

Short communication

ZrO₂–Nafion composite membranes for polymer electrolyte fuel cells (PEFCs) at intermediate temperature

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Abstract

Recast Nafion composite membranes containing three different percentages (5%, 10% and 20%, w/w) of commercial Zirconium(IV) oxide as an inorganic filler were developed by the Doctor-Blade casting technique in order to work in direct hydrogen polymer electrolyte fuel cells (DH-PEFCs) in critical operative conditions for the fuel cell at a temperature of about 120–130 °C.

By mixing a 10% (w/w) Nafion–dimethylacetamide (DMAc) dispersion with the inorganic compound, composite membranes were prepared. The developed membranes were characterised by water retention capacity (Wup%), ion exchange capacity (IEC, meq g⁻¹), thermo-gravimetric analysis and by X-ray measurements.

From XRD measurements, the ZrO₂ powder insertion was confirmed; the introduced amount was verified by TG analysis that highlighted the major thermal resistance of the developed membranes. Moreover, the chemical–physical results showed an increase of the water uptake and a decrease of the IEC with the increase of inorganic compound percentage. The introduction of the inorganic powder improved the mechanical characteristics of the developed composite membranes.

Moreover, the membranes were tested in a 5 cm² commercial single cell from 80 °C to 130 °C in humidified H₂/air with pressures of 3.0 abs. bar and the obtained results compared to a bare Nafion recast membrane (N16) developed through the same method and used as a reference.

Power density values of 604 mW cm⁻² and of 387 mW cm⁻² were obtained at 0.6 V and at $T = 110$ °C (100% of relative humidity) and $T = 130$ °C (85% RH), respectively, for the composite ZrO₂–Nafion membrane containing 10% (w/w) of inorganic filler.

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1. Introduction

Recently, the research interest in polymer electrolyte fuel cells (PEFCs) has been addressed to the increase of the working temperature above 100 °C with lower humidification levels [1,2]. For this reason, the activity has been focused on the components development for PEFCs (composite membranes and electrodes) containing hygroscopic and/or proton conductor compounds able to work at high temperature [3,4].

Generally, the most used electrolyte is a hydrated perfluorosulfonic acid polymer such as Nafion®; since this type of polymer needs water for proton conductivity, the operative conditions regarding temperature range are limited to below the

boiling point of water. The Nafion maximum conductivity occurs at 100% relative humidity (RH) and is quite constant with respect to temperature, around 0.083 S cm⁻¹ [5–7] with the membrane conditioned in water at 100 °C for 1 h.

By increasing the pressure, the temperature range could be extended, but PTFE-based materials such as Nafion polymer have a maximum operating temperature limited by the physical properties of the material itself.

Moreover, the membrane should be maintained fully hydrated at $T > 100$ °C because the water is necessary for proton conduction.

For all these reasons, the interest has been focused to the development of so-called composite membranes capable to work at a higher temperature than the classical temperature range for PEFCs.

This aim could be reached by using thermally resistant starting polymers or through the introduction of a hygroscopic

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and/or proton conductor second substance into the polymeric matrix.

In fact, the inclusion of inorganic species improves the mechanical properties because a specific interaction is favoured between the inorganic and organic components, assists in improving the membrane water management [8] and, moreover, the inorganic presence confers to the membrane a new structural arrangement that inhibits the direct permeation of reaction gases. For the introduction of the inorganic compounds, it is possible to act through different methods that include in situ formation of the inorganic powder in a preformed-membrane, in situ sol/gel reactions and dispersion of the inorganic solid into the cast solution.

Regarding the last procedure, hydrophilic and/or proton conductors compounds such as inorganic oxides (SiO_2 , TiO_2 , ZrO_2 , etc.) [9–11] and heteropolyacids (phosphotungstic acid—PWA, phosphomolibdic acid—PMoA, silicotungstic acid—SiWA, etc.) [12–15] have been used as fillers to modify a per-fluorinated sulfonic acid membrane such as Nafion [16,17].

In the present study, composite membranes containing different percentages of commercial ZrO_2 were developed through a simple dispersion by mixing the components in an ultrasonic bath of the inorganic compound in a 10% (w/w) Nafion solution in dimethylacetamide (DMAc) as a solvent.

The membranes were characterised in terms of ion exchange capacity (IEC), water uptake (Wup%), X-ray measurements and thermo-gravimetric analysis.

The electrochemical characterisation was carried out both in a commercial single cell feeding it with H_2 /air in the temperature range of 80–130 °C.

The results in terms of polarisation curves have been evaluated and compared to the commercial Nafion membranes and to a home-made bare Nafion membrane of comparable thickness.

2. Experimental

2.1. Membranes preparation

A 5% (w/w) Ion Power[®] alcoholic Nafion solution was chosen for membranes preparation.

From previously obtained results on the recast bare and composite Nafion membranes developing [4], a DMAc–Nafion solution was obtained drying the Ion Power solution to obtain a Nafion dry residue and then by dissolving it in the solvent.

Such 10% (w/w) solution was selected to cast three different membranes (NZr1, NZr2 and NZr5) by Doctor-Blade casting method with an amount of 5% (w/w), 10% (w/w) and 20% (w/w) of commercial Zirconium(IV) oxide powder (Ytria stabilized, ca. 8% Y_2O_3 , Aldrich Submicron Pwd 99.9%) that was added to the 10% (w/w) Nafion solution in DMAc and dispersed in an ultrasonic bath before the re-concentration phase necessary for the casting procedure. Through a slow re-concentration at low temperature under a magnetic stirring, suitable viscosity solutions were obtained and stratified on a glass sheet. The obtained films were dried on the hot plate at $T=80$ °C to evaporate the solvent and the membranes detached from the glass with distilled water. Successively, they underwent to a thermal treatment

Table 1
Tested membranes

Membrane	ZrO_2 (% w/w)	Thickness (μm)
N16	0	70
NZr1	5	70
NZr2	10	100
NZr5	20	90

until $T=155$ °C to increase the crystallinity and to improve the mechanical characteristics. A chemical treatment was carried out in a 7 M HNO_3 solution, 5% (v/v) H_2O_2 solution and in a 1 M H_2SO_4 solution with intermediate boiling steps in the distilled water.

The developed membranes together the sample used for comparison are scheduled in Table 1.

2.2. MEAs preparation

The membranes were assembled by hot-pressing between home-made electrodes to obtain the membrane-electrode-assemblies (MEAs). The electrodes preparation procedure based on a spraying technique is described elsewhere [18]. A 30% Pt/Vulcan (E-Tek Inc.) was used as an electro catalyst. Anodes and cathodes with the same Platinum (Pt) loading (0.5 mg cm^{-2}) in the catalyst layer and low polytetrafluoroethylene (PTFE) content in the diffusion layer were prepared.

2.3. Powder and membranes characterisation

2.3.1. Powder and membranes thermo-gravimetric analysis (TG)

The thermo-gravimetric analysis was carried out with a thermo-balance Netzsch (mod. STA 409) in air following the variation of the percentage mass loss in weight, in the temperature range between 25 °C and 1100 °C with a temperature rate of 5 °C min^{-1} .

2.3.2. Powder and membranes X-ray analysis

The X-ray powder diffraction (XRD) analysis was performed using a Philips X-ray automated diffractometer (model PW3710) with $\text{Cu K}\alpha$ radiation source. The 2θ Bragg angles were scanned between 5° and 100°.

2.3.3. Ion exchange capacity (IEC)

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 titrated 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:

$$\text{IEC} = \frac{V \times M}{m_{\text{dry}}} \quad (1)$$

where IEC is the ion exchange capacity (meq g^{-1}); V the added titrant volume at the equivalent point (mL); M the molar concentration of the titrant; m_{dry} is the dry mass of the sample (g).

2.3.4. Water uptake measurements

The water uptake (Wup%) was calculated by the difference between wet and dry samples weight. 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:

$$\text{Wup}\% = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100$$

where m_{wet} is the wet mass of the sample (g) and m_{dry} is the dry mass of the sample (g).

2.4. Electrochemical characterisation

Electrochemical tests were carried out in a 5 cm^2 commercial single cell supplied by GlobeTech connected to a Fuel Cell Technologies work station.

Membrane-electrode-assemblies with the different membranes were tested in a range of $80^\circ\text{C} < T < 130^\circ\text{C}$ in humidified H_2/air gases at 3.0 abs. bar maintaining a 100% RH of gas, except at $T = 130^\circ\text{C}$, wherein a RH of 85% was used.

The gas fluxes were fixed at 1.5 times the stoichiometry for the fuel and 2 times the stoichiometric value for the oxidant at a current density value of 1 A cm^{-2} .

The polarisation curves were recorded by means a test station equipped with a software for the automatic data acquisition and the cell resistance was measured with an Agilent milliohmeter by a static method at a frequency of 1 kHz.

The time-test on the NZr2 membrane was carried out at a constant value of cell potential (0.5–0.6 V) recording the current density variation as a function of time with time intervals of about 300 s for about 60 h with start up in the morning and shut down in the evening for a total of about 5–6 h per day.

3. Results and discussion

Fig. 1 shows X-ray measurements onto the used commercial ZrO_2 powder: crystalline ZrO_2 was present in the cubic phase (JCPDS data no. 27-997) and the peculiar peaks are highlighted through a star.

Fig. 2 shows X-ray analysis carried out on all developed composite Nafion– ZrO_2 membranes; in the square, the XRD profiles of commercial Nafion membrane (N115) compared to a home-made bare membrane (N16) developed with the same procedure are shown. The commercial (N115) and home-made (N16) membranes pattern is very similar, but the recast membrane as shown in the square presents a sharper peak at $15^\circ 2\theta$, probably due to the presence of bigger clusters with respect to the commercial membrane [19].

X-ray spectra related to the developed composite membranes show the peaks of the considered ZrO_2 powder confirming the

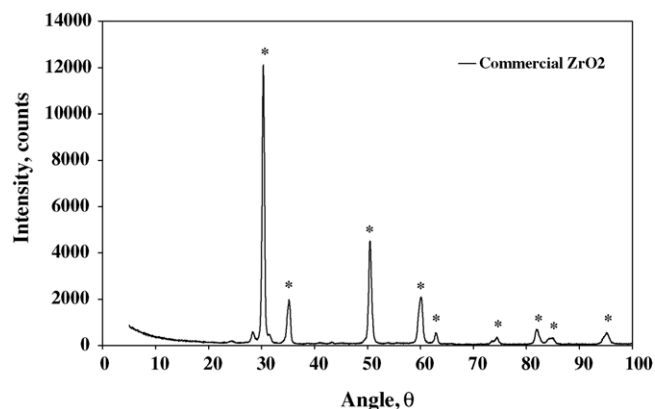


Fig. 1. X-ray diffraction (XRD) analysis on the commercial ZrO_2 powder (JCPDS data no. 27-997).

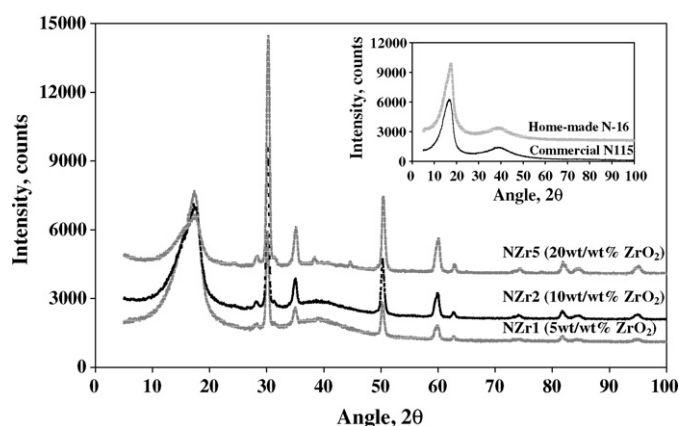


Fig. 2. X-ray diffraction (XRD) analysis on the composite Nafion– ZrO_2 membranes; in the square, commercial N115 and home-made bare (N16) membranes comparison is reported.

presence of the inorganic compound within the Nafion polymeric matrix.

Fig. 3 shows the TG analysis results. In the square, the comparison between commercial (N115) and N-recast (N16) membranes shows no significant difference; in fact, the curves are completely overlapped to be not distinguished. This means

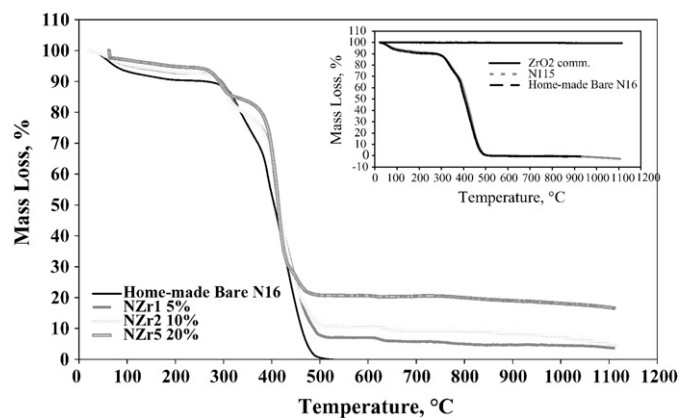


Fig. 3. Thermo-gravimetric analyses on the composite membranes compared to home-made bare Nafion membrane; in the square, commercial N115, home-made bare N16 membranes and ZrO_2 powder TG analysis comparison is shown.

Table 2
Chemical–physical results on the developed membranes

Membrane	Thickness (μm)	Water uptake (%)	IEC (meq g^{-1})
N16	70	20	0.89
NZr1	70	24	0.92
NZr2	100	24	0.85
NZr5	90	30	0.84

that the recast Nafion membrane preparation procedure did not produce substantial variations in the original polymer.

A mass loss at about 100°C corresponding to the water desorption is observable; at about 280°C , the de-sulfonation process begins and after 400°C , there is a complete decomposition of these materials.

Regarding to the composite membranes, if we consider that at $T = 700^\circ\text{C}$ all the polymer is surely burnt out, the remaining mass could be associated to the inorganic compound. In particular, a remaining mass of 5.7%, 9.2% and 20.4% was calculated for NZr1, NZr2 and NZr5, respectively.

In Table 2, the results of the chemical–physical characterisations on all tested membranes are reported.

In Fig. 4, the Wup% and the IEC behaviour as a function of inorganic percentage are shown; it is evident that the water uptake increases by increasing of the inorganic powder that is a softly hydrophilic compound, while the IEC value decreases due to the presence of ZrO_2 .

The membranes were tested in a single fuel cell in the range of temperature $80\text{--}130^\circ\text{C}$ with a 100% RH. In Fig. 5, the behaviour of the OCV as a function of temperature is reported. For all the MEAs, the OCV decreases by cell temperature increasing; the membrane with the highest content of ZrO_2 presents lower values, although the thickness of $90\ \mu\text{m}$, probably the presence of an excess of inorganic material, weakens the structure of the polymer matrix. This low value of OCV has a consequence on the performance at all the investigated temperatures.

Figs. 6 and 7 show the cell polarisation comparison at 80°C and 110°C , respectively. Until this cell temperature, the behaviour of MEAs is the same; the introduction of a small amount of ZrO_2 (NZr1) produces no evident changes in the cell performance, while a better performance with 10% (w/w) (NZr2) was obtained with a power density greater than $600\ \text{mW cm}^{-2}$ at $0.6\ \text{V}$ both at 80°C and 110°C .

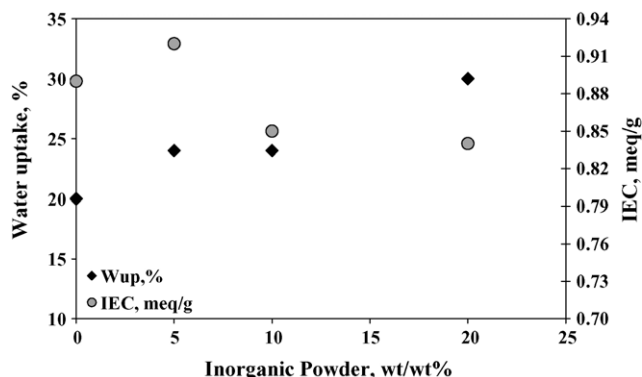


Fig. 4. Water uptake and IEC as a function of inorganic powder percentage.

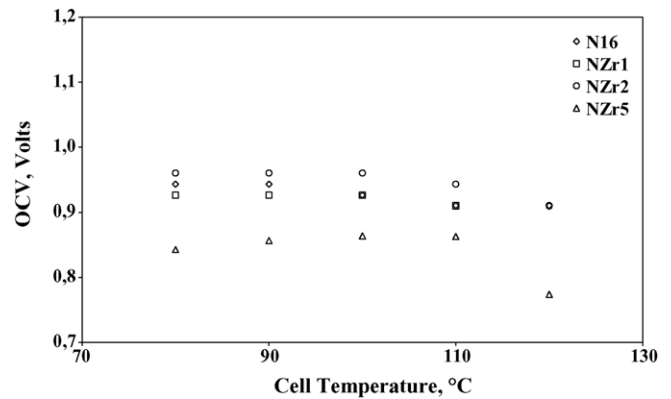


Fig. 5. OCV values of tested membranes as a function of temperature.

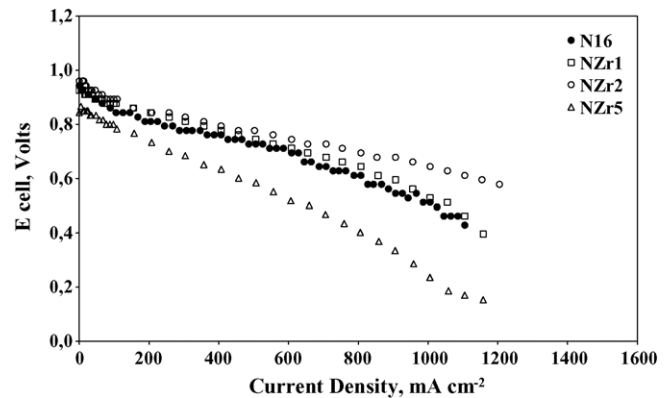


Fig. 6. Polarisation curves for all tested membranes at $T = 80^\circ\text{C}$.

The good performance of NZr2 membrane was maintained at 130°C with gas humidification of 85% RH. In Fig. 8, a plot showing the recorded power density as a function of current density is reported. A maximum power density of about $400\ \text{mW cm}^{-2}$ was obtained in the potential range of $0.5\text{--}0.6\ \text{V}$.

Starting from these results, a short stability test of about 60 h at this temperature in the potential range of $0.6\text{--}0.5\ \text{V}$ was carried out, in particular at a fixed value of $0.6\ \text{V}$ for 12 h and at $0.5\ \text{V}$ for the remained time. For this reason, the behaviour in terms of power density is reported (Fig. 9). A linear degradation of the membrane is observable with a power density loss of about

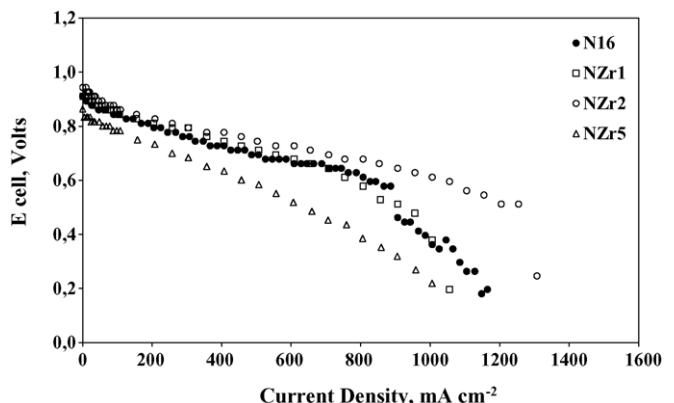


Fig. 7. Polarisation curves for all tested membranes at $T = 110^\circ\text{C}$.

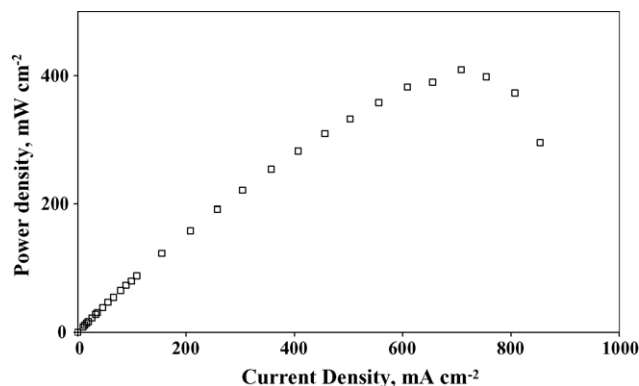


Fig. 8. Maximum power density curve for NZr2 membrane at $T = 130\text{ }^{\circ}\text{C}$ with 85% RH.

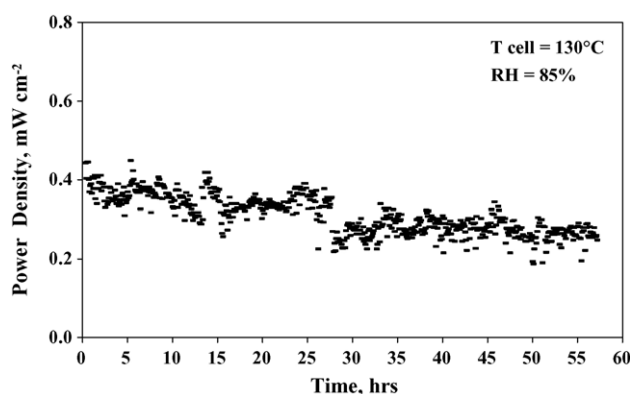


Fig. 9. Time-test for NZr2 membrane at $T = 130\text{ }^{\circ}\text{C}$ with 85% RH.

150 mW cm^{-2} in 60 h, even if the curve seems to show a drastic loss of 80 mW cm^{-2} after about 27 h of operation, coinciding with a shut down of two days. In fact, if we analyse the first part of the test, less than 50 mW cm^{-2} was lost in 27 h against 20 mW cm^{-2} in the second part. Probably, the membrane needs to maintain the humidity during the shut-down step. The evident scattering of stability test data could be due to the inhomogeneous dispersion of the inorganic powder in the polymer matrix.

4. Conclusions

Composite membranes with three different inorganic compound contents were investigated and characterised in terms of IEC, water uptake, XRD measurements and thermo-gravimetric analysis.

The membranes were prepared by mixing the inorganic compound with a 10% (w/w) Nafion solution in DMAc as a solvent.

The presence and amount of ZrO_2 was confirmed through TG and X-ray analysis.

A power density of 452 mW cm^{-2} and of 604 mW cm^{-2} at 0.6 V and at $T = 110\text{ }^{\circ}\text{C}$ was obtained for the composite membranes with a 5% and 10% (w/w) of Zirconia powder, respectively, against a 480 mW cm^{-2} power density for the bare home-made membrane used as a reference.

The membrane containing a 10% (w/w) of commercial Zirconium(IV) oxide tested at $T = 130\text{ }^{\circ}\text{C}$ (85% RH) has supplied a power density of about 400 mW cm^{-2} and the short stability test in these conditions has demonstrated that the membrane needs to maintain the humidity during the shut-down step.

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