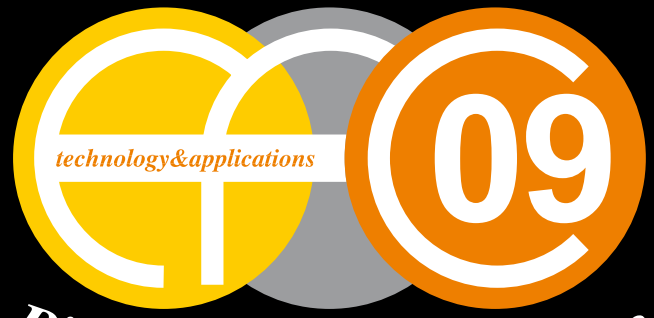

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ELECTRO-DEPOSITED PLATINUM ON ACTIVATED MULTIWALL CARBON NANOTUBES:SINGLE-CELL TESTS, MORPHOLOGICAL AND ELECTROCHEMICAL CHARACTERIZATIONS

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ABSTRACT
This work is focused on the electro-crystallization of Pt nanostructured particles on activated multiwall carbon nanotubes (MWCNTs) containing substrate to produce polymer electrolyte fuel cells gas diffusion electrodes.
An activation procedure to enhance the reactivity of multiwall carbon nanotubes surface toward electro-deposition has been studied and optimized. Electrochemical single-and multi-pulsed galvanostatic deposition has been applied defining the best operational parameters leading to a highly nanostructured electrode morphology. Electrochemical measurements (in half-cell configuration) and polarization curves in 5 cm^2 single-cell station have been carried out together with morphological analysis by means of scanning electron microscopy. Very promising results in term of maximum specific power density values similar or better than those of standard E-TEK electrode, prepared by conventional powder-type chemical technique, have been obtained for deposition of platinum particles on MWCNTs substrate electrodes, despite the extremely low amount of catalyst (up to 3 times lower than that of commercial electrodes).

INTRODUCTION
High surface carbon materials represent the fundamental components of the gas diffusion electrodes (GDE) used in polymer electrolyte fuel cells (PEFCs). It is widely turned out that carbon substrate and electro-catalyst present a mutual strong interaction giving enhanced performances in term of catalytic particles stability and activity. Besides, in PEFCs platinum electro-catalyst nanoparticles are usually deposited on high surface carbon substrates in order to reduce platinum quantity under the condition of keeping high catalytic activity.
At present, the primary carbon supports are represented by carbon powders (e.g. Vulcan XC-72R) but in recent years novel carbon structures have been proposed because of their interesting electronic and electro-active properties, nanometer sizes, high surface area and finally high electron transfer kinetics allowing to achieve high current density values.
Traditionally, platinum electro-catalysts are prepared by impregnation/chemical reduction process. This method requires a high amount of platinum (>0.3 mg cm-2) to achieve good performances because nanoparticles localisation in reaction sites results critical. Conversely the use of an electric field ensures platinum localisation only in reactant sites and the catalyst load can be noticeably reduced [1, 2]. Moreover, the electro-deposition technique offers considerable advantages:
- high purity of deposits
- catalyst uniform distribution on the support
- platinum particles of reduced size
- a easier procedure: lack of reducing agent and surfactants, as well as lack of hydrogen treatments at high temperature.

In the light of the problems above discussed, the aim of this work is to study and to evaluate the possibility of the PEFCs electrodes preparation by means of platinum electro-deposition on activated MWCNTs substrates.Before GDE substrate preparation, MWCNTs (Aldrich) have been subjected to a purification treatment based on boiling 3M nitric acid solution to remove amorphous carbon and catalyst nanoparticles coming from their synthesis process.

EXPERIMENTALS
Before GDE substrate preparation, MWCNTs (Aldrich) have been subjected to a purification treatment based on boiling 3M nitric acid solution to remove amorphous carbon and catalyst nanoparticles coming from their synthesis process.
After purification, carbon nanotubes have been mixed with a suitable amount of PTFE and sprayed onto a carbon paper substrate giving the Gas Diffusion Layer (GDL). MWCNTscontaining GDL has been again activated following the chemical method above described, improving their wettability and reactivity. On the uppermost surface of this activated substrate, platinum has been deposited by electrochemical single (GED) and multiple pulse (PED) galvanostatic technique.
The platinum loading (LPt) has been determined by UV-

VIS spectrophotometric analysis and electrochemical properties have been studied by Electrochemical impedance spectroscopy (EIS) and polarization curves in half-cell device.
The investigated materials have been then applied as gas diffusion electrodes (GDEs) and assembled with Nafion™ 112 membrane in the membrane-electrode-assemblies (MEAs).
These systems have been tested in single fuel cell station (Scribner) with a geometric area of 5 cm2 and fed with humidified H_2/O_2 at constant flow rates. The cell temperature has been maintained at 50°C. Nanoparticles morphology has been investigated by means of field emission gun scanning electron microscopy (FEG-SEM, LEO mod.1530).

DISCUSSION AND CONCLUSIONS

In Fig.1 and 2 micrographs at different magnifications (80KX and 500KX) of GED and PED samples have been reported. Both electro-deposited platinum particles have been homogeneously spread on the substrate and by PED a more uniform particle sizes have been deposited. The inset images show that different morphology could be obtained depending on the galvanostatic techniques: spherical (GED) and lamellar (PED) shapes.

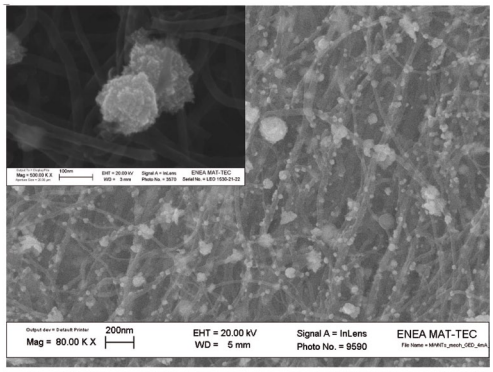

Figure 1: FEG-SEM micrographs (80KX and 500KX) of Pt on MWCNTs-GDLby GED (L_{Pt}= 0.070 mg_{Pt} cm^{-2}).

Figure 3 reports polarization curves of GED and PED samples obtained in half-cell device fuelled by air. It is evident the best performance showed by PED GDL despite the same platinum loading of GED. This result could be explained considering that PED particles morphology (Fig. 2-inset) have a extremely rough and lamellar surface giving high active catalytic surface. In fact, increasing current density values, the reaction takes place under activation control, strongly dependent on the active catalytic surface.
Cell tests (fig.4) confirm the results just discussed and the same GED and PED behaviors. Further works will concern the influence of electro-deposition parameters such as electrodeposition charge density Qdep, applied current density ip and duty cycle value on the platinum loading to improve the electrochemical performances.

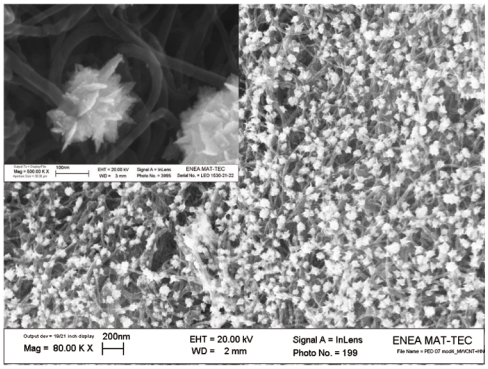

Figure 2: FEG-SEM micrographs (80KX and 500KX) of Pt on MWCNTs-GDLby PED (L_{Pt}= 0.050 mg_{Pt} cm^{-2}).

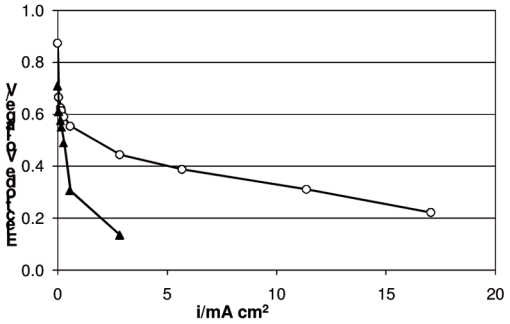

Figure 3: Half-cell polarization curves of Pt on MWCNTs-GDL by PED (○) and Pt on MWCNTs-GDLby GED (▲).

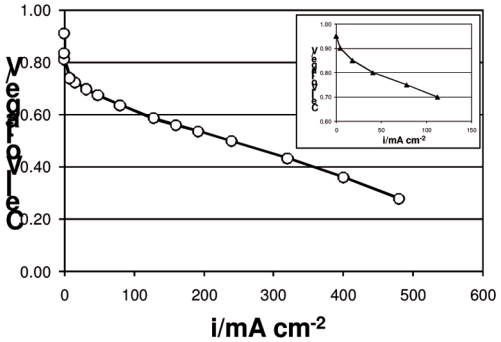

Figure 4: Cell polarization curve of Pt on MWCNTs-GDL by PED. Inset: Cell polarization curve of Pt on MWCNTs-GDL by GED.

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