

# **POLYMER ELECTROLYTE FUEL CELLS ELECTRODES**

## **A performance study**

A. CEMMI, C. PAOLETTI, A. POZIO

ENEA - Dipartimento Tecnologie per l'Energia, Fonti Rinnovabili e Risparmio Energetico  
Centro Ricerche Casaccia, Roma



ENTE PER LE NUOVE TECNOLOGIE,  
L'ENERGIA E L'AMBIENTE

# POLYMER ELECTROLYTE FUEL CELLS ELECTRODES

## A performance study

A. CEMMI, C. PAOLETTI, A. POZIO

ENEA - Dipartimento Tecnologie per l'Energia, Fonti Rinnovabili e Risparmio Energetico  
Centro Ricerche Casaccia, Roma

I contenuti tecnico-scientifici dei rapporti tecnici dell'ENEA rispecchiano l'opinione degli autori e non necessariamente quella dell'Ente.

The technical and scientific contents of these reports express the opinion of the authors but not necessarily the opinion of ENEA.

# POLYMER ELECTROLYTE FUEL CELLS ELECTRODES

A performance study

A. CEMMI, C. PAOLETTI, A. POZIO

## **Abstract**

*This work is focused on the study of electro-crystallization of Pt nanostructured particles to be used as a catalyst on carbon material support (carbon black and carbon nanotubes) for polymer electrolyte fuel cells electrodes. Electrochemical single and multiple pulse galvanostatic depositions have been applied defining the best operational parameters leading to a highly nanostructured electro-catalysts morphology. Electrochemical measurements such as cyclic voltammeteries have been carried out in order to determine the electrochemical active surface together with morphological analysis by means of scanning electron microscopy. The influence of electro-deposition parameters on the Pt loading have been extensively studied and optimized. The investigated materials have been then applied as gas diffusion electrodes (GDE) and characterized by means of polarization curves in half-cell and in single cell test station. A comparison with a standard E-TEK electrode, prepared by conventional powder-type technique, shows that the electrodeposited catalyst electrodes present comparable performances and their maximum specific power density values are similar or better than that of standard E-TEK cathode. These results strongly encourage the implementation of electrodes obtained by electro-deposition in a real-world device.*

**Key words:** Polymer electrolyte fuel cell, electro-catalyst, membrane electrode assembly (MEA), electro-deposition, carbon nanotubes.

## **Riassunto**

Il lavoro presentato nel seguente RT è stato svolto nell'ambito del Progetto di ricerca FISR 2005-2008 che riguarda lo sviluppo delle celle a combustibile e dei sistemi per le loro applicazioni.

Nell'ambito di questa ricerca sono state studiate metodologie elettrochimiche per la cristallizzazione di particelle di platino nanostrutturate su supporti di materiale carbonioso (polvere di carbone Vulcan XC72R e nanotubi di carbonio a parete multipla MWNTs) da impiegare come elettrocatalizzatori nelle celle a combustibile ad elettrolita polimerico.

I catalizzatori sono stati depositati mediante tecniche galvanostatiche a singolo e multiplo impulso (GED e PED rispettivamente) e caratterizzati dal punto di vista elettrochimico (voltammetrie cicliche) e morfologico (FEG-SEM). È stata studiata l'influenza dei parametri operativi sulla morfologia e sul carico di platino in modo da ottenere un catalizzatore con elevate prestazioni elettrochimiche e caratterizzato da una estesa nanostruttura superficiale.

I materiali sono stati quindi utilizzati nella preparazione di elettrodi a diffusione gassosa (GDE), degli assemblati membrana-elettrodo e caratterizzati attraverso curve di polarizzazione in semi-cella ed in cella. I risultati mostrano che i sistemi con catalizzatore elettrodepositato hanno elevate densità di potenza specifica e prestazioni del tutto paragonabili o migliori rispetto ad un elettrodo commerciale E-TEK.

**Parole chiave:** PEFC, tecniche di elettrodeposizione, elettrocatalizzatore, nanotubi di carbonio, MEA.



## INDEX

1. INTRODUCTION.....	7
2. EXPERIMENTAL.....	10
2.1 Electrode preparation	
2.2 Single fuel cell fabrication	
2.3 Single fuel cell testing	
3. PREPARATION OF SUBSTRATES AND THEIR CHARACTERIZATION.....	19
4. SINGLE FUEL CELL of 5 cm <sup>2</sup> .....	22
3.1 Electrode preparation	
3.2 Single fuel cells fabrication and characterization	
3.3 Conclusions	
5. SINGLE FUEL CELL of 2 cm <sup>2</sup> .....	30
3.1 Electrode preparation	
3.2 Single fuel cells fabrication and characterization	
3.3 Conclusions	
6. REFERENCES.....	39



## 1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have significant advantages such as the elimination of electrolyte leakage, lower corrosion, simplification of stack design. These promising attributes have stimulated many applications in areas such as consumer electronics, aerospace and transportation<sup>1</sup>. Nevertheless, several drawbacks in PEFCs need to be overcome including high costs, high catalyst loading and low CO tolerance.

From the perspective of electrode materials, the cost problem can be faced in two ways: improvement of the catalyst utilization and reduction of the catalyst loading. Progress in fuel cell research not only has led to increased power density and efficiency but also to an optimization of preparation techniques and materials fabrication.

It is worth noting that only the catalyst in contact with both membrane electrolyte and reaction gas is electrochemically active. In fact, in the catalytic layer the so-called “three-dimensional reaction interface” is recognized as the region in which electrons, protons and reactant gases performing reduction/oxidation reactions are present at the same time. For this reason, catalyst nanoparticles (Pt or alloy) deposited on high surface carbon support are requested to be covered by a Nafion<sup>TM</sup> ionomer solution, to ensure a good ionic conduction with polymeric membrane (acting as electrolyte).

This has been widely previously<sup>2-4</sup> demonstrated and obtained via impregnation of gas diffusion electrodes with solubilised ionomer (e.g. Nafion<sup>TM</sup>).

Common manufacturing methods do not allow a good localization of the catalyst and, as a consequence, utilization of Pt is definitely low. In order to obtain a large interface area between the polymer electrolyte and the catalyst, several novel fabrication processes, besides casting<sup>5</sup>, screen printing<sup>6</sup>, brushing<sup>7</sup>, spreading<sup>8</sup>, spraying<sup>9-11</sup> have been developed. By these alternative methods, the catalyst allow for depositing directly on the surface of carbon electrode or membrane, decreasing noble metal loading but maintaining adequate performances.

A novel method based on the electro-spray technique has been developed by Ben'ítez et al.<sup>12</sup> and characterized by different techniques, which showed both morphological and structural improvements contributing to a better catalyst utilization compared to conventional methods. Several electrode membrane assemblies (MEAs) have been fabricated with electrodes prepared by three different methods. MEAs obtained via electro-spray exhibited a power density three times higher than those prepared with impregnation methods and eight



times higher than those prepared by the spray technique with Pt loadings of  $0.5 \text{ mg cm}^{-2}$ . Moreover, the power density obtained was twice better than that of a commercial E-TEK electro-catalyst. However, the same researchers have studied Pt utilization in electrodes prepared by impregnation, spray and electro-spray methods and found that the impregnation method gives a higher Pt utilization than the other two methods. They attributed this behaviour to the high porous structure achieved from a complete solvent removal after a long period of impregnation, while in the other two methods, the immediate elimination of solvent leaves a poorly porous structure<sup>13</sup>.

Many efforts have been taken in developing electrodes with a high efficiency of noble metal catalyst improving by catalyst ink preparation<sup>14</sup> and novel Pt deposition methods.

Thus, common vacuum deposition methods that include physical<sup>15,16</sup> or thermal<sup>17</sup> vapour deposition have been employed. Sputtering technique is considered as one of the best approaches to the catalyst deposition onto the gas diffusion layers. However, this technique is not a massive production method and requires expensive vacuum equipments. Otherwise, electro-deposition<sup>18,19</sup> of noble metal catalyst on un-catalyzed carbon electrodes opens a promising route for increasing the present efficiency of metal catalysts.

In fact, the use of an electric field to deposit catalyst particles ensures their localization only in regions with a triple phase contact (carbon substrate/electro-catalyst/electrolyte), and the Pt loading can be noticeably reduced ( $L_{\text{Pt}} < 0.1 \text{ mg cm}^{-2}$ )<sup>20</sup>. Moreover, considerable advantages can be achieved:

- high purity of deposits
- catalyst uniform distribution on the support
- Pt particles of reduced size
- easier procedure: absence of reducing agent and surfactants, as well as hydrogen treatments at high temperature
- easier industrial scale-up

Electro-deposition techniques are the most studied by researchers who try to obtain smaller Pt particles in order to enlarge the catalytic area and, accordingly, to enhance the catalytic activity for structure-sensitive reactions<sup>21</sup>.

It is possible to find a significant correlation between electro-catalytic behaviours and nanoparticles structure. In fact, in a previous technical report<sup>22</sup> we found that electro-deposition parameters allow to significantly control the Pt particles morphology, leading to

spherical, dendritic and lamellar shapes. Results show that electro-catalytic properties are influenced by the deposit morphology: nanostructured globular surface shapes give the best electro-catalytic performances.

Finally, while activated carbon is still the most common support material for electrocatalysis, new forms of carbon such as fullerenes and nanotubes, which have become more available recently, have also been indicated as suitable materials for electrode and catalyst support in PEFCs.

In this work a preparation method based on the electrochemical deposition of low-loading Pt nanoparticles on PEFCs gas diffusion electrodes, giving improved performance and catalyst utilization versus commercial Pt catalyst is presented.

Pt nanoparticles electro-catalysts have been directly deposited on gas diffusion layers (GDLs) by means of galvanostatic polarization techniques: single and multiple pulse electro-depositions.

The subject has been thoroughly investigated not only in terms of deposition techniques optimization, but also by testing in-house prepared PEFCs in a single-cell station. This way, the actual performances of these new materials have been evaluated in real working conditions and a detailed description of the corresponding electrochemical performances is here reported.

Morphological features and Pt loading have been studied to characterize the electrodes and a correlation with their electrochemical performances has been found.

## 2. EXPERIMENTAL

Electrodes preparation and single fuel cell realization is schematically reported in the following:

1. diffusive ink preparation
2. diffusive layer spraying on *carbon paper*
3. thermal treatments
4. catalyst electrodeposition (electrochemical characterization and chemical analysis of deposits)
5. electrode/membrane/electrode assembly (MEA)
6. fuel cell test

### 2.1 ELECTRODE PREPARATION

Electrodes preparation has involved the following materials:

- TGPH-090 carbon paper (Toray Industries Inc.) of 0.3 mm thickness, 74% porosity and mass density of  $0.45 \text{ g cm}^{-3}$ ;
- Vulcan XC-72R carbon and Super-P<sup>TM</sup> carbon black powder;
- Multi-wall carbon nanotubes (Aldrich) 90% purity;
- Polytetrafluoroethylene (PTFE, Hoechst, Hostaflon TF5033 type, 35%wt solution);
- Isopropyl alcohol (Carlo Erba, 99.9% wt);
- Alcoholic solution of Nafion<sup>TM</sup> 5% (DuPont);

The diffusive layers have been prepared by the commonly used spray deposition method. A homogenous alcoholic suspension containing carbon powder and 20-30 %wt of PTFE has been immersed in an ultrasonic bath at room temperature. To facilitate the dispersion of carbon particles the suspension has been mixed with a water/isopropyl alcohol (1:1) solution.

The mixture has been stirred in ultrasonic bath during the whole procedure to remove the air trapped inside the extremely porous carbon particles, improving their wettability and homogeneity in the dispersion.

Then, the diffusive ink has been homogeneously sprayed onto the whole surface of a carbon paper support forming the gas diffusion layer (GDL, Fig.1). The carbon amount in the diffusion layer ranges from 1.5 and  $2 \text{ mg cm}^{-2}$ . Although this technique guarantees a certain

reproducibility, it is worth noting that about a 20-30 % of material loss has been observed and the thickness control is not very easy.

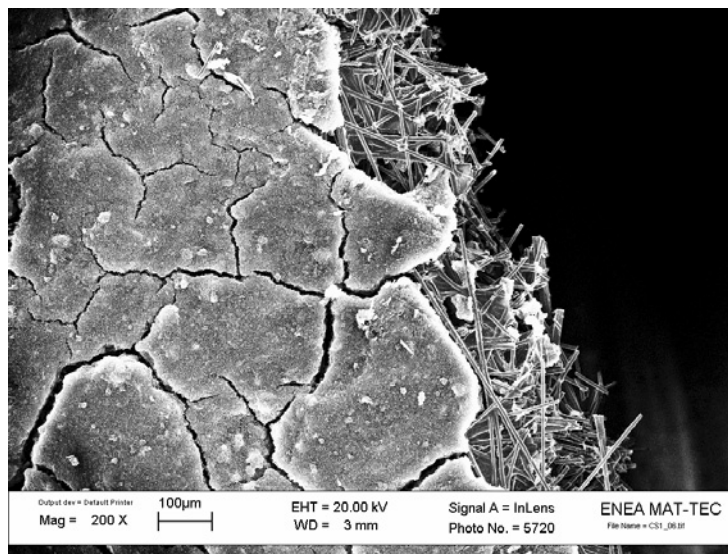


Fig. 1. – *GDL SEM image: carbon paper support and diffusive layer*

Afterwards, GDLs have been sintered in a oven at 120°C for 1 h, at 280°C for 2 h and at 350°C for 30 min. This thermal step is necessary to remove the dispersion agent contained in the PTFE suspension. Moreover, PTFE is molten, aggregating the carbon powder particles and giving an hydrophobic character to the gas diffusion layer.

#### *Pt electro-deposition onto the GDLs and characterization*

A sample of GDL with suitable size inserted in an electrode holder has been used as a working electrode before electro-deposition. A round plexiglass mask allowed for the contact between the electrode surface and the solution. (Fig.2)

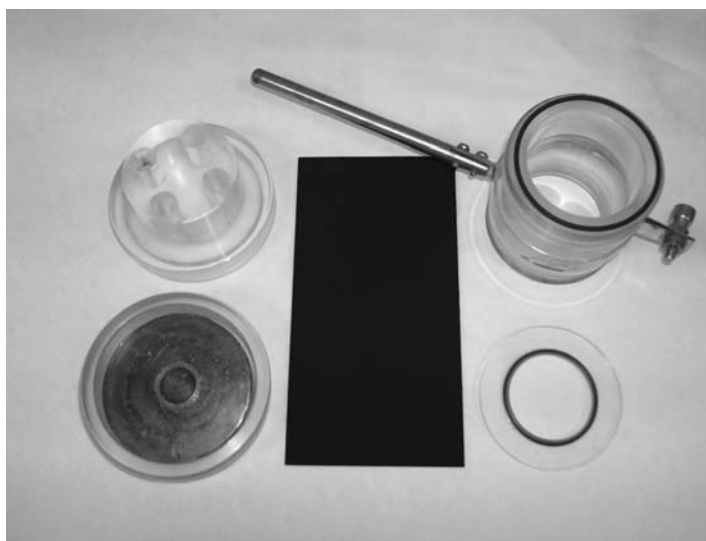


Fig. 2.- *Electrochemical cell*

Pt electro-deposition has been carried out by two techniques.

- single pulse galvanostatic polarization (GED)
- multiple pulse galvanostatic polarization (PED)

The electro-deposition bath containing  $\text{H}_2\text{PtCl}_6$  5 mM in  $\text{H}_2\text{SO}_4$  1 M at 30 °C and an electrochemical cell in a three-electrodes configuration has been used.

The counter electrode has been a graphite stick. The electrode potentials have been measured with respect to a saturated calomel (SCE) reference electrode (0.244 V vs. NHE at 30 °C).

Electro-deposition tests and electrochemical characterizations have been done using a potentiostat-galvanostat PAR EG&G mod.273A controlled by a computer using an appropriate software (CORRWARE, Scribner Inc.) (Fig.3).

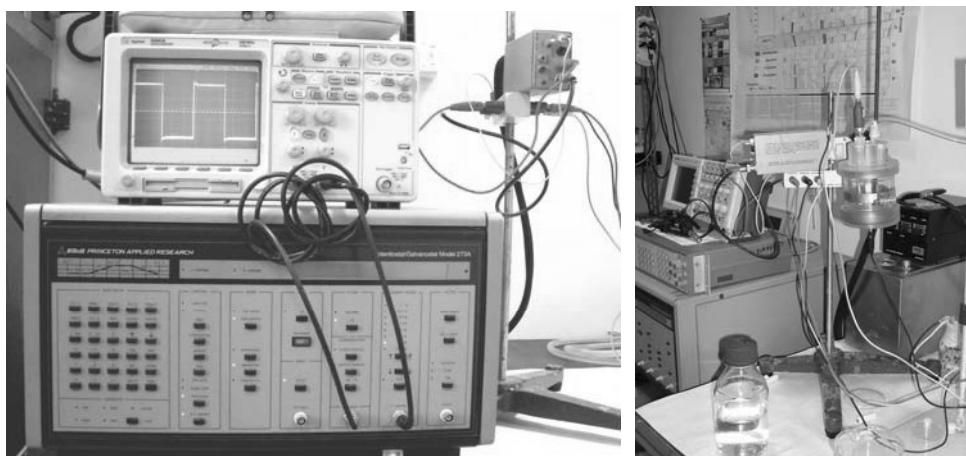


Fig.3. –*Electrochemical cell and instruments used for Pt electrodeposition and electrochemical characterizations*

#### *Electrochemical characterization of Pt deposits*

After Pt particles deposition, the electrode has been cleaned with deionized water. Then the Pt/CNTs and Pt/CP deposits have been investigated by means of cyclic voltammetry (CV) to determine the Pt electrochemical active surface (ERS) and study its activity towards hydrogen adsorption/desorption processes. CVs have been carried out in  $\text{H}_2\text{SO}_4$  1 M at 30°C in nitrogen flux. A typical CV curve is reported in Fig.4.

The hydrogen desorption charge  $Q_{\text{Hdes}}$  ( $\text{mC cm}^{-2}$ ) has been determined by integrating the current density in the potential range between -0.2 and 0.3 V after the subtraction of electrochemical double layer current density. The electrical charge  $Q_{\text{H}}^0$  necessary for a hydrogen monolayer to desorb from a smooth Pt electrode ( $1 \text{ cm}^2$ ) is  $0.21 \text{ mC cm}^{-2}$ .

The ratio between  $Q_H$  and  $Q_H^0$  allow to calculate the platinum real surface (ERS)

$$ERS = \frac{Q_H}{Q_H^0}$$

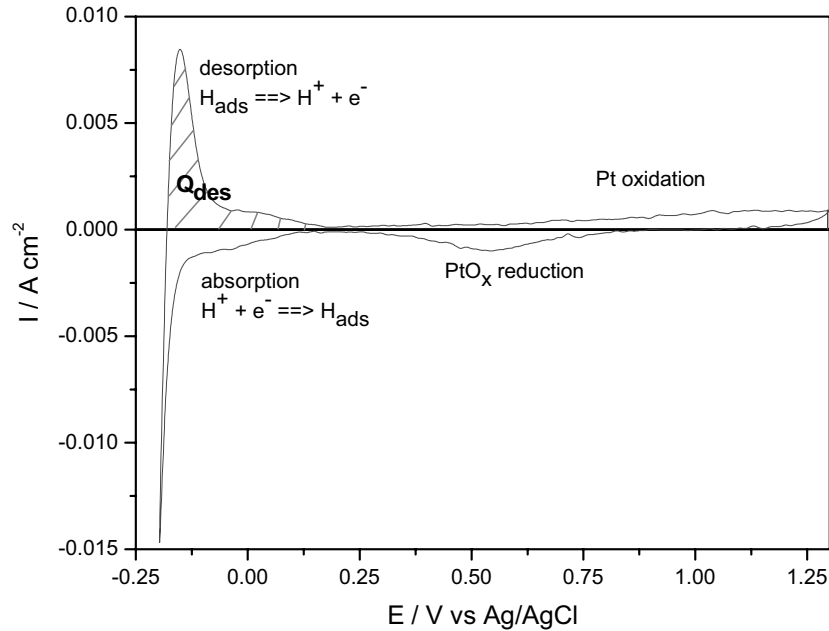


Fig.4. – Typical cyclic voltammetry curve.

#### *Morphological study of Pt deposits*

Since the different Pt electro-crystallization techniques may lead to deposits with various morphologies, a high resolution field emission gun - scanning electron microscope (FEG-SEM) has been used for a detailed study of the surface at a nanoscale level.

#### *Chemical analysis of deposits*

The platinum load ( $L_{Pt}$ ) on GDL has been determined by spectrophotometric analysis (Fig.5) (UV-VIS spectrometer, Beckman mod. DU65) at  $\lambda=403$  nm, with the method described in the following.



Fig. 5. - *UV-VIS Spectrometer*

In a solution containing chloride ions, Pt(IV) can be reduced to Pt(II) by Sn(II) species. After reduction, Pt(II) ions react quantitatively with  $\text{SnCl}_3^-$ , forming an anionic complex  $[\text{PtSn}_4\text{Cl}_4]^{4-}$  with an intense yellow colour. The measurements have been carried out in a quartz cuvette with an optical path of 1 cm. Water has been used as a reference.

The analytical procedure has been the following:

- preparation of Sn (II) chloride solution: 25 g of  $\text{SnCl}_2$  have been dissolved in hot concentrated HCl (37 %wt) and water added up to 50 mL;
- removal of Pt deposition from electrode by hot dissolution for 3 min in  $\text{HNO}_3/\text{HCl}=\text{v/v}$  1:3;
- the resulting solution has been dried to remove nitric acid and then immersed again in 1 mL of HCl 1N;
- 0.5 mL of  $\text{SnCl}_2$  solution have been added to the previous one reaching a final volume ( $V_f$ ) of 5 mL with water;
- a calibration plot has been constructed (Fig. 6) by plotting the absorbance data (after blank subtraction) as a function of Pt amount (expressed as ppm, [Pt]) contained in different standard solutions, prepared by dilution of AECP 20 ppm in HCl 1N;
- $L_{\text{Pt}}$  ( $\text{mg cm}^{-2}$ ) has been calculated by considering the  $S_g$  geometric surface of the analysed GDE, with the following equation

$$L_{\text{Pt}} = \frac{[\text{Pt}] \cdot V_f \cdot 10^3}{S_g}$$

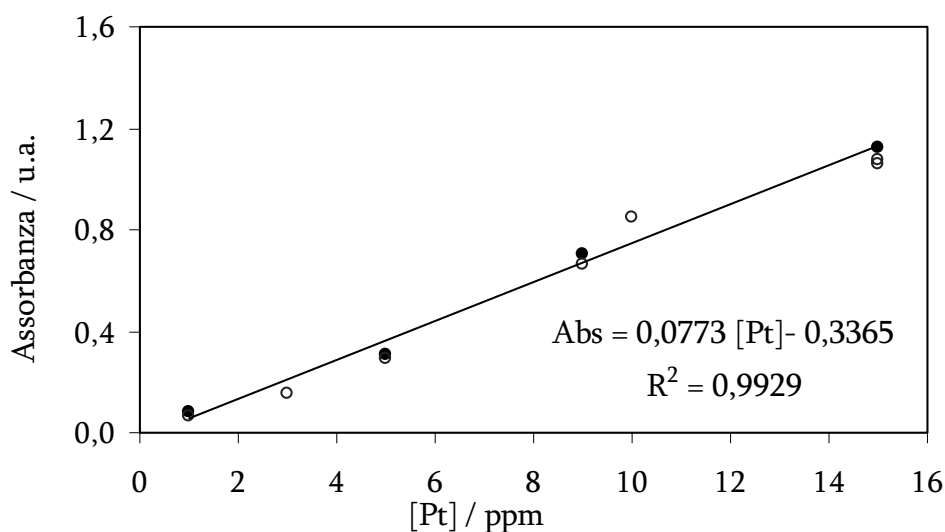


Fig. 6. – Typical calibration plot for Pt analysis

Pt electrochemical active surface (EAS) is calculated, using  $Q_H$  ( $\text{mC cm}^{-2}$ ),  $Q_H^\circ$  and the platinum load  $L_{Pt}$  ( $\text{mg cm}^{-2}$ ) measured by chemical analysis, with the following equation:

$$\text{EAS} = \frac{Q_H}{Q_H^\circ \cdot L_{Pt} \cdot 10} \quad (\text{m}^2 \text{ g}^{-1})$$

## 2.2 SINGLE FUEL CELL FABRICATION

### *Nafion™ membrane*

A Nafion™ (DUPONT DE NEMOURS) membrane has been used.

The Nafion™ membrane is supplied in large sheets and in acidic form but without any particular preservation cares, so that a pre-purification step is required to eliminate organic impurities.

The membrane purification procedure is quickly described. Firstly, the membrane has been cut in a suitable size and then submitted to the following treatments:

- 1 hour in a boiling  $\text{H}_2\text{O}_2$  5%wt solution followed by cooling at room temperature
- 1 hour in boiling deionized water followed by cooling at room temperature
- 1 hour in a boiling  $\text{H}_2\text{SO}_4$  1 M solution point followed by cooling at room temperature
- 1 hour in boiling deionized water followed by cooling at room temperature

Now the membrane is ready to be used and it can be kept in deionized water for several weeks.



### *Membrane electrode assembly (MEA)*

The preparation procedure of MEAs is described in the following, MEAs with two different dimension ( $5\text{ cm}^2$  and  $2\text{ cm}^2$ ) have been prepared.

Firstly, electrodes previously submitted to electro-deposition have been soaked with a Nafion™ 5%wt solution, dried in a oven at  $130^\circ\text{C}$  for 1 hour allowing Nafion™ polymerization and then cut in a suitable size.

Subsequently, the following items have been overlapped one by one: a Teflon sheet, two filter paper sheets, the first electrode (with a catalytic layer on its top face), the wet Nafion™ membrane, the second electrodes (with a catalytic layer turned towards the membrane), two filter paper sheets and an other Teflon sheet.

The whole package has been moved under press pre-heating at  $100^\circ\text{C}$ , applying a pressure below 10 bars and the temperature has been set at  $130^\circ\text{C}$  for 5 min. The assembly has been quickly removed and cooled at room temperature between two stainless steel plates.

The MEA (Fig.7a) obtained can now be tested in a fuel cell station or preserved totally immersed in deionized water or between wet filter paper sheets.

During the assembly procedure filter paper sheets are left in contact with the electrodes. These facilitate evaporation of solvents still present in the catalytic ink which avoid a perfect adhesion to the contact surfaces.

### *MEA/Gasket assembly (MEGA)*

In the case of a  $5\text{ cm}^2$  MEA, a Membrane Electrode Gasket Assembly (MEGA) has been prepared sealing the MEA, previously prepared, with a silicone-based gasket. This process consists in the insertion of MEA in a mould where a silicone-based polymer blend has been injected. This mould has been then kept around  $70^\circ\text{C}$  to speed up the hardening process.

Figure 7b shows the MEGA obtained through this process. With respect to the commonly used Viton gaskets or rubberized clothes, a number of advantages and innovative aspects are found:

- a fast preparation as well as an easy insertion in single cell facilities or stacks;
- an easy preservation of the system, which becomes easy to handle and ready to use;
- a higher Nafion™ membrane saving.

The points above listed remark very important results for a possible industrial scale development aiming at optimizing economic (membrane and labour costs) and technological factors (ease of assembly, reproducibility and quality control).

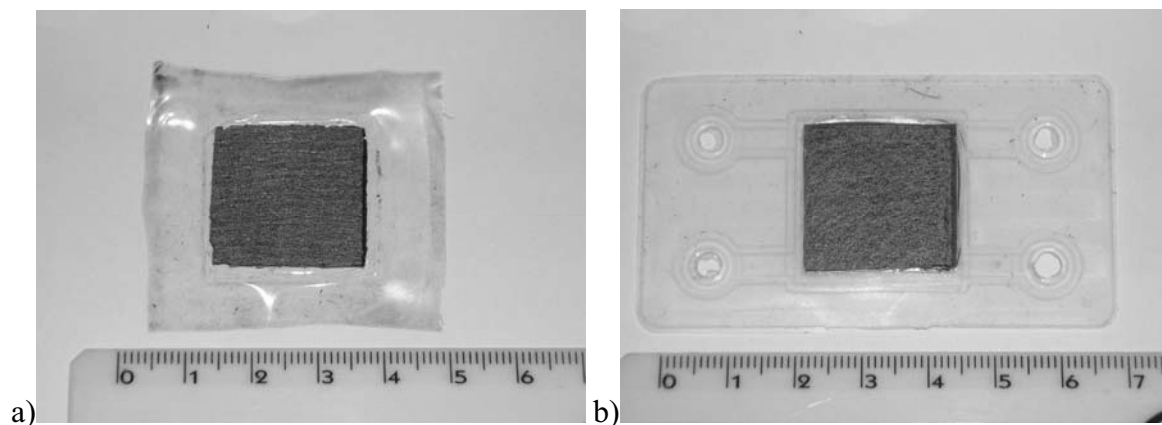


Fig. 7. – a) MEA and b) MEA/gasket (MEGA)

## 2.3 SINGLE FUEL CELL TESTING

### *Single cell start-up*

The single cell start-up is a critical phase in the characterization measurements.

In fact, during preparation and insertion in the cell, MEAs can undergo damages which can compromise electrochemical performance. The critical steps of preparation process are: thermal and compression treatment necessary to prepare MEA; silicone blend injection and *gasket* formation; MEA locking inside single fuel cell test facility.

Generally, thermal treatments occur in a temperature range wherein used materials are stable. Nevertheless a Nafion™ membrane dehydration is seen to occur. Pressure applied on the MEA is instead dangerous to diffusive and catalytic layers, leading to possible worsening of morphological properties (thickness and porosity), hence, electrochemical performance. Sometimes different performances can be ascribed to problems due to the reproducibility of MEA fabrication process. Finally, also the presence of impurities in the system influences its electrochemical performances.

Since at the beginning a MEA could not be in the optimal condition for working, the first single cell start-up should be led in a different way. In order to ensure a suitable humidification of Nafion™ membrane, the single fuel cell is left for several hours at constant temperature under fuel and oxidant humid gas flow: thus, a progressive hydration of the Nafion™ membrane is guaranteed.

This phenomenon is clearly characterized by an ohmic resistance decreasing during the current application.

### *Electrochemical characterization*

Each single MEAs/MEGAs have been separately investigated by electrochemical characterization.

Electrochemical measurements (impedance spectroscopy and polarization curves) have been carried out by means of a potentiostat-galvanostat Autolab PGSTAT 30 combined with a Current Booster (ECO CHEMIE). Finally, data analysis has been done using the software FRA.

Measurements have been performed in a two electrode symmetrical configuration: working electrode and counter electrode as an anode and cathode of the fuel cell respectively, both fed with hydrogen. This way makes it possible to compare the behaviour of the different anodes because the obtained results can be related to a reference cathode, equal for every cell. Some measurements, instead, have been recorded feeding the cathode with oxygen and the anode with hydrogen, simulating normal working condition of a fuel cell.

Electrodes prepared by electro-deposition have been used as anodes, while a in-house electrode EFE3 obtained by spraying and prepared with a catalytic ink (containing 30%wt Pt,  $L_{Pt}=0,54 \text{ mg/cm}^2$ ), has been used as a cathode in all the measurements.

The possibility of evaluate and compare single assemblies before the realization of a stack, early discarding those systems that do not reach a fixed standard, represents a promising and interesting perspective for a forthcoming industrial scale-up. The “death rate” of assemblies is nowadays one of the biggest technological obstacles to PEFCs’ industrial scale-up. To overcome this problem we aim at the development of totally reusable assemblies. For example, the systems studied and characterized in this work will be used again for further scale-ups.

### 3. PREPARATION OF SUBSTRATES AND THEIR CHARACTERIZATION

Electrodes are made by a hydrophobic sheet of *carbon paper* as a support over which a layer of carbon black powder or CNTs is deposited. In common electrodes this layer acts as a *gas diffusion layer* (GDL).

The carbon powders used in this work have been the Vulcan XC-72 and the Super P. These two types of carbon show very different morphological features which may influence the final product of the spraying step.

Figures 8a and 8b show SEM images of the carbon powders Vulcan XC-72 and Super P while Figure 8c shows multiwall carbon nanotubes (MWCNTs) SEM image. From the analysis of these images it can be turned out that the two powders are made by different particle compositions. The first appears heterogeneous with big and small particles, while the second show a higher homogeneity.

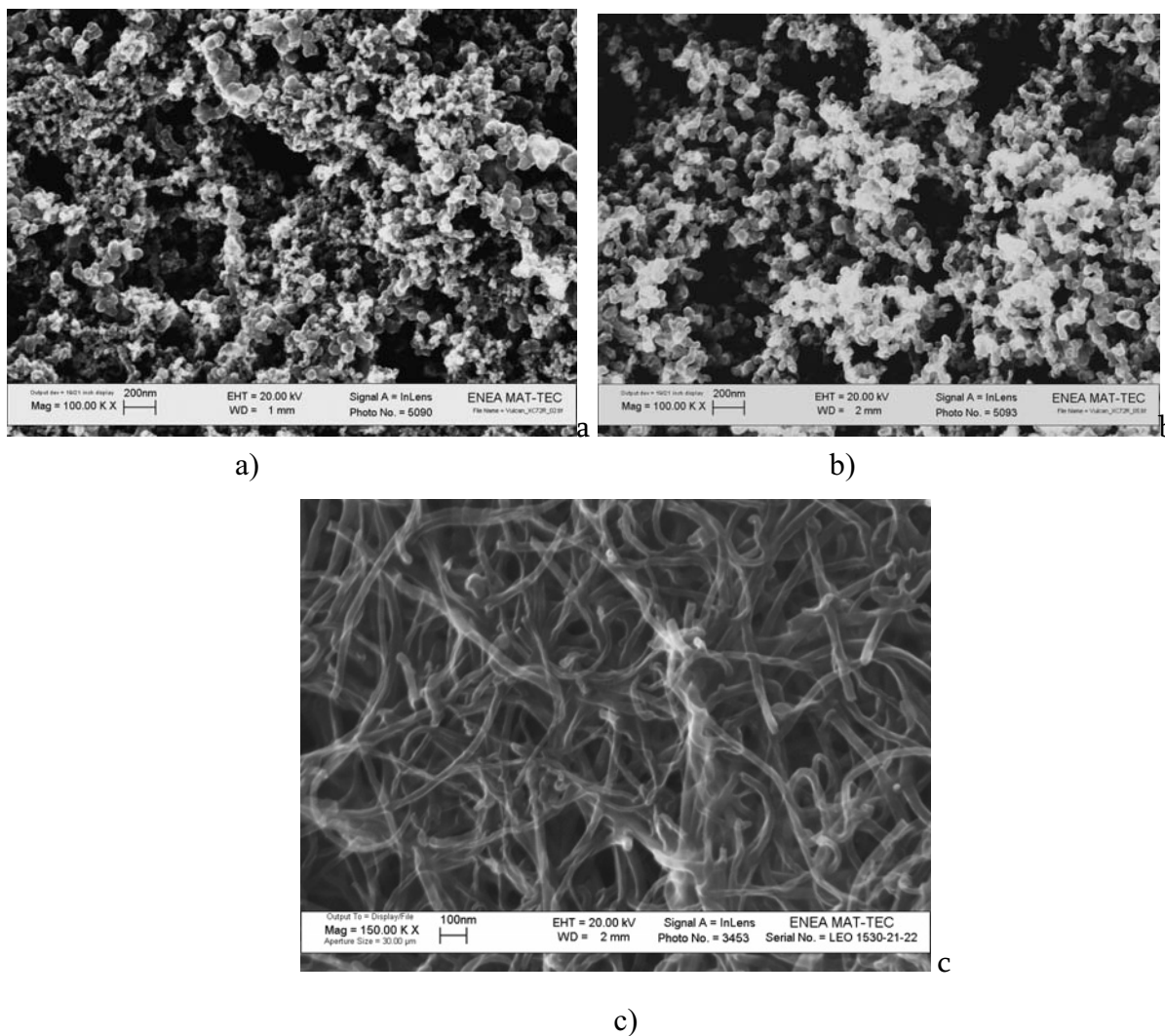


Fig. 8. – Carbon substrates: a) Vulcan XC-72; b) Super P; c) MWCNTs.

Figures 9a and 9b show GDL electrodes prepared by spraying over *carbon paper* the two above mentioned carbon powders and CNTs (Fig. 9c). In order to decide which GDL electrode is the most suitable for the use in GDE, all GDLs have been morphologically analysed.

From SEM images it is clear that in the case of Vulcan XC-72 the spraying procedure to obtain GDLs led to not unusable electrodes. In fact, the *carbon paper* surface is not homogeneously covered – *carbon paper* fibres are evident – probably due to poly-dispersion of carbon particles' dimensions.

GDL from Super P carbon powder is instead superficially homogeneous, even though some cracks are visible due to solvent evaporation upon thermal treatments.

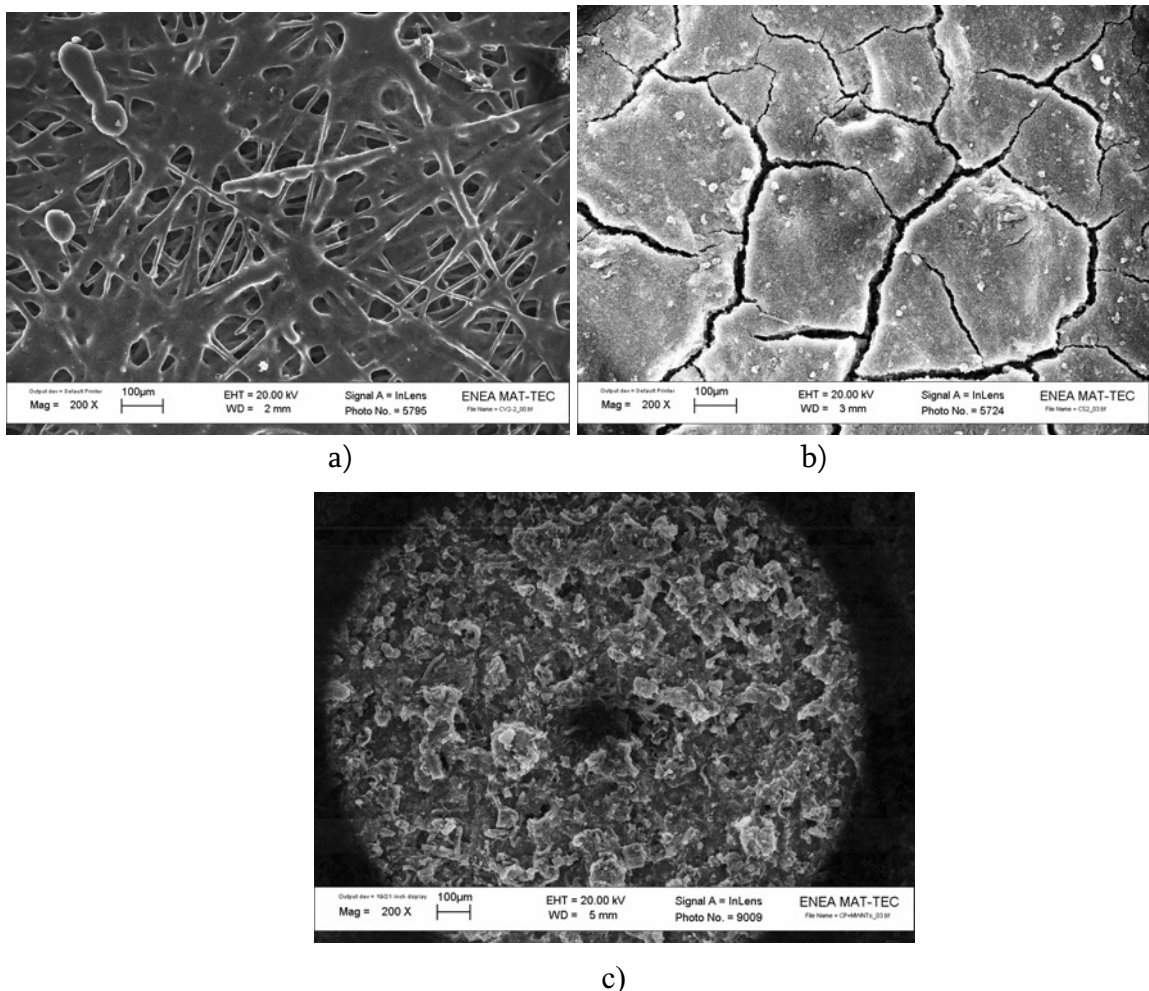


Fig. 9. - SEM images resulting from spraying depositions: a) Vulcan XC-72; b) SuperP ; c) MWCNTs over carbon paper

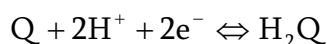
### *Pt electrodeposition over GDLs and their characterization*

Before deposition, electrodes have been cycled between oxidative and reductive potentials in order to increase the hydrophilicity of the carbon surface, for the reasons explained in the following paragraphs.

During electro-deposition, the thickness of catalytic layer is controlled by the electrolyte penetration depth into the un-catalyzed carbon electrode, this being depending on the hydrophilic character of the electrode carbon. In the case of an excessive hydrophilicity, the electrolyte penetrates too deeply and the resulting catalytic layer is thicker than desired. Conversely, a highly hydrophobic carbon deposit leads to thin catalytic layer possibly affected by dendritic formation. Thus, the surface properties of carbon support must be optimized in order to obtain particles and catalytic layers of the desired dimensions and thickness.

The Super P and CNTs substrates have been treated with 50 voltammetric cycles (CV) in the voltage range  $-0.3 \div 1.2$  V vs. SCE in a  $\text{H}_2\text{SO}_4$  1 M +  $\text{CH}_3\text{OH}$  0.1 M solution. This is the treatment leading to the formation of hydrophilic groups favouring the electrolyte permeability.

Then a CV of a bare GDL has been recorded in  $\text{H}_2\text{SO}_4$  1 M after  $\text{N}_2$  purging to eliminate oxygen (Fig. 10). It is visible the absence of current signals due electrodic reactions in the whole voltage range except around 0.3 - 0.5 V vs. SCE where a reversible peak is ascribed to the redox couple quinone/hydroquinone ( $E^\circ=699$  mV vs. NHE at  $\text{pH}=0$  and  $T=25$  °C) according to the equilibrium:



Such a couple is easily found on various types of carbon. Anyway, due to its low intensity, this redox feature is negligible in presence of deposited Pt.

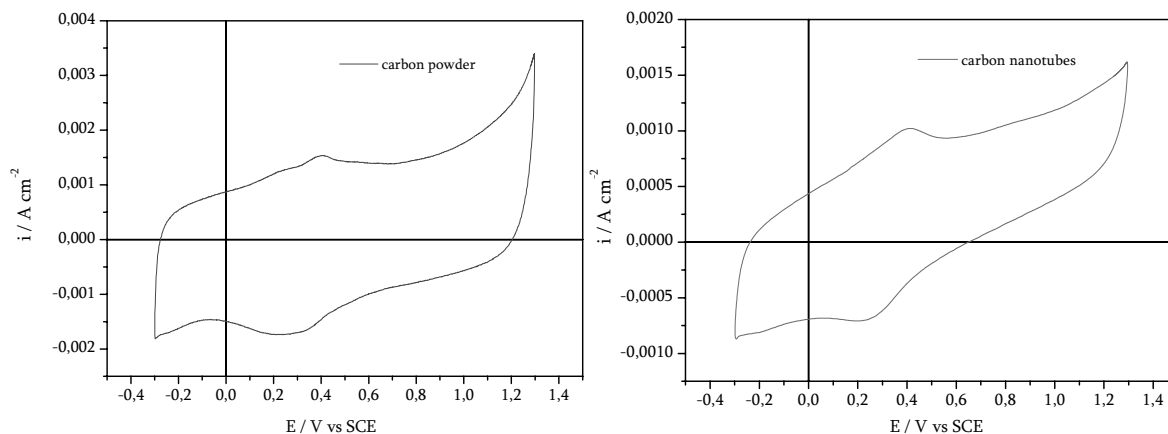


Fig. 10. – *Super P and CNTs' CVs after treatment in  $\text{CH}_3\text{OH}$*

## 4. SINGLE FUEL CELL of 5 cm<sup>2</sup>

### 4.1 ELECTRODES PREPARATION

Electrocatalyst deposition has been conducted over an un-catalyzed GDL. Ten different electro-depositions have been done changing the electric charge in order to obtain nanostructured particles. The parameters of each deposition are:

- “Ged 0”: GED  $Q_{ED}=97.7 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over Super P GDL
- “Ged I”: GED  $Q_{ED}=977.1 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over Super P GDL
- “Ged II”: GED  $Q_{ED}=977.1 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over Super P GDL
- “Ged III”: GED  $Q_{ED}=977.1 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over Super P GDL
- “Ged B”: GED  $Q_{ED}=977.1 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 0.1M over Super P GDL
- “Ged C”: GED  $Q_{ED}=1068.7 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 0.1M over Super P GDL
- “Ged D”: GED  $Q_{ED}=1206.1 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 0.1M over Super P GDL
- “Ped A”: PED  $Q_{ED}= 899.1 \text{ mCcm}^{-2}$ , 150s  $t_{on}=0.4$   $t_{off}=0.5$  in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 0.1M over Super P GDL
- “CNTs 32”: GED  $Q_{ED}= 244.3 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over MWNTs GDL
- “CNTs 96”: GED  $Q_{ED}= 732.8 \text{ mCcm}^{-2}$ , 150s in AECP 5mM+H<sub>2</sub>SO<sub>4</sub> 1M over MWNTs GDL

The completion of electrocatalyst deposition has been confirmed by a CV in H<sub>2</sub>SO<sub>4</sub> revealing peaks associated to Pt and PtOx reactions (Fig.11).

The morphological analysis (Fig.12) evidences that a uniform deposition with nearly mono-dispersed particles is possible to obtain.

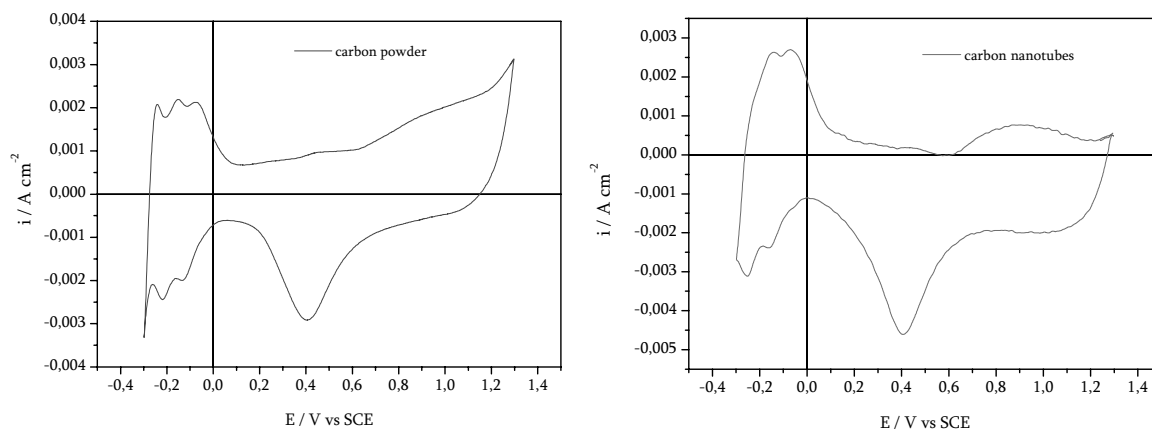


Fig. 11. – *Super P and CNTs' CVs after Pt electrodeposition*

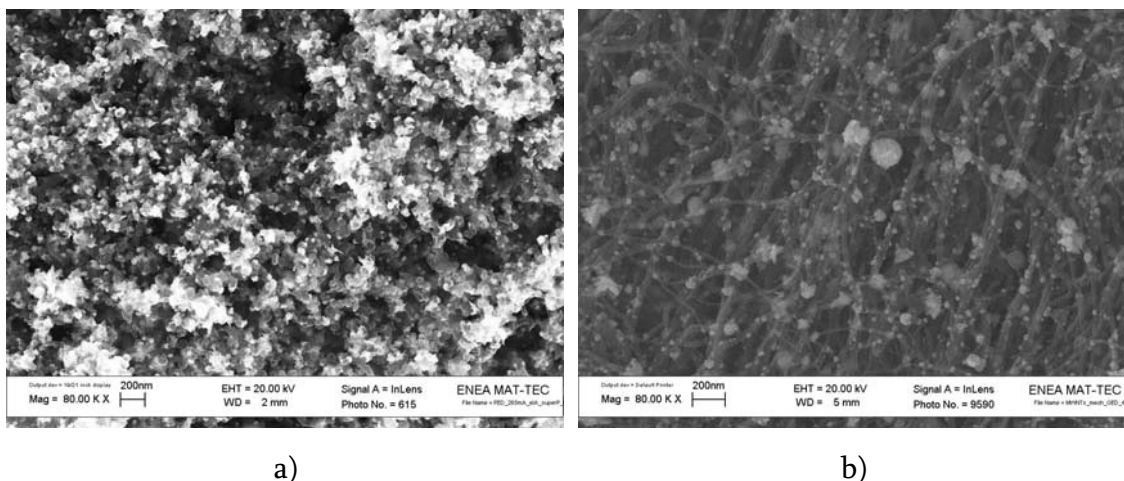


Fig. 12. –SEM images resulting from electro-depositions over a) Super P and b) CNTs

Parameters extracted from electrochemical and chemical characterizations are resumed in the following table:

Sample	Ged 0	Ged I	Ged II	Ged III	Ged B	Ged C	Ged D	Ped A	CNTs32	CNTs96
$L_{Pt}$ ( $\mu\text{g}/\text{cm}^2$ )	11,9	47,6	49,7	50,2	57,7	18,6	18,0	8,34	35,5	67,8
ERS ( $\text{cm}^2$ )	138,9	332,5	467,3	607,5	529,9	100,2	39,2	176,8	416,4	641,5
EAS( $\text{m}^2\text{g}^{-1}$ )	1167,4	698,4	940,3	1210,2	918,4	538,8	217,7	2120,6	1173,0	946,1

#### 4.2 SINGLE FUEL CELLS FABRICATION AND PREPARATION

Usually, PEFCs electrodes are made by three adjacent carbon layers (carbon paper, diffusive layer, catalytic layer). In this work, instead, the electrocatalyst has been more easily deposited directly over the diffusive layer, forming a few microns penetrating catalytic layer.

Figure 13 shows a MEA cross section made by a EFE3 cathode and an electrodeposited anode. During the sample preparation for SEM analysis the carbon paper support detached from the rest of the anode. EDX analysis shows Pt localization in the catalytic layer of EFE3 cathode and electrodeposited anode (Fig. 13 c).

The SEM image clearly shows the 5 different layers and their thickness. The Nafion™ 112 has a thickness around 30  $\mu\text{m}$  (dark layer in the middle). Then, on the cathodic side a more compact catalytic layer and a diffusive layer with PTFE and carbon agglomerates are evident. It is worth noticing the different thickness of the two electrodes. The EFE cathode has been prepared by spraying over the GDL a alcohol based ink containing a Pt/C 30 %<sub>w</sub> powder and Nafion™, as a catalytic layer. While the anode has been prepared *via* Pt electro-



deposition directly over the GDL and then covering with Nafion™, as already mentioned above. Thus the anode results much thinner.

#### *Electrochemical characterization*

Every electrochemical measurement has been carried out in a test facility FUEL CELL LOAD UNIT series 890 (Scribner Associates, Inc).

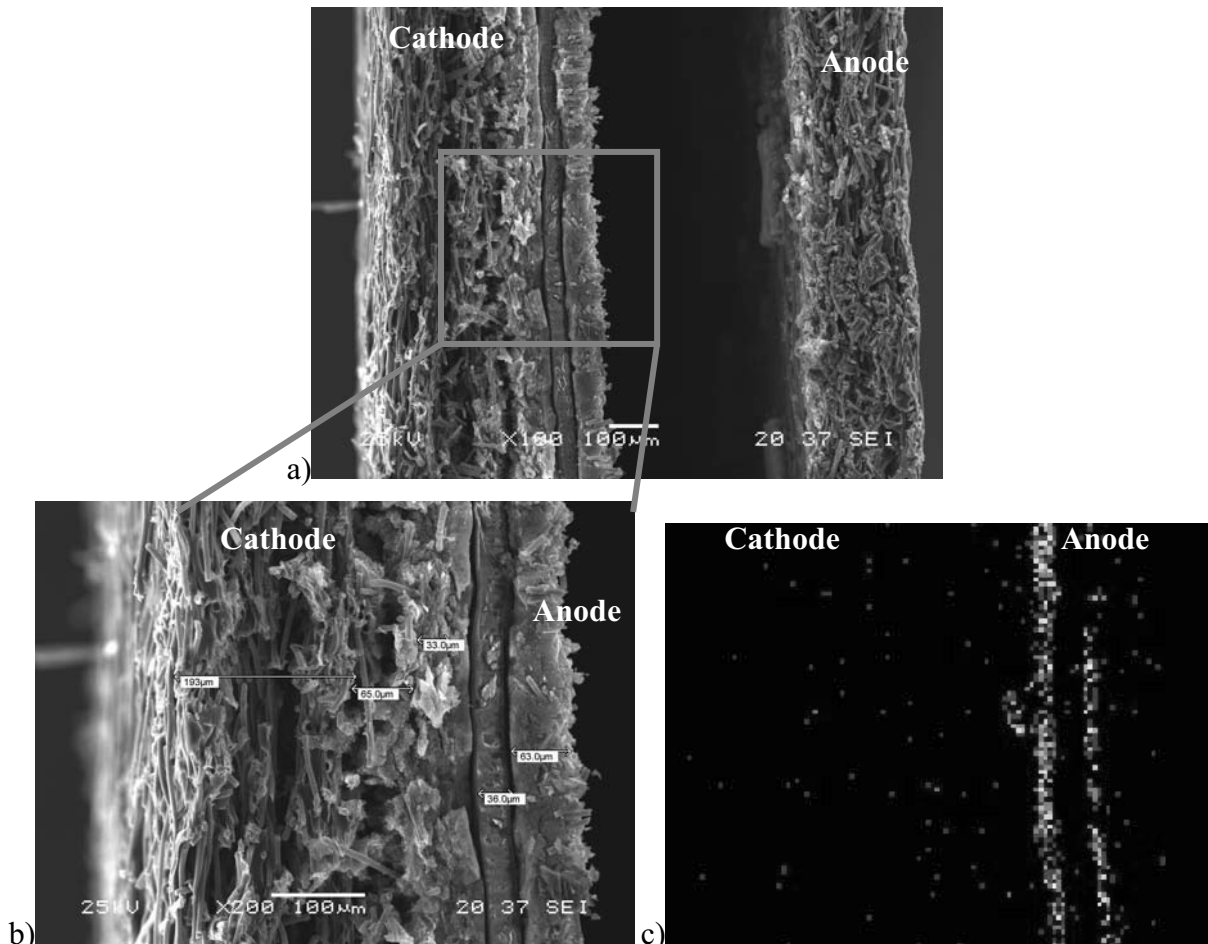


Fig. 13. – a) and b): SEM cross-section images of MEA; c) EDX analysis evidencing the Pt deposits.

Measurements have been conducted at equilibrium potential applying a sinusoidal tension of 10 mV amplitude in the frequency range 15-0.1 kHz. Electrode flux was 200 mL min<sup>-1</sup> at maximum humidification conditions. The high frequency real part of impedance represents the cell resistance  $R_{\Omega}$ , which is the sum of different contributions (membrane, electrodes, aluminium and graphite plates). Spectra consist mainly of a half-circle, described, according to Boukamp<sup>23</sup>, by an equivalent circuit  $R_{\Omega}(R_pC)$ . Here,  $R_{\Omega}$  is the sum of electrodes and electrolyte resistance,  $R_p$  the polarization resistance coming from the sum of ohmic,

charge transfer and diffusion contributions and  $C$  is the pseudo-capacity of the electrode/electrolyte interface (accounting for the electrochemical double layer too).

The first tested cells have been those made by Ged I, Ged II, and Ged III samples. The primary problem to face has been how much Nafion™ had to be deposited over the electrodes. Previous studies<sup>2</sup> reported that the optimum amount of Nafion™ to mix together with the catalytic ink ranges from 10% to 15% of the Pt/C ratio. In this case these percentages could not be applied due to the very low Pt load after electrodeposition.

Thus, the three cells have been realized with the same conditions for anodic electrodepositions but with different amounts of Nafion™: in Ged I higher than 15% (120 mg Nafion™ 5%), in Ged II without Nafion™ and in Ged III with Nafion™ in the range 10%-15% (0.1 mg Nafion™ 5%).

Figure 14 shows the Nyquist plot obtained by measuring the cell impedance at OCV, 25°C and optimal humidification conditions.

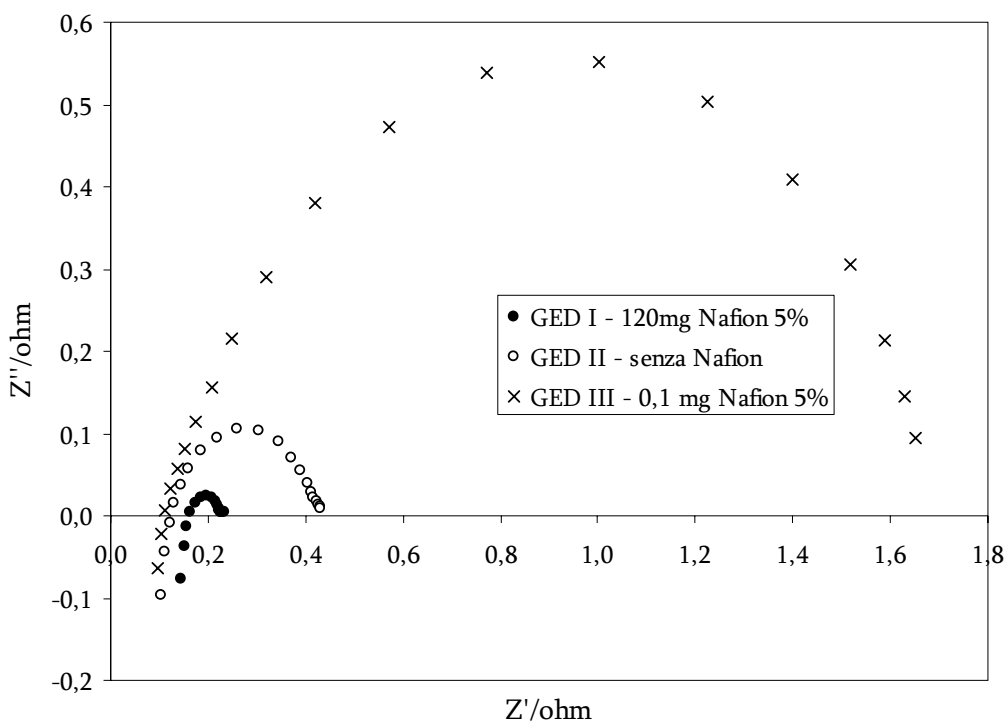


Fig.14.- Nyquist plot at OCV, 15-0.1 kHz for electrodeposited carbon powder electrodes.

In Table I the total resistance values are reported. Data in last column represent the ratio between the measured cell resistance ( $R_{cl}$ ) and a standard cell resistance with Nafion™ 112 ( $R_{Nafion™}$ , around 0.18-0.20  $\Omega\text{cm}^2$ ).

Table I. Results of impedance measurements on cells with different amounts of Nafion™

Sample	$Z'/\Omega$	$R_{LF}/\Omega$	$R_{el}/\Omega \text{ cm}^2$	Nafion 112
Ged I (120 mg Nafion™5%)	0.16	0.233	0.82	4.1
Ged II without Nafion™	0.12	0.432	0.61	3.0
Ged III (0.1 mg Nafion™5%)	0.11	1.653	0.55	2.8

Ohmic resistance is calculated by the intercept of the half-circle with abscissa axis in the high frequency region. The lowest ohmic resistance is found for the cell with an intermediate Nafion™ amount, while the higher resistance is found for the higher amount of Nafion™. Polarization resistance has a different trend and is found to be the lowest for the highest amount of Nafion™ and highest when the membrane amount is low. Polarization resistance decreases as electrochemical area increases. The obtained result is explained by considering that Pt particles are dispersed inside the diffusive layer and only partially at the membrane/electrode interface. Thus, a high amount of Nafion contributes increasing the most inner catalytic sites reducing the polarization resistance, but increasing the resistance at the membrane/electrode interface.

In other words, when a high amount of Nafion™ is present, although it is more difficult to reach the reaction sites, this effect is balanced by the higher amount of active Pt. This explanation is consistent with literature findings<sup>24</sup> reporting that the amount of Nafion™ to add is inversely proportional to the Pt load. The ohmic resistances of 15% and 0% Nafion™ electrodes are similar because they are due to the superficial Pt in contact to the membrane. Nevertheless the presence of too little Nafion™ does not increase very much the active area and obstacles the gas diffusion to active sites at the interface.

The second aspect arisen from these first test measurements has been the too low quantity of deposited Pt, unable to make the cell run. Hence, a deposition with the same applied charge has been conducted but in a more diluted H<sub>2</sub>SO<sub>4</sub> solution to increase the process efficiency. Figure 15 shows Nyquist plots for cells with anode Ged III and Ged B and in table II results are reported.

It is evident that the impedance of the electrode obtained from a more diluted acid solution is lower than Ged III's. In fact chemical analysis revealed a higher Pt load, hence a lower polarization resistance.

Table II. Results of impedance measurements on cells with electrodeposited Pt in 1 M and 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions

Sample	Z'/Ω	R <sub>LF</sub> /Ω	R <sub>el</sub> /Ω cm <sup>2</sup>	Nafion 112
Ged III H <sub>2</sub> SO <sub>4</sub> 1M (~0.1 mg Nafion 5%)	0.11	1.653	0.55	2.8
Ged B H <sub>2</sub> SO <sub>4</sub> 0.1M(~0.1 mg Nafion 5%)	0.09	0.411	0.43	2.1

In the case of electrode CNTs96 preliminary chemical analyses reported a high Pt load, encouraging to use this electrode for a cell. The higher amount of catalyst electrodeposited along with the electroactive and high kinetics properties of this material allowed to achieve higher current than previous cases (Table III and Fig.16). This results is noteworthy if compared to the commercial PEFCs working with 10 times higher Pt loads.

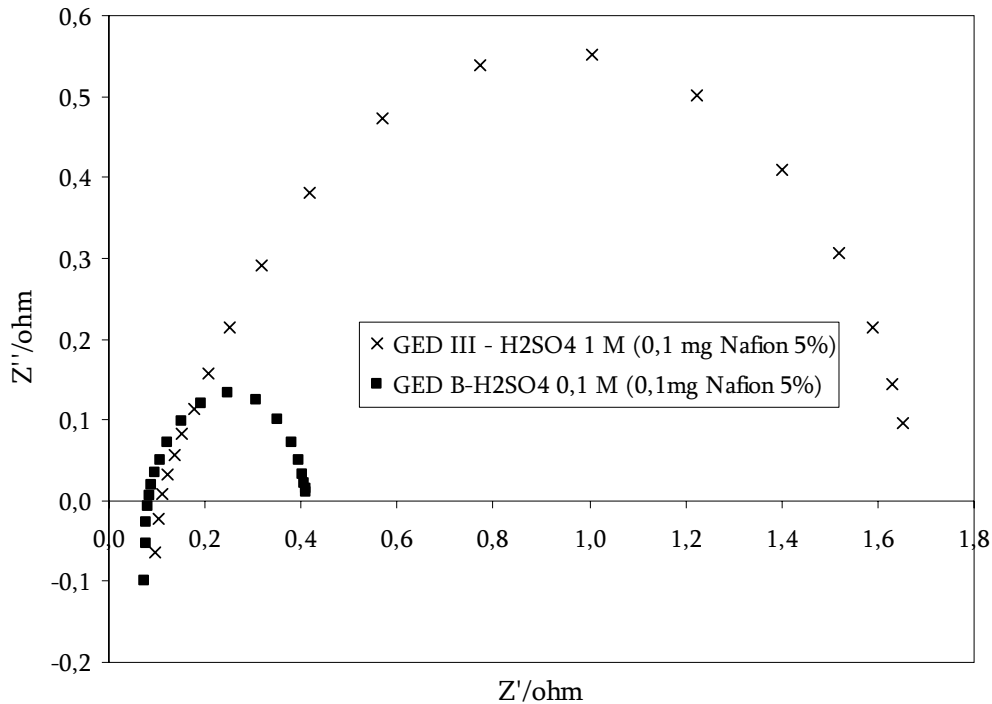


Fig.15.- Nyquist plot at OCV, 15-0.1 kHz for electrodeposited carbon powder electrodes.

The results here obtained are referred to a preliminary research step. Future plans will be focused on the possibility of depositing higher Pt loads by controlling the electrodeposition times and on the study of the correlation between Pt load and optimum Nafion amount. Electrodes realized with nanomaterials such as CNTs will be the main object of our investigations.

E/V	0.95( $E_{ocv}$ )	0.90	0.85	0.80	0.75	0.70
i/ mA	0.02	4.43	18.04	40.8	78.1	112.2

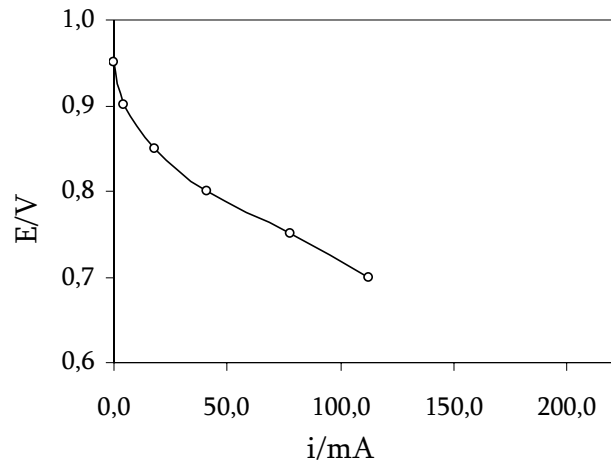


Table III and Fig.16.- Polarization curve obtained from CNTs96 anode cell.

#### 4.3 CONCLUSIONS

This work has been focused on the fabrication of a prototypical polymer electrolyte fuel cell at the ENEA-Casaccia R.C., putting in evidence technological problems and promising results.

The MEGA technology has shown to be effective and reliable, offering a number of advantages:

- operative quickness both in the preparation of assemblies and their cell setting-up;
- possibility of storing the assemblies as ready-to-reuse devices for indefinite time;
- qualitative direct observation and control on *ante-operam* characterization in single-cell systems (critical during experimental phase and especially during production);
- polymeric membrane saving;
- the silicone-based material used for gaskets is chemically and morphologically inert, with mechanical properties indifferent to repeated use.

The experiments conducted show the validity of the system under different point of views.

The electrochemical impedance spectroscopy (EIS) allowed for useful comparisons between different electrodes *via* the interpretation of the associated equivalent circuit models. These measurements demonstrated, as a drawback, that the electrode/electrolyte interface resistance is 2 to 4 times higher than for a standard cell.

EIS experiments also evidenced the positive influence exerted by the addition of Nafion on the cell resistance, while regarding the Pt load deposited over the diffusive layer, a compromise value has been determined taking into account points like Pt saving and increase of cell resistance.

The cell prepared from CNTs based electrode has resulted in the system with the best electrochemical properties thanks to the higher number of Pt catalytic sites, being the total Pt load the same as the other systems. In addition, a higher electroactivity and faster electron transfer kinetics allowed to achieve higher current densities.

Results obtained in this preliminary phase are still to be optimized together with the investigation on procedures allowing for depositing higher amounts of active Pt and optimal Nafion quantities.

## 5. SINGLE FUEL CELL of 2 cm<sup>2</sup>:

### 5.1 ELECTRODES PREPARATION

Seven different electro-depositions have been done changing the electric charge in order to obtain nanostructured particles. In the following table the parameters of each deposition are described.

Table I: Platinum loading ( $L_{Pt}$ ), electro-deposition charge density ( $Q_{dep}$ ) and duty cycle PED parameter of GED, PED and SD platinum electro-catalysts.

Samples	$L_{Pt} / \text{mg}_{Pt} \text{ cm}^{-2}$	$Q_{dep} / \text{C cm}^{-2}$	Duty cycle %
SD 01	0.82	-	-
GED 01	0.66	36	-
GED 03	0.06	8	-
PED 05	1.15	76	66
PED 06	1.08	36	33
PED 07	0.30	8	33
PED 08	1.11	76	33

### 5.2 SINGLE FUEL CELLS FABRICATION AND PREPARATION

The MEAs have been tested in single fuel cell station (Scribner) with a geometric area of 2 cm<sup>2</sup> (2.1cm x 0.9cm) and fed with humidified H<sub>2</sub>/O<sub>2</sub> at constant flow rates (50 cm<sup>3</sup> min<sup>-1</sup> with a  $T_{\text{humidi.}} = 80^{\circ}\text{C}$  and 100 cm<sup>3</sup> min<sup>-1</sup> with a  $T_{\text{humidif.}} = 65^{\circ}\text{C}$ , respectively), at the same pressure both for anode and cathode (1.2 bar abs). The cell temperature has been maintained at 70°C.

In Fig.17 the best polarization curves of the MEAs obtained in the experimental conditions previously described are displayed.

The cathode used in these MEAs is prepared by different deposition method: SD 01 by spraying deposition, GED 01 ( $Q_{dep} = 36 \text{ C cm}^{-2}$ ) by single pulse galvanostatic electro-deposition and PED 07 ( $Q_{dep} = 8 \text{ C cm}^{-2}$ ) by multiple pulse galvanostatic electro-deposition.

The membrane electrode assembly has been prepared using a Nafion<sup>TM</sup> 115 membrane. It is worth to note that even if the MEAs performances are comparable, their Pt loadings are very different: SD 01 presents the highest  $L_{Pt}$  (0.84 mgPt cm<sup>-2</sup>) with respect to GED 01 (0.66 mgPt cm<sup>-2</sup>) and PED 07 (0.29 mgPt cm<sup>-2</sup>).

These results are confirmed taking into account the maximum specific power density values ( $P_{\max}$ ,  $\text{kW m}^{-2} \text{g}_{\text{Pt}}$ ), as shown in Fig.18.

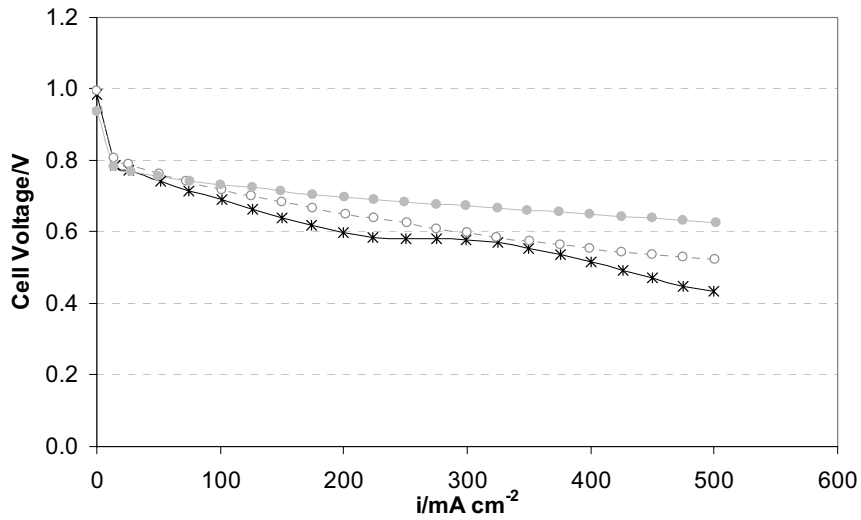


Fig.17. - Polarization curves of MEAs prepared by multiple pulse galvanostatic electro-deposition ( $-\ast-$  PED 07), single pulse galvanostatic electro-deposition ( $--\circ--$  GED 01) and spraying deposition ( $-\bullet-$  SD 01).

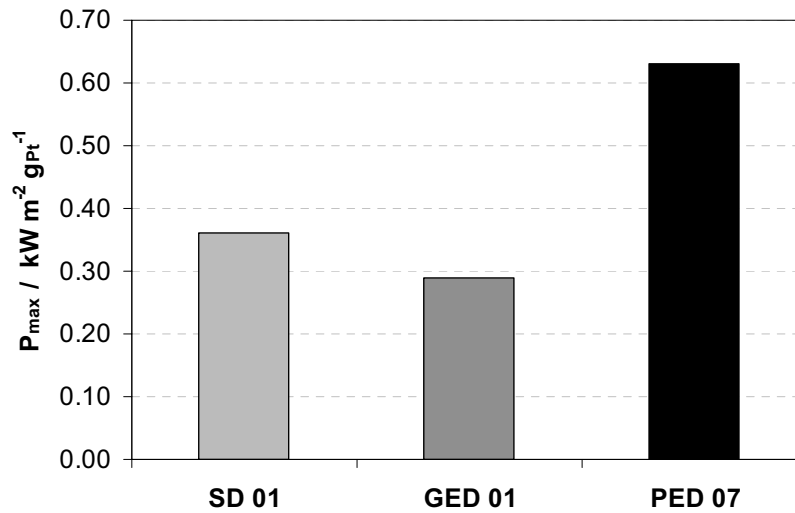


Fig. 18. - Maximum specific power density values for SD 01, GED 01 and PED 07.

It is clear that the PED technique gives a good nanostructured Pt particles localization, achieving higher catalyst utilization. The smaller  $P_{\max}$  value of GED 01 is probably due to the morphology of its Pt deposits: the catalyst particles are almost ten times bigger than those of PED 07 (Fig. 19 a and b) and the nanostructured surface presents longitudinal ridges for GED 01 while lamellar triangular shapes for PED 07 (Fig. 19 c and d).



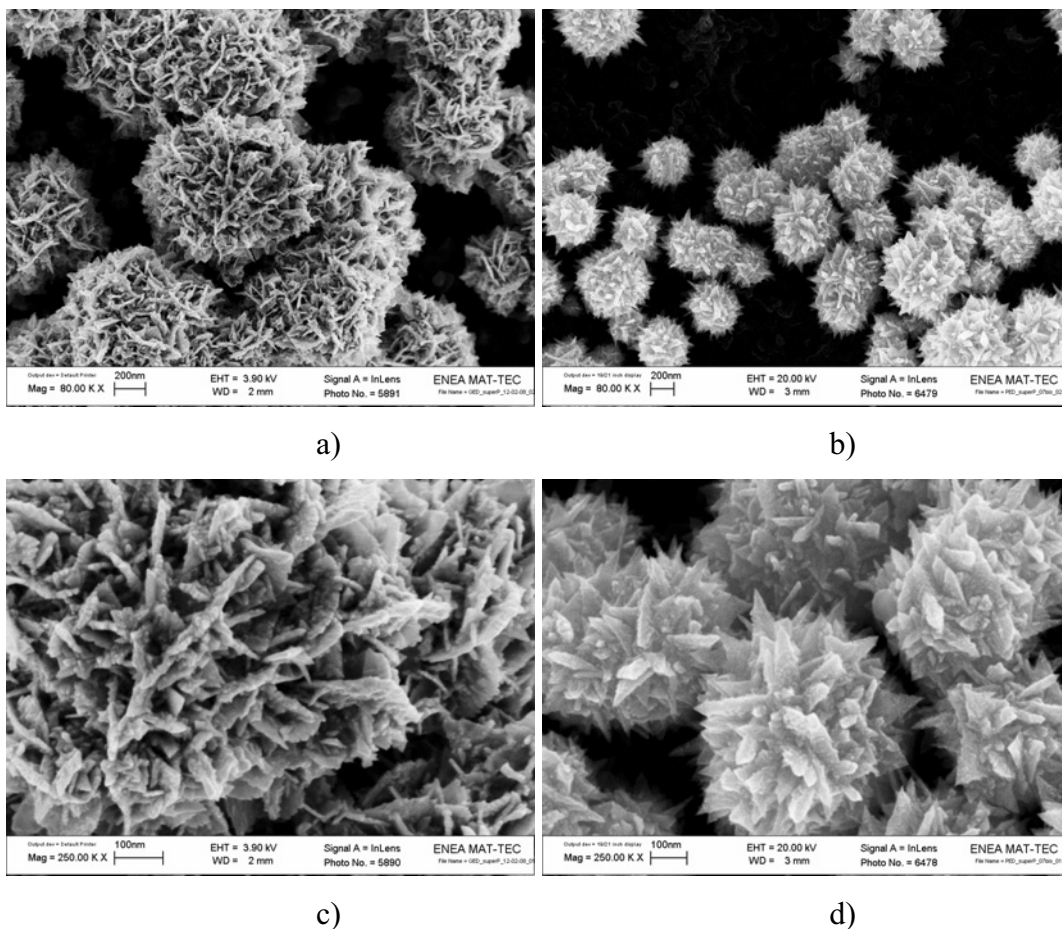


Fig. 19. - FEG-SEM images at 80KX for a) GED 01 and b) PED 07; at 250KX for c) GED 01 and d) PED 07.

Based on these results our attention has been turned to the effect of PED parameters on the electrocatalyst behaviour.

Fig.20 shows the cell tests results of three MEAs prepared by PED at 33% duty cycle and at different charge densities values ( $Q_{dep}=8 \text{ C cm}^{-2}$ ,  $Q_{dep}=36 \text{ C cm}^{-2}$ ,  $Q_{dep}=76 \text{ C cm}^{-2}$ ). Increasing charge density, MEAs performances tend to decrease, especially for the PED 08 ( $L_{Pt}= 1.11 \text{ mg cm}^{-2}$ ) deposited with the highest  $Q_{dep}$ .

Note that PED 07 and PED 06 show almost the same performance but the former has a  $L_{Pt}$  three times lower than the latter. Further, the Pt loading is similar in PED 06 and PED 08 but the performance obtained are very different.

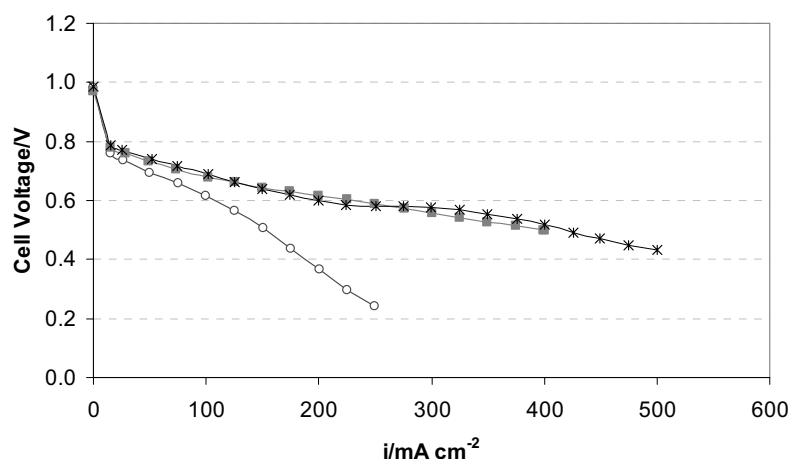


Fig.20. - Polarization curves of MEAs prepared by multiple pulse galvanostatic electro-deposition at 33% duty cycle (—\*— PED 07,  $Q_{dep}=8\ C\ cm^{-2}$ ), (—■— PED 06,  $Q_{dep}=36\ C\ cm^{-2}$ ) and (—○— PED 08,  $Q_{dep}=76\ C\ cm^{-2}$ ).

These behaviours can be associated with the influence of the morphology on Pt particles catalyst activity. Charge density exerts an important effect on properties such as size, shape and distribution of the deposit. When a high charge density is used for deposition, particles aggregate, resulting in large Pt islands not homogeneously spread on diffusive layer surface (Fig.21 a, b and c). Moreover, at increasing charge density the particle size of the deposit become bigger losing their nanostructured surface (Fig.21 d, e and f).

An interesting evidence of PED technique carried out in acidic solution is represented by the non-linear trend (Fig.22) of Pt loading vs applied electro-deposition charge density, as commonly expected.

$L_{Pt}$  rises drastically at the beginning, together with the deposition charge density and then tends to stabilize around a constant value. This is due to the reduction of Pt deposition efficiency. At the beginning only Pt deposition reaction occurs on the substrate, because  $H^+$  discharge overpotential is very high on carbon materials. As the metal loading increases on the surface, this overpotential noticeably decreases and the applied current is shared with the  $H^+$  reduction, lowering Pt deposition efficiency.

In conclusion, the electric field is responsible of Pt cluster aggregation and of nanoparticles migration on the exposed Pt surface, losing the characteristic nanostructured morphology of the deposits, strictly related to their electro-catalytic activity. This electric field effect is as much marked as the deposition time is long.

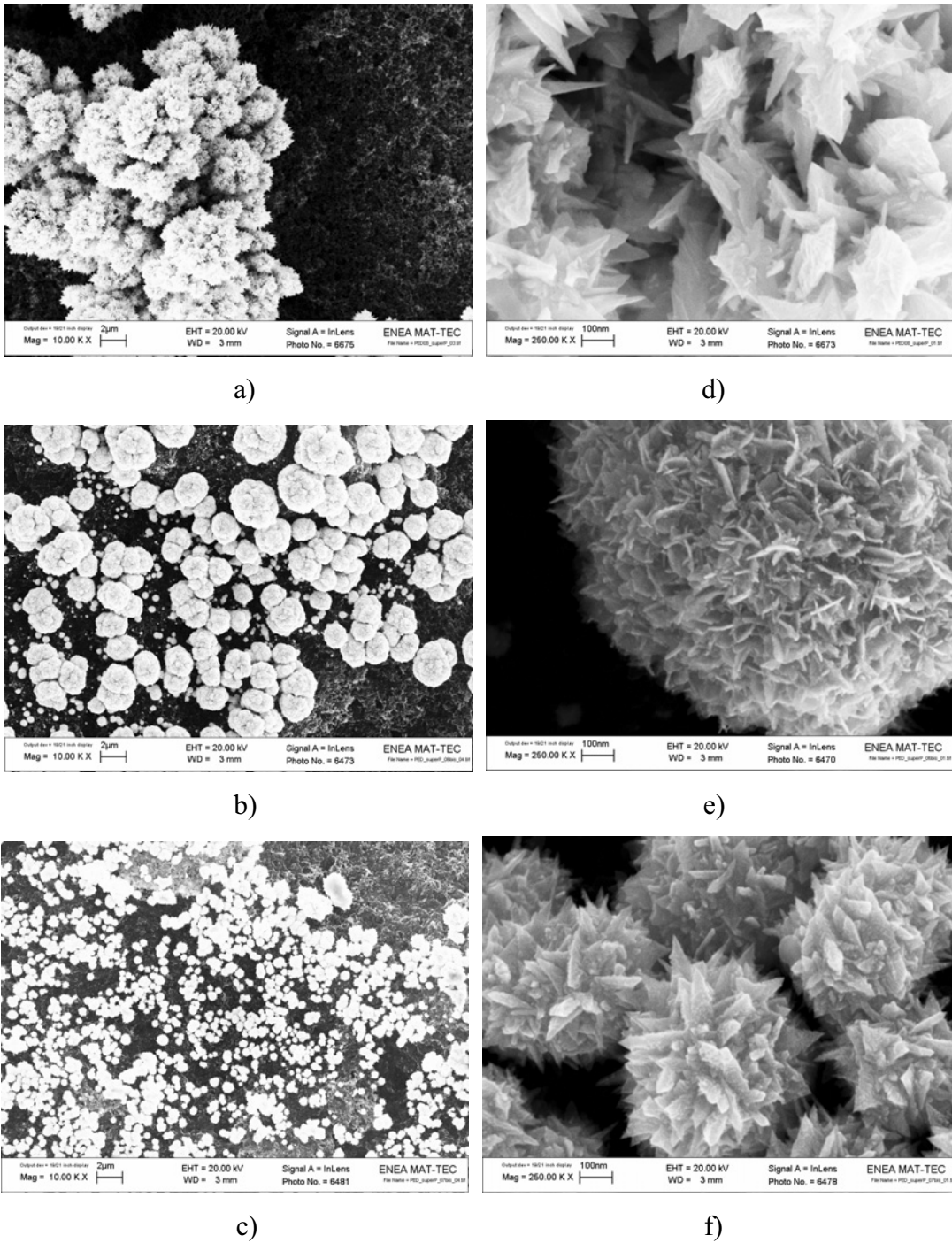


Fig.21. - FEG-SEM images at 10KX for a) PED 08, b) PED 06 and c) PED 07; at 250 KX for d) PED 08, e) PED 06 and f) PED 07.

In order to study thoroughly the influence of PED parameters on the performances of the deposits, two different duty cycles (33% and 66%) have been chosen. PED 08 at 33% and PED 05 at 66% duty cycle with the same deposition charge density of  $76 \text{ C cm}^{-2}$  have been

thus prepared and the corresponding polarization curves have been presented in Fig.23. Although the Pt loading of PED 05 and PED 08 is nearly the same (around  $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ), remarkable differences in cell tests results have been shown, probably due to the Pt particles activity and morphology.

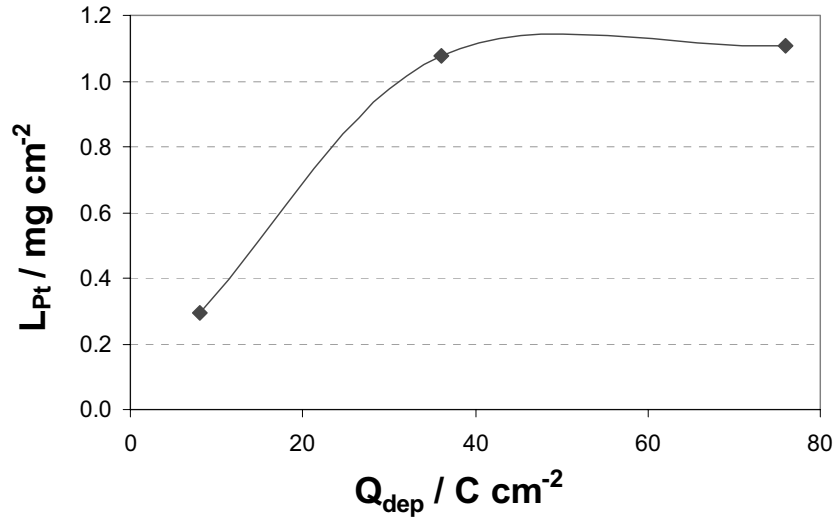


Fig.22. - Pt loading ( $L_{\text{Pt}}$ ) vs applied charge density ( $Q_{\text{dep}}$ ) in a multiple pulse electro-deposition.

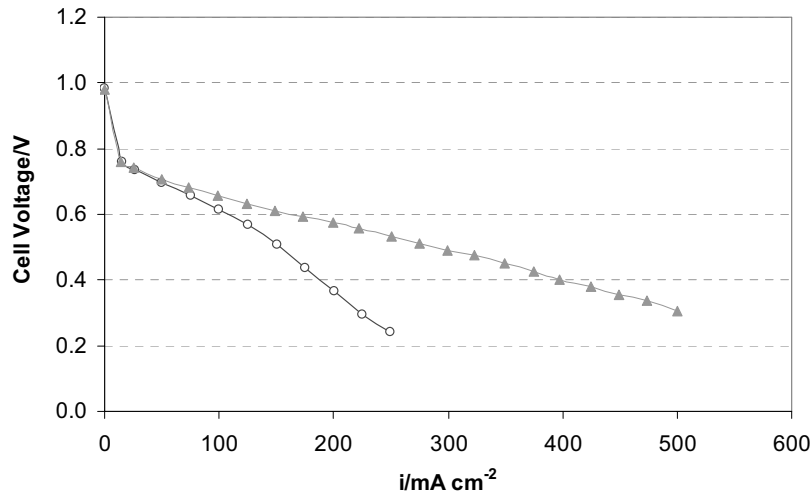


Fig.23. - Polarization curves of MEAs prepared by multiple pulse galvanostatic electro-deposition at 33% duty cycle ( $\text{---}\circ\text{---}$  PED 08,  $Q_{\text{dep}}=76 \text{ C cm}^{-2}$ ) and at 66% duty cycle ( $\text{---}\blacktriangle\text{---}$  PED 05,  $Q_{\text{dep}}=76 \text{ C cm}^{-2}$ ).

In fact, comparing SEM images at 250 KX, Pt particles surface of PED 08 deposit (Fig.21d) appears smoother than that of PED 05 (Fig.24a) and each particles is characterized by a thin and peaked structure, not active in the catalytic reaction. Despite the different PED parameters varied during deposition, the Pt particles distribution observed for both samples (Fig.21a PED 08 and Fig.24b PED 05) is characterized by islands formation exclusively depending on the applied charge density value ( $Q_{dep}=76 \text{ C cm}^{-2}$ ).

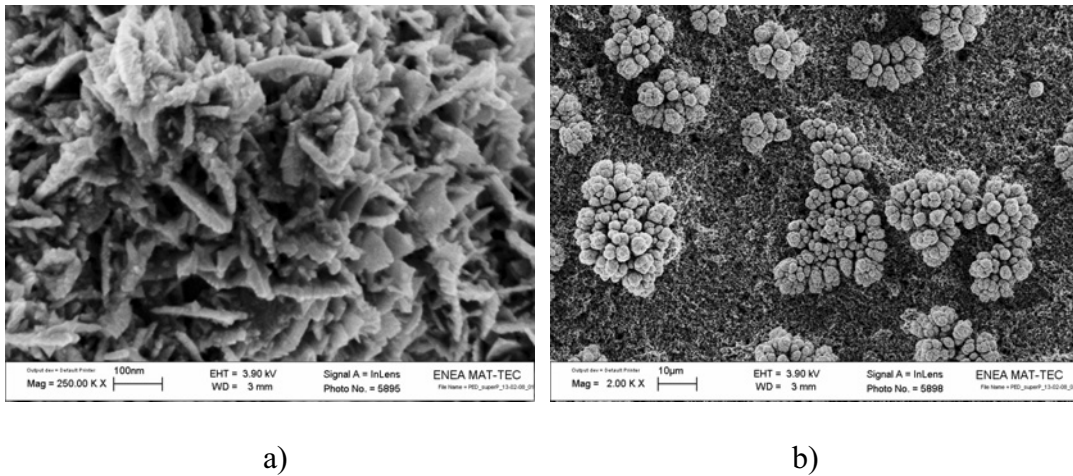


Fig.24. - FEG-SEM images for PED 05 a) at 250KX and b) at 2KX.

Finally, since the best result has been obtained for PED deposited with  $8 \text{ C cm}^{-2}$  another GDE has been prepared by GED at the same charge density. The spectrophotometric analysis of sample GED 03 gave a Pt loading of  $0.06 \text{ mg}_{Pt} \text{ cm}^{-2}$  but no polarization curve has been recorded for GED 03 MEA due to the extremely low  $L_{Pt}$ .

It is very interesting to compare the cell tests results with the electrochemical characterization by CVs (Table 2). In particular, the EAS values are extremely different: nearly ten times higher for SD 01 than those of PED deposits. This evidence is not in agreement with the cell tests, since their performances are quite comparable.

This behaviour could be explained considering the triple interface contact as the active reaction site accessible both to electrons and protons. In CVs this zone is formed by Pt nanoparticles deposited on carbon substrate and by the electrolyte liquid solution, while in cell experiment it is constituted by Pt/C electro-catalyst and by the polymer electrolyte membrane (Nafion™). Hence, in CVs since the electrolyte can easily reach the whole Pt/substrate surface, all the active reaction sites are detected. In the cell tests the active

electrocatalyst particles are only those in direct contact with the solid electrolyte membrane or linked to that by the continuous Nafion™ film.

In conclusion, electro-deposition techniques represent an extremely suitable method to Pt localization in reaction sites, improving catalyst utilization and lowering Pt loading with high PEFC performances.

Table II: Electrochemical active surface (EAS) for PED deposits and SD 01.

<b>Samples</b>	<b>EAS / m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup></b>
SD 01	113.02
PED 05	9.90
PED 06	8.32
PED 07	10.81
PED 08	9.46

### 5.3 CONCLUSIONS

This work aims to investigate an alternative procedure respect to the traditionally used spraying technique to PEFC electrodes manufacturing. By Pt localization on the uppermost GDL surface, it is possible to decrease the thickness of the catalyst layer as well as the Pt loading giving a noteworthy increase of the efficiency in the noble metal usage.

Results indicate that single and multiple galvanostatic electro-depositions are suitable for the fabrication of electrodes characterized by very low Pt loading and high catalyst utilization.

By varying the experimental parameters, such as charge density or duty cycle, it is possible to control deposits morphology and Pt particles distribution. Generally, GED produces a more homogeneous distribution of catalysts onto the surface substrate than PED. An island growth, large Pt clusters and smooth particles show the worst electrochemical and electro-catalytic results. The best structure is identified as the lamellar triangular shape with a fine extended nanostructured surface.

It is necessary to compare the electrochemical CVs results with those of cell tests in order to evaluate the real electro-catalytic performances strictly dependent on Pt localized in the active reaction sites.

## 6. REFERENCES

1. A.J. Appleby, F.R. Foulkes, in *Fuel Cell Handbook*, edited Van Norstand Reinhold, New York, N.Y. (1989)
2. L. Giorgi, A. Pozio, E. Antolini, *J. Power Sources* 77, 136 (1999)
3. E. Passalacqua, L. Lufrano, G. Squadrito, A. Patti, L. Giorgi, *Electrochim. Acta* 46, 799 (2001)
4. K. Petrov, K. Xiao, E. R Gonzalez, S. J. Srinivasan, A. J. Appelby and O. J. Murphy. *Int. J. Hydrogen Energy* 18, 907 (1993)
5. M. Song, S.Y. Cha and W.M. Lee, *J. Power Sources* 94, 78 (2001)
6. E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti and L. Giorgi, *Electrochim. Acta* 43, 3665 (1998)
7. G. Sasikumar, J.W. Ihm and H. Ryu, *J. Power Sources* 132, 11 (2004)
8. K. Makino, K. Furukawa, K. Okajima, M. Sudoh, *J. Power Sources* 166, 30 (2007)
9. G.S. Kumar, M. Raja and S. Parthasarathy, *Electrochim. Acta* 40, 285 (1995)
10. L. Giorgi, E. Antolini, A. Pozio and E. Passalacqua, *Electrochim. Acta* 43, 3675 (1998)
11. F. Lufrano, E. Passalacqua, G. Squadrito, A. Patti and L. Giorgi, *J. Appl. Electrochem.* 29, 445 (1999)
12. R. Ben'ítez, A.M. Chaparro and L. Dazaa, *J. Power Sources* 151, 2 (2005)
13. R. Ben'ítez, J. Soler and L. Dazaa, *J. Power Sources* 151, 108 (2005)
14. S.-J. Shin, J.-K. Lee, H.-Y. Ha, S.-A. Hang, H.-S. Chin, I.-H. Oh, *J. Power Sources* 106 146 (2002)
15. L. Giorgi, L. Piloni, R.Giorgi, E. Serra, M. Alvisi, G. Galtieri, A. Cemmi, C. Paoletti, M. Pasquali; in *Proceedings of the 3<sup>rd</sup> European PEFC Forum*, File N° P124 (2005)
16. E. Slavcheva, I. Radev, G. Topalov, E. Budevski, *Electrochim. Acta* 53, 362 (2007)



17. A. Caillard, C. Coutanceau, P. Brault, J. Mathias, J.-M. Léger J. Power Sources 162, 66 (2006)
18. D. Martel, A. Kuhn, P. J. Kulesza, M. T. Galkowski, M.A.Malik, Electrochim. Acta, 46, 4197 (2001)
19. H. Kim, N.P. Subramanian, B.N. Popov, J. Power Sources 138, 14 (2004)
20. Z.D. Wei, S.H. Chan, L.L. Li, H.F. Cai, Z.T. Xia, C.X. Sun, Electrochim. Acta 50, 2279 (2005)
21. T. Hanaoka, T. Hatsuta, T. Tago, M. Kishida, K. Wakabayashi, Appl. Catal. 190, 291 (2000)
22. “*Nanostructured electrocatalysts for polymer electrolyte fuel cells*”, RT/2008/5/FIM
23. B.A. Boukamp, Solid State Ionics 20, 3 (1986)
24. G. Sasikumar, J.W.Ihm, H. Ryu, Electrochimica Acta 50, 601 (2004)



Edito dall' **ENEA**  
Funzione Centrale Relazioni Esterne  
Unità Comunicazione

Lungotevere Thaon di Revel, 76 - 00196 Roma

*[www.enea.it](http://www.enea.it)*

Stampa: Laboratorio Tecnografico ENEA - CR Frascati

Finito di stampare nel mese di ottobre 2008