

# Comparative Study on Composite Electrodes for Medium Temperature PEFC

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**Abstract:** The purpose of the present study consists in the development of a MEA (Membrane-Electrode-Assembly) for Polymer Electrolyte Fuel Cells (PEFCs) applications at intermediate temperatures ( $T > 100^{\circ}\text{C}$ ) through the introduction of inorganic compounds within the catalytic layer of the electrodes. For this aim, composite electrodes containing three inorganic compounds, with different chemical and physical properties, were developed with percentages ranging between 0-14 wt% of zeolite H-BETA, titania ( $\text{TiO}_2$ ) and yttria stabilized zirconia (YSZ) maintaining the same Platinum loading of  $0.5 \text{ mg/cm}^2$  and assembling the electrodes to a commercial N115 membrane. Electrochemical studies in terms of V-I curves were carried out in a temperature range of  $80\text{-}130^{\circ}\text{C}$  in order to select the optimal content of filler.

A comparison between the standard electrode and the best composite electrode containing the optimal amount for each investigated inorganic material was carried out. The role of inorganic materials is to limit the ionomer swelling by maintaining the mechanical characteristics of the polymer quite unaltered and to enhance the durability of the electrocatalyst to degradation phenomena during the fuel cell operation at a temperature over the critical one. For each inorganic material, a different optimal amount was found to be dependent on their chemical-physical properties, in particular the particle size, acidity and intrinsic proton conductivity. At high temperature ( $130^{\circ}\text{C}$ ), the beneficial effect of oxides introduction is more evident: a reduced cell resistance, a reduced Tafel slope, increased OCV values and improved fuel cell performance for composite electrodes than the standard one. It was supposed that a limit in the oxide introduction exists and it depends on physical properties of the inorganic filler, in particular the grain size, the acidity, the intrinsic proton conductivity and the physical properties of the polymeric matrix used as an ionomer.

**Keywords:** Inorganic compounds, Ionomer swelling, Catalytic layer, Composite electrodes, PEFC.

## 1. INTRODUCTION

Polymer Electrolyte Fuel Cells (PEFCs) represent an important research area because they offer a highly efficient energy source and low environmental impact. These electrochemical devices are being pursued for a wide variety of systems. In fact, although a significant development of PEFCs for stationary applications has taken place, many developers now focus on automotive and portable applications [1, 2]. For these reasons, in the last years not only the academic and industrial but also the public interest towards the PEFC is increased. There are, however, several obstacles to be overcome such as the high cost and short lifetime of these systems. These factors have to be prevented for the use of fuel cells in mass markets. In fact, the catalyst, membrane and cell hardware - some of fuel cell components - are very expensive determining a high initial cost. Moreover, PEFCs are becoming an interesting power source in different application fields, from small electronic portable units to medium size

stationary systems. Each application needs a fuel cell working under specific operative conditions. This wide range in power output and operative conditions imply a great variation of the active area size and Membrane Electrode Assembly (MEA) properties depending on the application. In particular, for automotive application, many efforts have been carried out to increase the operative temperature over  $100^{\circ}\text{C}$ , with the aim of minimising the catalyst poisoning at the anode when reformed  $\text{H}_2$  is used, improving the reaction kinetic, rendering more easy the water management, improving the heat rejection and waste heat [3-7]. Unfortunately, over  $100^{\circ}\text{C}$ , the hydration level and mechanical properties of the main typical polymer electrolyte (Nafion) used for membranes decrease with a consequently reduction of its proton conductivity. So, the research has moved on the development of composite membranes containing inorganic fillers that act as a mechanical reinforcement and permit to operate at higher temperatures without a sensitive reduction of proton conductivity [8, 9].

The same phenomena that affect the membranes could be found in the electrodes when they operate at medium temperatures, due to the utilisation of Nafion as an ionomer in the catalytic layer. In fact, over  $100^{\circ}\text{C}$ ,

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the mechanical properties of Nafion are lowered due to the ionomer swelling provoking: a) a reduction of the electrode-membrane interface; b) a worsening of the ionomer/catalyst contact; c) a reduction of the effective contact area. In addition, another important issue is represented by the durability of the electrocatalyst, that is subjected to degradation phenomena during the fuel cell operation, due to the corrosion of carbon support that produces agglomeration of platinum nanoparticles. Thus, the role of inorganic materials is to limit the ionomer swelling by maintaining the mechanical characteristics of the polymer quite unaltered at a temperature over the critical one [8, 10] associated to a better resistance of the electrocatalyst to the corrosion [11-19]. For this purpose, different metal oxides have been considered according to the following properties: high resistance to the electrochemical corrosion, high stability in acidic media; compatibility with the electrodic structure, intrinsic proton conductivity, etc.

In this work, composite electrodes containing percentages ranging between 0-14 wt% of each studied inorganic compound were developed and a comparison between the standard electrode and the best composite electrode containing the optimal amount for each inorganic material was carried out. The aim is to correlate the chemical-physical properties of the inorganic compounds with the electrochemical behaviour in fuel cell operation at high temperature and relative humidity, that can be considered drastic conditions for the ionomer swelling and electrocatalyst corrosion.

Zeolite, titania and yttria stabilized zirconia, having different chemical-physical properties were selected as inorganic fillers to be used in the ionomer dispersion before to obtain the catalytic ink.

As expected, at 80°C the inorganic compound introduction does not cause an evident performance improvement. On the contrary, at higher temperature (130°C), the beneficial effect is more evident: a reduced cell resistance, reduced Tafel slope, increased Open Circuit Voltage (OCV) values and fuel cell performance if compared to the standard electrode.

By considering the diffusive region of the polarisation curve, whereas the water management and the mass diffusion problems are more evident, limiting currents of 850mA/cm<sup>2</sup> for TiO<sub>2</sub> and 960mA/cm<sup>2</sup> for YSZ and H-BETA electrodes were recorded, Such values are higher than those obtained using the standard electrode (800mA/cm<sup>2</sup>), confirming an enhanced electrode structure.

## 2. MATERIALS AND METHODS

### 2.1. Powders Preparation and Characterisation

As inorganic material to be introduced in the catalytic layer, the following compounds were used: commercial Yttria stabilised Zirconia (Y<sub>2</sub>O<sub>3</sub> 8% mol) (Aldrich Submicron Powder 99,9% Purity); commercial zeolite H-BETA (CP811E-75, Zeolyst with a molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 75, in hydrogen form and with a surface area of 650m<sup>2</sup>g<sup>-1</sup>) and synthesised nanometric TiO<sub>2</sub> powder.

The last one was synthesised by a hydrolysis per hydrochloric acid of Titanium tetraethoxide (Ti(OEt)<sub>4</sub> supplied by Aldrich) by the sol-gel method, according to the reference [20]. The prepared powder was calcined for 4 hrs at 400°C in order to obtain the anatase structure.

The powders were characterised by using X-ray diffraction (XRD) analysis and a field emission scanning electron microscopy (FE-SEM) to verify the morphology.

The X-ray diffraction (XRD) analyses were performed by using a Philips X-ray automated diffractometer (model PW3710) with Cu-K $\alpha$  radiation source. The 2 $\theta$  Bragg angles were scanned between 5° and 100°.

A field emission Scanning Electron Microscope (Philips mod. XL30 S FEG) equipped with Energy Dispersive X-Ray probe (EDX) was used to study the morphology of the powders.

For SEM-EDX analyses all the samples were fixed on an adhesive stab and a graphite coverage was successively carried out to make them electrically active.

### 2.2. Electrodes and MEAs Preparation

The electrodes were prepared by using a spray technique [8, 10] on carbon cloth support (Textron). Composite electrodes were obtained by mixing different percentages (0-14 wt%) of the inorganic powders in the catalytic ink. The Pt loading was maintained as a constant at about 0.5 mg/cm<sup>2</sup> and the ionomer content was maintained as 33 wt% respect to the catalyst amount for all electrodes prepared.

A previous study on the selection of the best amount of YSZ and H-BETA to be introduced into the

catalytic layer [8, 10], has highlighted that the proper amount for both the oxides corresponded to a 8 wt%. This amount was used to prepare the composite electrodes in order to have a comparison of the performance among the different electrodic structures.

Regarding the composite TiO<sub>2</sub>-based electrodes, an evaluation of different amount (0-4 wt%) introduced into the catalytic layer was carried out.

The characteristics of the developed electrodes are reported in Table 1

**Table 1: Characteristics of Prepared Electrodes**

Electrodes	Inorganic Compound	Inorganic Content, (wt/wt%)
CNR-SE	-	0
TiO-2	TiO <sub>2</sub>	2
TiO-4	TiO <sub>2</sub>	4
YSZ-8	YSZ	8
H-BETA-8	Zeolite	8

The membrane electrode assemblies (MEAs) were obtained by pressing the electrodes on the commercial Nafion 115 membranes at 130°C with a pressure of 20kg/cm<sup>2</sup> for 3 min. The same electrode was used both for anode and cathode.

### 2.3. Electrodes Characterisation

EDX mapping on the composite electrodes was performed by using a field emission Scanning Electron Microscope equipped with EDAX microprobe. Platinum, Fluorine and respectively Ti, Si and Y were mapped for composite electrodes, utilising the lines M for Pt, K for F, Si and Ti and L for Y. The spectral line of Y was detected instead of Zr because it is overlapped to Pt line. Mapped surface is of about 20x10 μm and the used mapping matrix had a dimension of 256x 200.

### 2.4. Electrochemical Characterisation

Fuel Cell tests were carried out in a 5 cm<sup>2</sup> commercial single cell. MEAs were characterised in a temperature range between 80°C-130°C in H<sub>2</sub>/air with humidified gases (100% RH) at 3.0 abs. bar. The gas fluxes were fixed at 1.5 and 2 times the stoichiometric at a current density value of 1.0 A/cm<sup>2</sup> for fuel and oxidant, respectively. The polarisation curves were performed in a galvanodynamic mode.

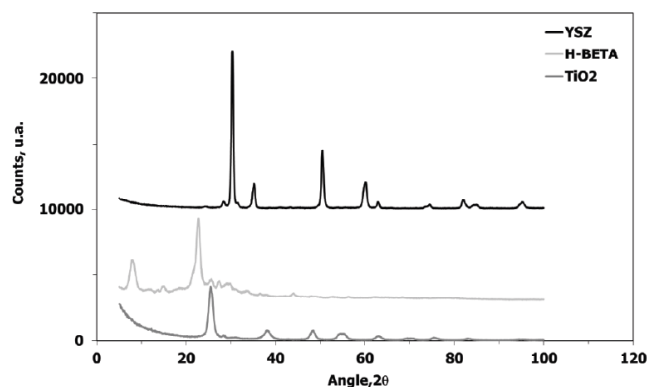
The cell resistance was measured at open circuit voltage (OCV) by using a HewlettePackard (type HP4338B) milliohmeter at a frequency of 1 KHz.

## 3. RESULTS AND DISCUSSION

The aim of this work is to understand how the different properties of the filler used for composite electrodes preparation can influence the optimal loading in the catalytic layer. In particular the grain size, the acidity and the intrinsic proton conductivity.

At first, the inorganic powders were characterised in order to verify the crystalline structure and the grain size of agglomerates.

In Figure 1, XRD patterns of the different oxides are compared in the range of the scanned 2θ angles.



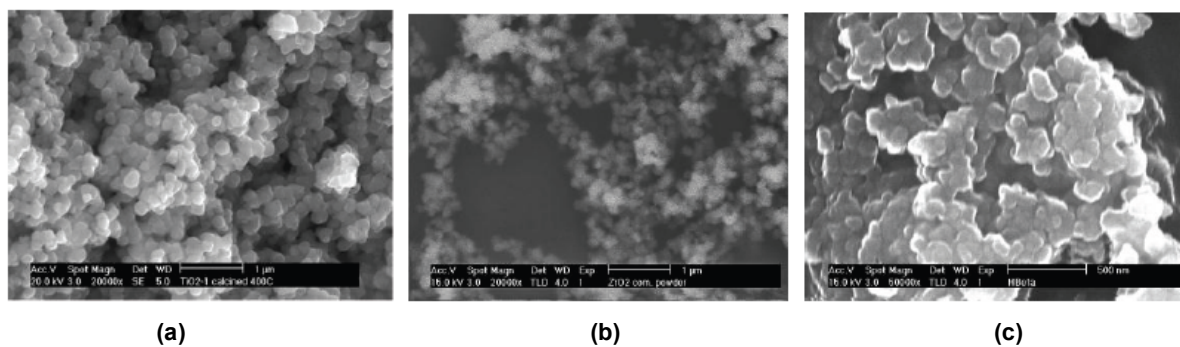
**Figure 1:** XRD patterns comparison of inorganic compounds.

The titanium oxide presents a definite crystalline structure corresponding to the Anatase phase as reported in the JCPDS card N° 71-1166 and other phases are not visible meaning that the synthesis has been successful.

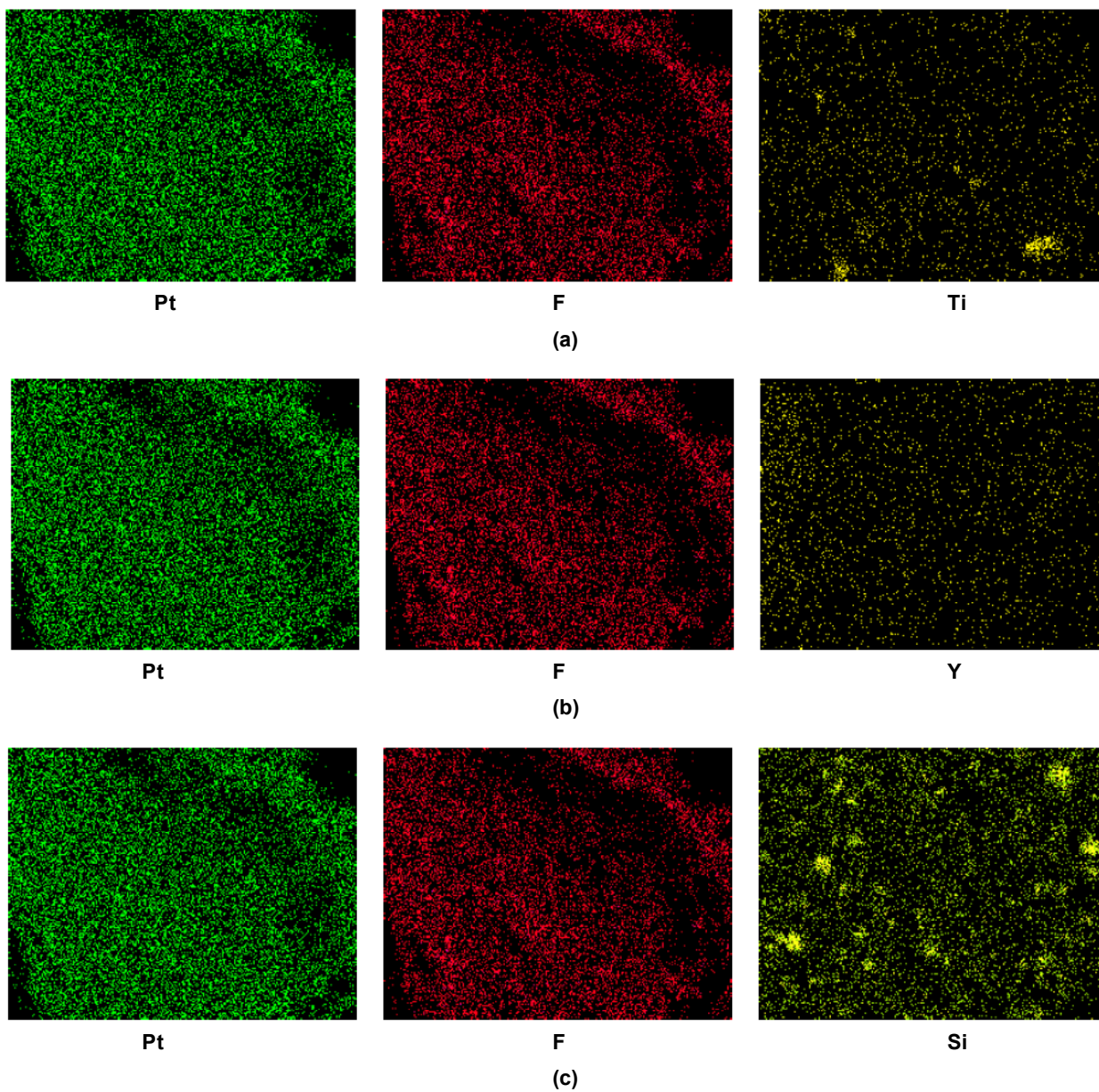
Regarding commercial YSZ, a crystalline structure corresponding to a cubic phase (JCPDS N° 27-997) was confirmed.

XRD pattern of zeolite presents two main peaks centred at 8° and 22° 2θ indicating a well defined crystalline structure corresponding to a typical H-BETA zeolite class [21, 22]

In Figure 2 a-c the comparison of the SEM images is reported for the three powders. It is possible to notice that all the samples present spherical particles but a different grain size. In particular, TiO<sub>2</sub> presents a grain size between 5-20 nm (Figure 2a), YSZ between 100-



**Figure 2:** SEM images of the used inorganic oxides, **a)** TiO<sub>2</sub>, **b)** YSZ and **c)** H-BETA.



**Figure 3 a-c:** EDX mapping of the developed composite electrodes, **a)** TiO-4, **b)** YSZ-8 and **c)** H-BETA-8.

150 nm (Figure 2b) and H-BETA between 40-100 nm (Figure 2c).

Concerning to the composite electrodes chemical-physical characterisation, EDX mapping has confirmed



that the inorganic powders are uniformly distributed on the electrodes surface. In fact, as shown in Figure 3 a-c, Pt and F are more visible due to their highest content in the electrodes, but in any case the other elements contained in the inorganic powders are well visible and are uniformly distributed respect to Pt and F.

After the chemical physical characterisation, electrochemical tests were carried out on the developed electrodes. In Figure 4 a-b, the polarisation curves related to developed electrodes containing different titania percentage at 80°C and 130°C are reported.

At 80°C the titania introduction seems to have no influence, in fact the standard electrode has better performance than the other two ones, this is because the optimal operative temperature for Nafion, so, at this temperature the effect of the inorganic compound introduction is not so evident. In particular, the introduction of TiO<sub>2</sub> produces a reduction of cell performance proportionally to the increasing of the introduced amount. The composite electrodes show worse performance than the standard electrode (CNR-SE) at 80°C with a current density at 0.6V of 407 and 254 mA/cm<sup>2</sup> for TiO-2 and TiO-4, respectively instead of 859 mA/cm<sup>2</sup> for the standard electrode. This is in accordance with the Tafel slope that increases with the increase of the inorganic content in the electrode (91mV/dec, 121mV/dec and 133mV/dec for CNR-SE, TiO-2 and TiO-4 respectively).

By increasing the operative temperature at 130°C, the beneficial effect due to the introduction of inorganic compound is more evident, even if the behaviour of composite electrodes is different. TiO-2 sample shows a worse performance than CNR-SE and TiO-4 one.

The last one reaches the highest performance with a current density of 506 mA/cm<sup>2</sup> at 0.6V and the lowest Tafel slope (88 mV/dec). This effect could be attributable to an enhanced electrode structure due to an improved mechanical resistance of the ionomer that limits the swelling and consequently the softening effect between the catalyst and the ionomer.

A similar study on the optimal amount of YSZ and H-BETA powders to be introduced was carried out [8, 10] by varying their percentages in the range 0-14 wt%. In both cases, an optimal different content if compared to titania was obtained. In particular, a loading of 8 wt% was found for the two different fillers.

Successively to the optimisation of each inorganic material in the electrodes catalytic layer, a comparison among the best composite electrodes in terms of V-I curves at 80°C and 130°C was carried out, as reported in Figure 5 a-b.

At T=80°C, the electrodes CNR-SE, YSZ-8 and H-BETA-8 show a similar performance. On the contrary, TiO-4 has the worst behaviour. In particular, the electrodes containing an inorganic compound with a similar particle size (YSZ and H-BETA) show the best and comparable performance.

In addition, as shown in Table 2, the electrochemical parameters such as cell resistance and OCV at 80°C highlight that the introduction of fillers in the catalytic layer produces a slight reduction of OCV values, while a different behaviour is found for cell resistance ( $R_{cell}$ ). In fact, this parameter remains quite unaltered when YSZ is present, it undergoes a slight increase with TiO<sub>2</sub> and a reduction with H-BETA introduction. Moreover, Tafel slope is reduced with YSZ, it is increased with TiO<sub>2</sub> and again it is reduced

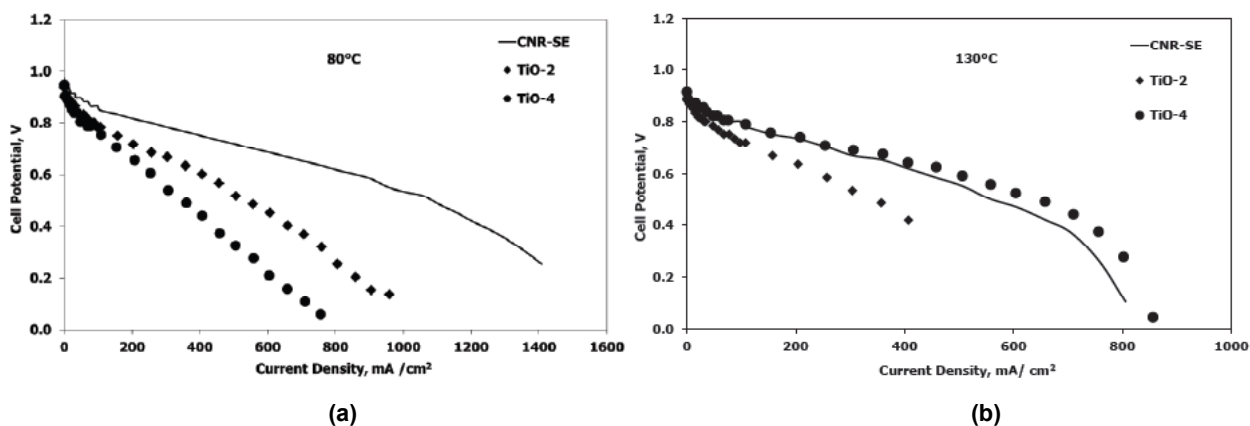
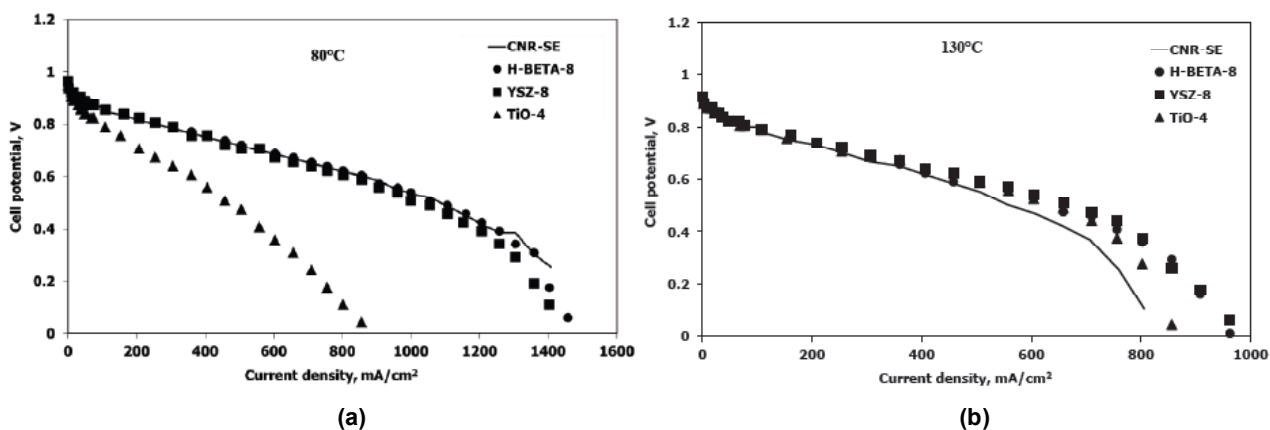


Figure 4 a-b: Comparison of polarization curves among composite TiO<sub>2</sub>-based electrodes and standard one, a) 80°C, b) 130°C.



**Figure 5 a-b:** Comparison of polarization curves among composite electrodes with optimized inorganic compound loading and standard one, **a)** 80°C, **b)** 130°C.

**Table 2: Electrochemical Parameters Comparison of Developed Electrodes**

Electrodes	Inorganic Content, wt%	Slurry pH	$R_{cell}$ , $\Omega\text{cm}^2$		OCV, V		Tafel Slope, mV/dec	
			80°C	130°C	80°C	130°C	80°C	130°C
CNR-SE	-	-	0.136	0.160	0.976	0.907	91	106
YSZ-8	8	5.9	0.130	0.130	0.965	0.914	72	83
TiO-4	4	5.3	0.140	0.115	0.948	0.916	133	88
H-BETA-8	8	4.3	0.110	0.120	0.955	0.909	65	87

with H-BETA if compared to CNR-SE. This behaviour could be explained taking into account the different properties of the fillers. YSZ has an intrinsic proton conductivity [23-25] that starts at  $T \geq 100^\circ\text{C}$  and a quasi-neutral slurry pH. So, at 80°C the effect on the  $R_{cell}$  is not so evident, but the contribution is more pronounced when the Tafel slope is considered, meaning that a better reaction kinetic occurs on the catalytic layers of the electrodes. Regarding the introduction of  $\text{TiO}_2$ , all the electrochemical parameters are worsened. Since no additive strong acidity ( $\text{pH}_{slurry}=5.3$ ) and no intrinsic proton conduction are recorded, this filler is considered as an inert and the benefit should be evidenced only at higher temperatures than 80°C, where the mechanical properties of the ionomer are improved. On the contrary, H-BETA possesses acidic sites ( $\text{pH}_{slurry}=4.3$ ) and the effect of additional protons is visible in the cell resistance reduction and also in the Tafel slope, that is the lowest than the others. The influence of these filler properties is reflected on fuel cell performance. In fact, YSZ and H-BETA show a similar performance than CNR-SE, while  $\text{TiO}_2$  shows a strong reduction of the

polarisation curve in the whole investigated region (activation, ohmic and diffusion).

Increasing the temperature up to 130°C, the benefit of the fillers introduction should become more evident because at this operative temperature with fully humidified gases, the effect of ionomer swelling on the interface contact should occur.

At this temperature the performance is improved for all the composite electrodes respect to CNR-SE (Figure 5 b), in particular the limiting current is increased from  $\sim 800 \text{ mA/cm}^2$  to  $\sim 850 \text{ mA/cm}^2$  and  $\sim 970 \text{ mA/cm}^2$  passing from the CNR-SE to TiO-4, YSZ-8 and H-BETA-8 electrodes.

The electrochemical parameters also highlight the benefit of filler introduction, in fact OCV values are higher for composite electrodes than standard one. The cell resistance and the Tafel slope are lower, meaning that different contributions of each oxide are fundamental for a good fuel cell operation. In particular,  $\text{TiO}_2$  acts as a mechanical reinforcement, due to its

inert characteristic, avoiding the detrimental effect of the ionomer swelling. Regarding to YSZ and H-BETA, besides the mechanical reinforcement effect, they possess an intrinsic proton conductivity and additive proton sources that contribute to the catalytic reaction rate at the three-phase boundary. Moreover, an improved limiting current was recorded, confirming an enhanced electrodic structure able also to participate to the water management during the fuel cell operation.

Because of different optimal amount was found for the different inorganic compound introduced in the catalytic layer, it was supposed that exists a limit in the oxide introduction depending on physical properties of the inorganic filler, in particular the particle size, the acidity or the intrinsic proton conductivity and the physical properties of the polymeric matrix used as an ionomer.

## CONCLUSIONS

Composite electrodes containing different inorganic compounds in the catalytic layer were developed and characterised in order to improve high temperature PEFC electrodes performance.

The study was carried out considering three inorganic compounds having different chemical and physical properties. The selected materials were a synthesised titania, a commercial yttria stabilized zirconia and a H-BETA zeolite that were introduced in the catalytic layer.

For each inorganic material, a different optimal amount was found depending on their chemical-physical properties, in particular the particle size, acidity and proton conductivity. For titania powder, a nominal amount of 4 wt% was found as optimal loading to be introduced into the catalytic layer, instead of 8 wt % for YSZ and H-BETA zeolite, as reported in a previous study.

A homogeneous distribution of the inorganic compounds in the electrodes was highlighted by SEM-EDX mapping.

A comparison among the best developed electrodes was performed in terms of V-I curves at 80°C and 130°C. As expected at 80°C, the inorganic compound introduction does not cause an evident performance improvement. At 130°C, all the composite electrodes reached a higher performance than CNR-SE. In particular, the electrodes containing YSZ and H-BETA show the best and comparable performance. The

limiting current was increased from ~ 800 mA/cm<sup>2</sup> to ~ 850 mA/cm<sup>2</sup> and ~ 970 mA/cm<sup>2</sup> passing from the CNR-SE to TiO-4, YSZ-8 and H-BETA-8 electrodes, wherein the water management is predominant, confirming an enhanced electrode structure.

It was supposed that a limit in the oxide introduction exists depending on physical properties of the inorganic filler, in particular the grain size, the acidity or the intrinsic proton conductivity and the physical properties of the polymeric matrix used as an ionomer.

## LIST OF ABBREVIATIONS

- PEFCs: Polymer Electrolyte Fuel Cells
- MEA: Membrane Electrode Assembly
- OCV: Open Circuit Voltage
- H-BETA: Zeolite Beta type
- YSZ: Yttria stabilised Zirconia
- XRD: X-ray diffraction
- FE-SEM: field emission scanning electron microscopy
- EDX: Energy Dispersive X-Ray

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