested in a single cell.

Fig. 4 shows the polarisation curves in humidified H$_2$/air from 80 to 130 °C for the NT1 membrane compared to the curves obtained for the commercial membrane with a similar
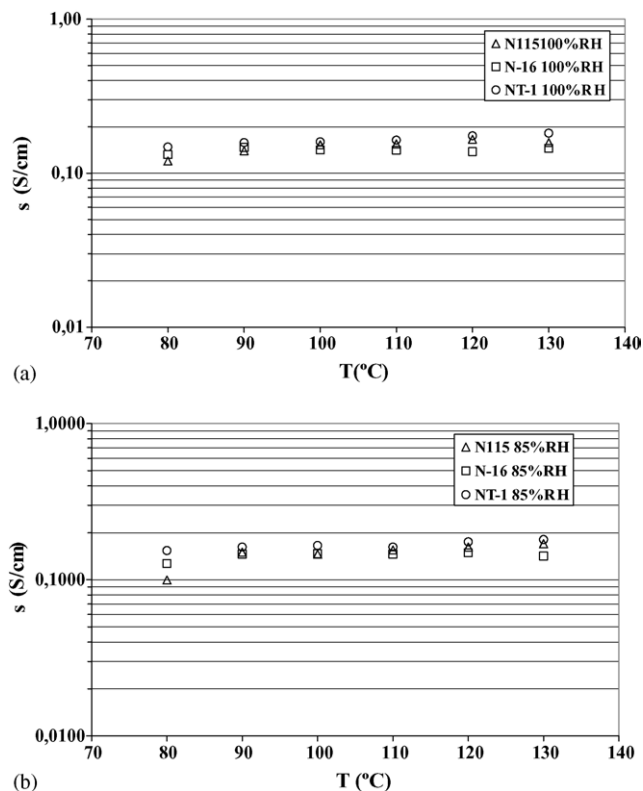

Fig. 3. (a and b) Ionic conductivity as a function of temperature at 100 and 85% RH.
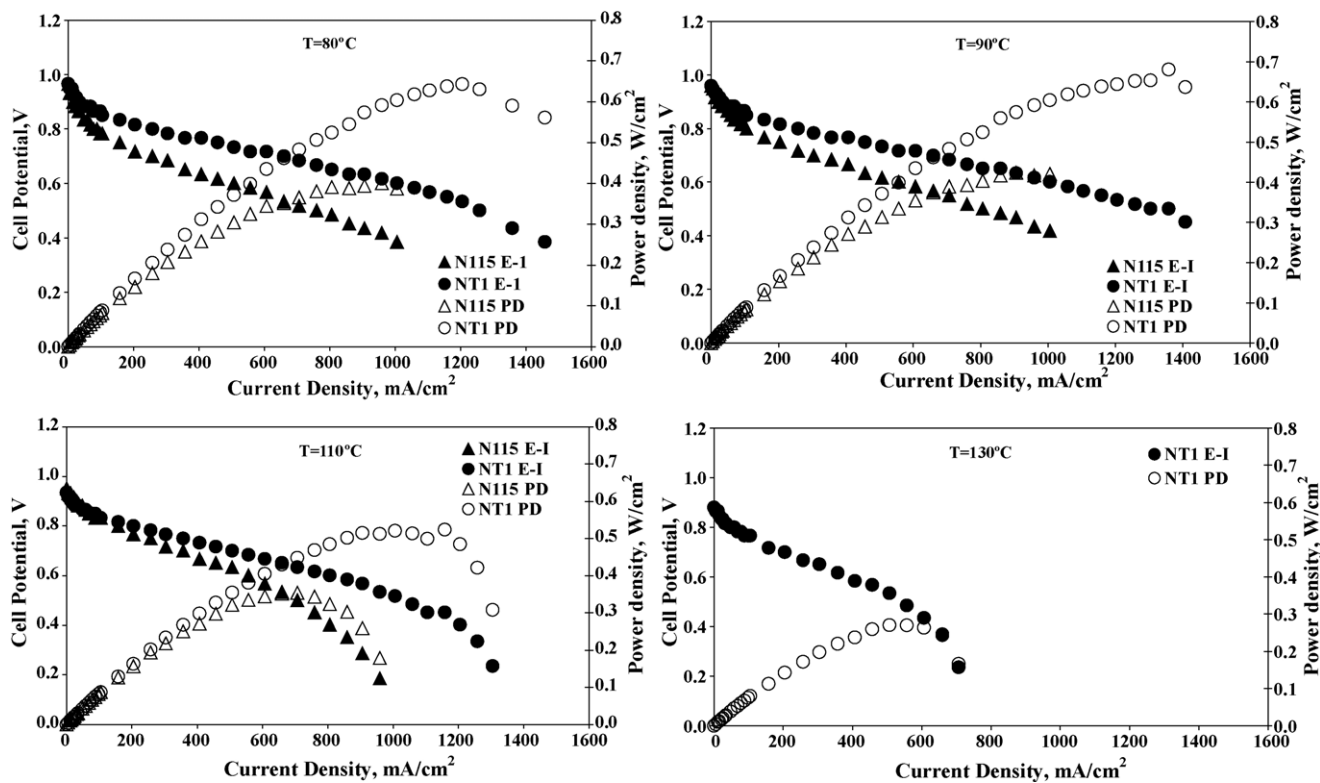

Fig. 4. Electrochemical performance for Nafion–Titania membrane compared to N115, in terms of polarisation (E–I) and power density (PD) curves, in H$_2$/air in the range 80–130 °C.
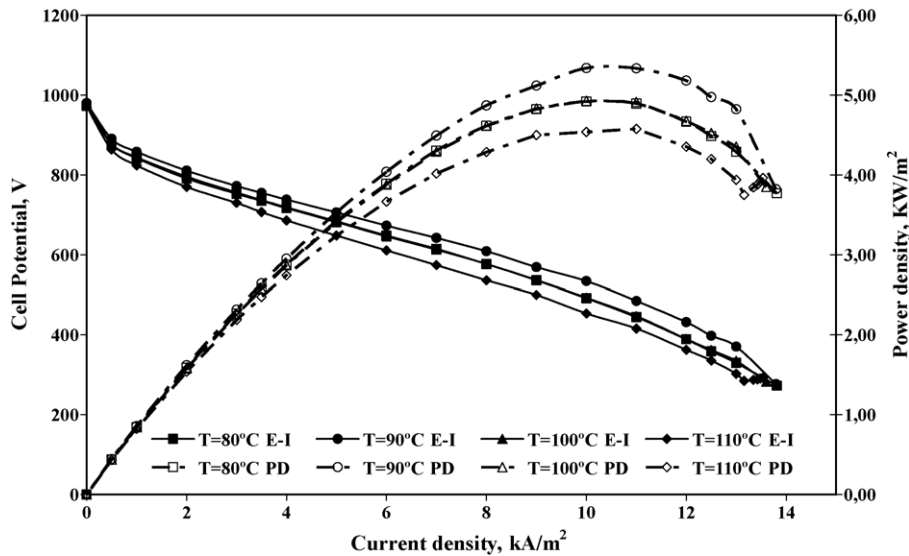
Fig. 5. Polarisation curves in pure H_2/air.

thickness. The composite membrane showed a better performance than the commercial membrane in the whole investigated temperature range.

A power density of 0.514 W cm^{-2} for NT1 against to 0.354 W cm^{-2} for N115 at 0.56 V and at $T = 110\,^\circ$C was recorded. At $T = 120\,^\circ$C, N115 was damaged while the NT1 membrane continued to work up to 130 $^\circ$C by reaching a power density of about 0.254 W cm^{-2} at 0.5 V.

In any case, the best performance and the maximum power density values were obtained for both the membranes at 90 $^\circ$C (0.680 and 0.420 W cm^{-2} at 0.5 V for NT1 and N115, respectively).

The cell resistance for N115 decreased from 0.122 to 0.106 Ω cm^2 until reaching 100 $^\circ$C and increased above this temperature, while for NT1 it decreased from 0.099 to 0.088 Ω cm^2 until 110 $^\circ$C, then increased with increasing temperature. This confirms that the presence of TiO_2 is able to decrease the cell resistance above 100 $^\circ$C.

A similar behaviour was observed in another set of tests performed at 3.5/4.0 abs. bar (H_2/air) on the same membrane (NT1) with a 16 cm^2 single cell and with the commercial electrodes. As shown in Fig. 5, the best performance was obtained at 90 $^\circ$C.

Preliminary tests were carried out by feeding the cell with steam reforming synthetic fuel (10 ppm CO; 20% CO_2; 75% H_2; 1% CH_4). Fig. 6 shows a comparison between polarisation curves at 110 $^\circ$C in pure H_2 and SR for the nanocomposite membrane. For both fuels, the measured OCV values were good, almost reaching 1 V.

A power density value of about 0.182 W cm^{-2} at 0.6 V in synthetic fuel versus the 0.366 W cm^{-2} value in pure hydrogen was obtained. As evident, the performance for tested MEA fed with SR is lower by about 50% if compared to the performance in pure hydrogen, but such a loss could be min-
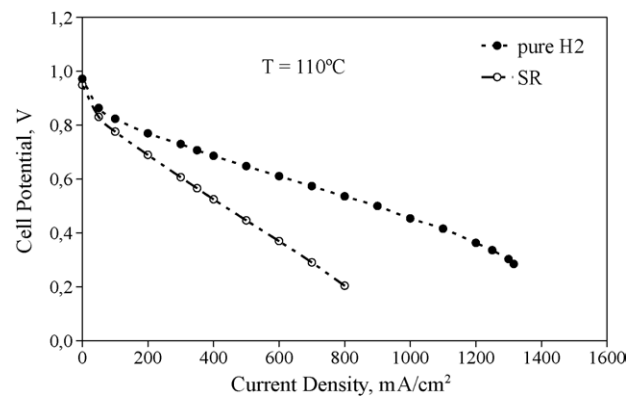

Fig. 6. Polarisation curves in pure H_2 and SR at $T = 110\,^\circ$C for the NT1 membrane.

imised by using suitable electrodes containing Pt-Ru as an electro-catalyst.

4. Conclusions

A synthesized nanometre TiO_2 powder was used to form a membrane for medium temperature PEFC. A standardized and reproducible method for film preparation based on the Doctor Blade technique was developed. The introduction of the inorganic filler supplies the composite membrane with a good mechanical and thermal resistance and improves the water uptake and IEC values if compared to the commercial Nafion membrane. The composite membrane is able to work at $T = 110\,^\circ$C with a power density value of 0.514 W cm^{-2} (at 0.56 V). Preliminary tests were carried out using steam reforming synthetic fuel up to 110 $^\circ$C that have highlighted the benefit of the inorganic filler introduction when

PEFC operates at a medium temperature and with processed hydrogen.

Acknowledgement

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