

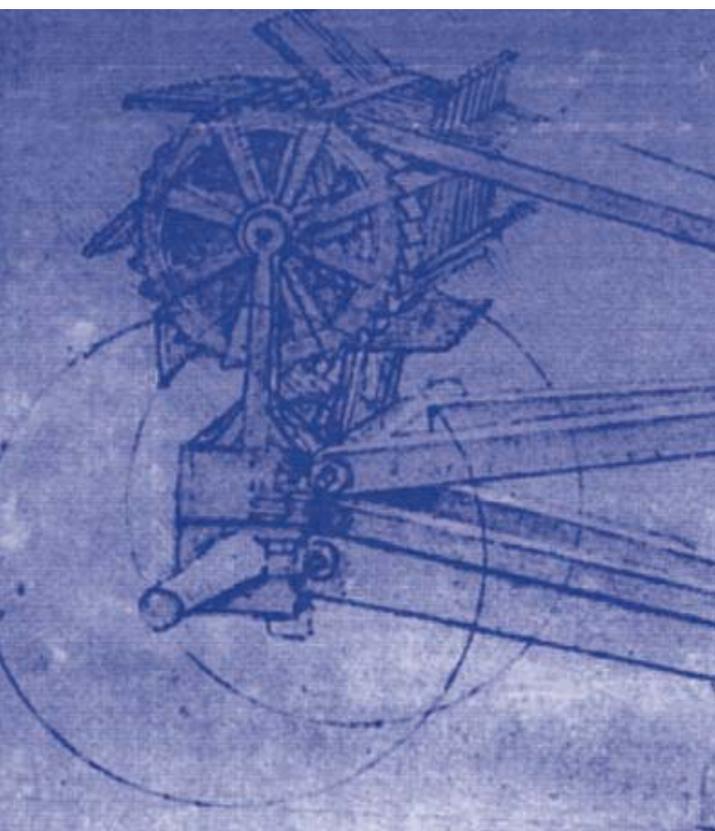


# 10th ICATPP Conference on Astroparticle, Particle, Space Physics, Detectors and Medical Physics Applications

Villa Olmo, Como (Italy) 8-12 October 2007

Instrumentation as a tool for detection of radiation and radiation effects in particle physics, astroparticle physics, space and medical applications

The conference will be devoted to physics and physics requirements, survey of technologies and performance of detectors employed (or to be employed) in fundamental and particle physics experiments at accelerators, underground laboratories, deep-sea facilities, and in space environment (including Earth magnetosphere and heliosphere) for astroparticle physics experiments and astrophysics research, special applications like medical imaging, radiotherapy, simulation code (GEANT4) for dose estimate in radiotherapy, radiation effects on devices, synchrotron radiation and new advanced detectors.



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Presentations include the following subjects: advances in physics from present and next generation experiments, advanced detectors, calorimetry, tracking devices, particle identification, data transmission, data acquisition, semiconductors, medical applications, radiotherapy, radiation damage effects, software and simulation developments, GEANT4 applications.

All contributions relevant to the Conference issues are welcome.

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# **RADIATION EFFECTS ON PLATINUM NANOSTRUCTURED ELECTROCATALYSTS FOR POLYMER ELECTROLYTE FUEL CELLS**

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Polymer Electrolyte Fuel Cells (PEFCs) offer low weight and high power density and are being considered for automotive and stationary power production besides space and electronic applications. In this work, gamma radiation effects on carbon materials (carbon powder and multiwalled carbon nanotubes) used as substrates in PEFCs electrodes, were studied. The enhancing of free radicals formation (especially on carbon powder) was observed and studied by EPR spectroscopy. This evidence leads to a significant activation of carbon materials because paramagnetic sites represent the preferential position for platinum electrocatalyst nucleation. Galvanostatic techniques were applied to deposits platinum nanoparticles on carbon substrates while FEG-SEM characterization and cyclic voltammetry (CV) were carried out to study the morphology and the electrochemical performances of PEFCs electrodes.

## **1. Introduction**

### **1.1. PEFCs generalities**

Polymer Electrolyte Fuel Cells (PEFCs) are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on both side. In a typical fuel cell, gaseous fuels, i.e. hydrogen and oxygen (from air), are fed continuously to the anode (negative electrode) and to the cathode (positive electrode) compartment, respectively.

Therefore, the electrochemical reactions take place at the electrodes to produce electric current. The electrolyte in the PEFCs is an ion-exchange membrane (fluorinated sulfonic acid polymer or other similar polymers) which is an excellent proton conductor. The desired function of the ion-exchange membrane is to provide an ion conductive gas barrier. The only liquid in this type of fuel

cell is water, thus corrosion problems are minimal. Water management in the membrane is critical to achieve efficient performances. In fact, to maintain the membrane well hydrated, the fuel cell must operate such that the by-product water does not evaporate faster than inside produced. Because of the limitations on the operating temperature imposed by the polymer and because of problems with water balance, maximum PEFCs working temperature is around 70-90°C. However, PEFCs deliver high power density, offering low weight and extremely reduced volume. The immobilized solid electrolyte membrane simplifies sealing in the production process, reduces corrosion and provides for longer cell and stack life. PEFCs operating at low temperature allow to faster start-ups and immediate response to the power demand changes. The PEFC system is believed to be suitable for vehicular power applications as well as for smaller scale stationary power supplies and electronic devices.

In the field of space engineering, fuel cells have been applied to spacecrafts, like GEMINI, since the 1960s. Because fuel cell produces water as a by-product from electricity generation, it is very attractive for manned operations in a closed environment. Furthermore, because of fuel cells present high potentiality related to the very high energy densities of fuel gases, these systems are still advantageous for application to large spacecrafts in short-term missions [1–3]. For the above mentioned reasons, nowadays PEFCs are beginning to receive again considerable attention in aerospace applications: one example is the Stratospheric Platform Project [4–7]. In fact, a light weight and a long duration generating system is now required to maintain the altitude and position of an aircraft or airships in the stratosphere. Lately, a lot of missions, among which transfer vehicle in low-Earth orbit, are proposed providing PEFCs on-board [9, 10].

### **1.2. *Aim of the work***

The PEFCs gas diffusion electrodes are catalyzed by deposition of platinum nanoparticles on carbon substrates. Such particles must be localized on the electrode surface to achieve high electrocatalyst utilization. The traditional techniques for the electrocatalyst deposition (impregnation followed by chemical reduction of metal precursors) do not allow a surface localization and therefore it is necessary to deposit high quantity of platinum [11-12].

In order to reduce platinum quantity and improve electrocatalyst performances, platinum nanoparticles are usually deposited on high surface carbon substrates. Recent studies show that the use of an electric field to deposit the catalyst particles allows to have platinum nanoparticles localisation only in active reaction sites, accessible both to electrons and protons (carbon

substrate/electrocatalyst/ membrane triple interface), lowering highly platinum loading ( $< 0.1 \text{ mg cm}^{-2}$ ) [13-15].

In this work, we aim to enhance carbon substrate performances in platinum deposition by gamma-rays irradiation. In fact, radiation induces the free radicals formation: this paramagnetic sites are preferential position to the platinum nucleation.

The effect of dose and dose rate were also investigated by means of the electron paramagnetic spectroscopy (EPR).

Electrocatalysts were prepared by single pulse galvanostatic polarizations (GED), electrochemical activities were studied by cyclic voltammeteries (CV) and morphological analysis were carried out by scanning electron microscopy (FEG-SEM).

## 2. Experimentals

### 2.1. Materials

Carbon Black Vulcan XC72R (CB Vulcan,  $191 \text{ m}^2\text{g}^{-1}$ ) and SuperP (CB SuperP,  $60 \text{ m}^2\text{g}^{-1}$ ), *in-house* Gas Diffusion Layer (GDL) and Multiwalled Carbon Nanotubes (CNTs,  $50 \text{ m}^2\text{g}^{-1}$  Aldrich) are used in this work as raw substrate materials.

### 2.2. Irradiation

Carbon substrates were irradiated at the Calliope  $^{60}\text{Co}$  plant, placed in the Research Centre ENEA-Casaccia (Rome, Italy) at the increasing doses from 50 kGy to 1 MGy at dose rate of 500 Gy/h, 1270 Gy/h and 4530 Gy/h.

The radiation induced free radicals formation was investigated by EPR measurements performed at room temperature after at least 50 min from the stop of irradiation or followed in time in order to investigate the radical decay kinetic. A Bruker EMS104 ESR analyzer (9.8 GHz) was used and the adopted parameter settings are the following ones: microwave power 10 mW, scan width 200 G, modulation amplitude 16 G, sweep time 10.5 s, filter time constant 20.5 ms, receiver gain 30 dB, field offset and receiver offset 0.

The EPR peak-to-peak intensity is proportional to the free radicals number present on investigated materials.

For each sample EPR spectrum was normalized to the mass and, in order to evaluate the free radical concentration effectively due to gamma radiation, the signal associated to radicals present in the un-irradiated filler was subtracted to each measurement.

### 2.3. Electrode preparation and electrochemical characterization

Platinum nanoparticles were electrodeposited on the CBs and CNTs substrates by galvanostatic polarization at constant current (GED), from 5 mM  $\text{H}_2\text{PtCl}_6$  + 1 M  $\text{H}_2\text{SO}_4$  aqueous solution.

In Fig. 1a, a typical pulse profile is shown:  $t_p$  is the polarisation time and  $i_p$  is the applied current density. Charge electrodeposition ( $Q_{\text{ED}}$ ) is calculated as the product between  $i_p$  and  $t_p$ .

The following parameters  $t_p = 300$  s and  $i_p$  varying from 0.1 to 0.6  $\text{mA cm}^{-2}$  are used to prepare the electrocatalysts.

In order to obtain CBs and CNTs electrodes, platinum was electrodeposited onto a rotating glassy carbon disc electrode (RDE), with a geometric surface of 0.125  $\text{cm}^2$ . An homogeneous alcoholic suspension of CBs or CNTs and Nafion solution was sprayed over the cleaned glassy carbon surface and then dried.

The GED depositions were carried out in a standard three-electrode cell: an high purity (99.9999 %) platinum foil served as the counter electrode, an Ag/AgCl saturated electrode (SSC) used as the reference electrode and the RDE as the working electrode.

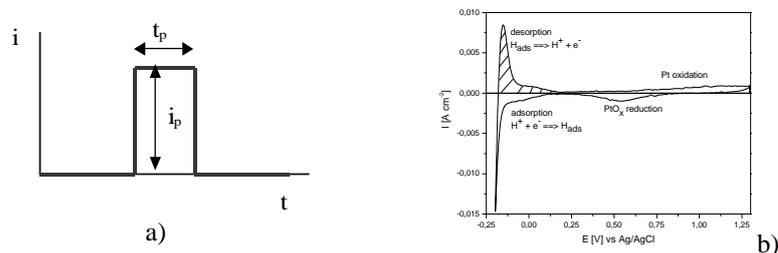


Figure 1 . a) GED profile b) Typical CV of platinum on carbon substrate in 1 M  $\text{H}_2\text{SO}_4$  solution.

Cyclic voltammeteries were recorded in 1 M  $\text{H}_2\text{SO}_4$  with potential cycled between -0.2 and +1.3V vs. SSC (Fig.2). The electrochemical real surface was calculated from the density charge required for hydrogen desorption from platinum surface.

Electrodeposition tests and electrochemical characterisations were done using a potentiostat-galvanostat PAR EG&G mod. 273A. All experiments were carried out at room temperature.

### 3. Results and discussion

In Fig.3 EPR spectra of CBs Vulcan and SuperP are reported. CBs morphology, porosity and surface area are key parameters for the EPR signal [16, 17]. In fact,

as you can see, the line shape is completely different: rather broad and asymmetric for the first, narrow and symmetric for the second. The broad lines are due to radicals associated with polymer aromatic chains, while the narrow signals are due to the oxygen functional groups on carbon aggregates surface. Moreover, EPR spectra before and after irradiation present the same shape for both CBs. These results, supported by SEM analysis, allow to assign an unhomogeneous and not ordered structure for CB Vulcan and a more finely dispersed aggregates distribution for CB SuperP.

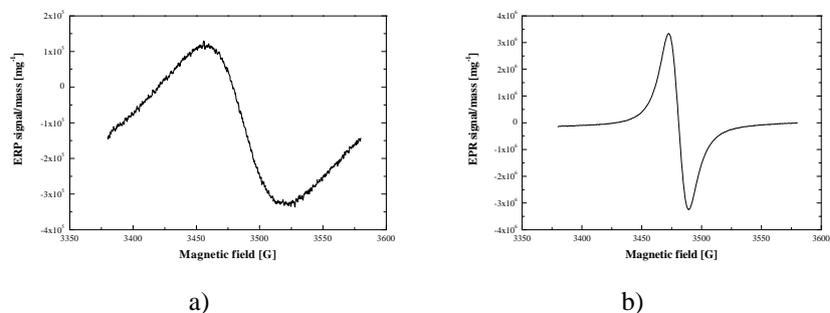


Figure 3 . EPR spectra of CB a) Vulcan and b) SuperP.

In Fig.4 the EPR signals vs dose for the carbon substrates at 1200 Gy/h and at 4500 Gy/h are reported. Analyzing these trends, for each samples it is possible to single out the different conditions that produces a significant increase of the radicals species.

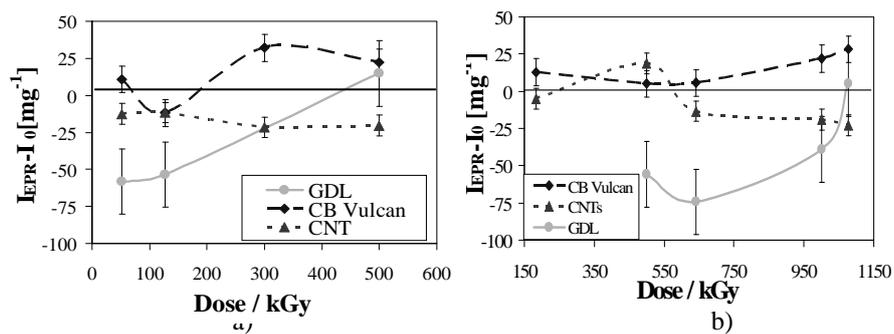


Figure 4 . EPR signal dependence on dose at a) 1200 Gy/h and b) 4500 Gy/h.

For CB Vulcan at 1200 dose rate, electrochemical results (Fig.5) confirm the evidences of EPR spectroscopy. In fact, the best electrochemical performances

are obtained for the 300 kGy irradiated sample, showing the highest EPR peak-to-peak intensity, while the 126 kGy irradiated sample presents the worst results.

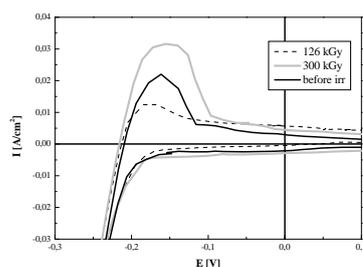


Figure 5 . Vulcan CV profiles depending on dose.

Morphological analysis (Fig.6) of irradiated carbon substrates show that platinum is more uniformly dispersed on the whole surface. Moreover, platinum particles present an homogeneous size distribution as well as a fine nanostructured surface. This evidence might be caused by the significant effect of radiation regarding induced free radicals formation on carbon materials above discussed.

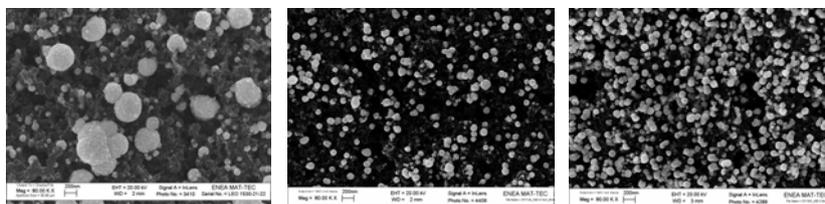


Figure 6 . CB Vulcan SEM images a) before irradiation b) at 126 kGy and c) at 300 kGy.

#### 4. Conclusions

CB Vulcan, CB SuperP, CNTs and GDL are used as platinum electrocatalysts carbon substrates in PEFCs.

By means of gamma-rays irradiation it is possible to induce free radicals formation, enhancing carbon substrates performances related to the following platinum deposition.

The dose and dose rate conditions, leading to the best activation results for each carbon materials, were singled out.

As EPR spectroscopy results, a narrow and symmetric spectrum is presented by CB SuperP, indicating a finely dispersed aggregates distribution, while a broad

and asymmetric spectrum by CB Vulcan, related to unhomogeneous and not ordered structure.

Free radicals formation improves platinum electrodeposition yield, increasing the electrochemical real surface.

On irradiated carbon substrates platinum deposits show homogeneous nanoparticles size and uniform distribution.

### Acknowledgments

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