

# Plasma sputtering deposition of platinum into porous fuel cell electrodes

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**Abstract.** Platinum is deposited into porous carbon materials relevant for fuel cell electrodes using plasma sputtering techniques. The resulting platinum concentration profile extends up to 2  $\mu\text{m}$  into the porous carbon and is well fitted by a generalized stretched Gaussian function, which displays the non thermal nature of the penetration process. Platinum deposits are observed to grow as clusters. On the outermost carbon particles, platinum nano-cluster sizes of 3.5 nm have been measured. In tests using actual PEM fuel cells, current densities as high as 1000  $\text{mA}\cdot\text{cm}^{-2}$  have been obtained at 400 mV with 25  $\text{cm}^2$  plasma electrodes. This compares favourably with commercially available electrodes but the present electrodes have a platinum density 4.5 times lower and hence can be considered to be significantly more efficient.

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The Proton Exchange Membrane Fuel Cell (PEMFC) is a promising power source due to its high energy conversion efficiency at relatively low operating temperature (near 80° C). Such power sources are being seriously considered for use on portable power source for laptop computers and cellular phones, for transportation such as buses, cars, and for stationary applications like auxiliary power sources for domestic use in housing possibly in conjunction with gas turbines. A way to increase fuel cell efficiency and to reduce costs is to improve the electrode characteristics. In particular, a reduction of the amount of noble metal catalyst (typically platinum) and in the way it is distributed in the gas diffusion electrodes would be of great value. Conventional electrodes are fabricated by coating a carbon cloth with an ink composed of carbon particles (carbon black), clusters of platinum catalyst and polytetrafluoroethylene (PTFE) particles. This coating is called the gas diffusion layer and is 50 $\mu$ m thick with a platinum catalyst content of 0.35 mg.cm<sup>-2</sup>. Some attempts have been made to reduce the amount of catalysts [1] and one way is simply to expose the uncatalyzed gas diffusion layer (Figure 1) to a flux of platinum, which then diffuses into the gas diffusion layer to a sufficient depth so that adequate fuel cell performance is reached. A technique that meets these conditions is plasma sputtering because plasma sputtering has the advantage of controlling depth profile. Earlier experiments [2, 3, 4, 5, 6, 7, 8] have shown great promise for this technique, but a clear description of catalyst penetration into the uncatalyzed diffusion electrodes and resulting concentration profiles remain to be established.

In order to obtain more detailed information on the deposition process, a low pressure Very High Frequency (VHF) inductive plasma sputtering system has been constructed (APRIM VIDE) as displayed in figure 2. An argon plasma is created in the stainless steel deposition chamber 18 cm inner diameter and 25 cm long by using an external planar antenna (also known as TCP antenna) at 30 W input power and an argon pressure of 5 10<sup>-3</sup> mbar. The excitation antenna is powered by a tunable frequency generator operating for the present experiments at 100 MHz. The electrodes are placed on a movable grounded substrate holder in front of the sputtering target with a target - substrate distance of 4.5 cm. A base pressure of P<sub>0</sub> = 2. 10<sup>-8</sup> mbar could be achieved by a primary/turbomolecular pump combination and during the experiment, an argon flow is fixed to 5 sccm using a mass flow meter. Langmuir probe measurements at the substrate position are employed to determine the plasma potential (V<sub>p</sub>), the electron density (n<sub>e</sub>) and electron temperature (T<sub>e</sub>). Typical values are V<sub>p</sub> = 15 eV, n<sub>e</sub> = 4. 10<sup>10</sup>cm<sup>-3</sup>, and k<sub>B</sub>T<sub>e</sub> is 4 eV. The Pt target was biased with a continuous (DC) potential of V<sub>b</sub> = -300 V which was chosen as it was close to the maximum sputtering efficiency for Ar<sup>+</sup> on Pt: 0.86 Pt atom per incident Ar ion [9]. Moreover, using a simple one-dimensional calculation, the Thompson energy distribution function of the sputtered Pt atoms, and their mean kinetic energy, when travelling across the Ar gas on the 4.5 cm target to substrate distance, can be deduced [10, 11]. On Figure 3, the energy distribution function f(E<sub>Pt</sub>) of the sputtered Pt atoms with kinetic energy E<sub>Pt</sub> is plotted assuming a kinetic energy of the sputtering argon ions, E<sub>i</sub> = 315 eV. The mean kinetic

energy  $\langle E_{Pt} \rangle$  of Pt atoms reaching the substrate is then calculated to be 6.5 eV.

Argon ions fall through the sheath of the negatively biased Pt target and Pt atoms are sputtered and travel across the plasma to the electrode which holds the porous carbon film. In such a process, simultaneously with the deposition, the grounded electrode is subjected to low energy plasma ion bombardment (here they have the energy  $E_{Ar^+}^s = eV_p = 15$  eV) [12, 13]. Such ion bombardment can be an important contributor in controlling the deposition [12, 13, 14], especially in favouring cluster growth with low size dispersion [12, 14, 15].

Coated electrodes were analyzed by high resolution scanning electron microscopy (Hitachi S-4500 in Montpellier and S-4200 in Orléans) to determine cluster sizes at the surface and the evolution of the porosity, i.e. to display if the build up of platinum on the carbon black granules is reducing pore size. Rutherford Backscattering was used to measure both the total Pt content and to quantify Pt penetration into the diffusion layer. Fuel cell tests were conducted using 5x5 cm<sup>2</sup> electrode fixed on a membrane-electrode assembly acting as a true fuel cell (figure 4). This sputtering deposited electrode was placed at the fuel cathode where oxygen reduction takes place, while a conventional E-TEK electrode (80% Carbon 20% PTFE 50 $\mu$ m thick) with Pt loading of 0.35 mg.cm<sup>-2</sup> is fixed at the anode where H<sub>2</sub> oxydation occurs. This configuration was chosen as the influence of the sputtered electrode is greater at the cathode than at the anode because oxygen reduction is more sensitive to Pt loading and distribution than hydrogen oxydation at the anode. The results are then compared to the effectiveness of a reference fuel cell which had standard electrodes.

RBS measurements were performed to determine the Pt content depth profile within the electrode diffusion layer. A 2 MeV  $\alpha$  (He<sup>+</sup>) particle beam issued from a Van de Graaf accelerator (CERI, Orléans), is directed onto the Pt catalysed diffusion layer and  $\alpha$  particles are backscattered after colliding with a carbon atom, a fluorine atom (from PTFE - (CF<sub>2</sub>)<sub>n</sub> -) or a Pt atom. In their trajectory into the substrate, the impinging  $\alpha$  particles loose kinetic energy before being elastically reflected. Consequently, these backscattered  $\alpha$  particles have an energy distribution that reflects the depth profile of the reflecting species. Energy loss also depends on the mass, which makes RBS sensitive to the composition. Figure 5 show a typical RBS spectrum of a plasma electrode after 20 min Pt deposition time. The left side of the spectrum, at low backscattering energies, corresponds to carbon and fluorine substrate contributions, whereas on the right side, the asymmetrical peak originates from  $\alpha$  particles scattered by Pt atoms. The area under this Pt peak is directly related to the number of the platinum atoms inside the diffusion layer. In this example, there are 250 10<sup>15</sup> Pt atoms cm<sup>-2</sup> i.e. 0.08 mg.cm<sup>-2</sup>, say 4.5 times less than that of conventional electrodes. The deposition time  $t$  is 20 min. The tail on left side of the Pt peak indicates that the Pt atoms have diffused into the porous carbon layer and hence it is possible to deduce the Pt depth profile from

this spectrum. By fitting the experimental spectrum with a simulated spectrum (using SIMNRA software [16], for example) the depth profile can be recovered by an iteration process until the simulated spectrum matches the experimental spectrum. The resulting depth profile corresponding to Figure 5 is plotted in the Figure 6.

This profile is best fitted by using a generalized stretched Gaussian function, which is an exact solution of non linear equation for anomalous diffusion [17, 18]. This function reads  $\rho(z) = [1 - (1 - q)\beta z^\lambda]^{1/1-q} / Z$ .  $q, \beta, \lambda, Z$  are fitting parameters. In figure 6,  $q = 1.8$  and  $\lambda = 0.8$  are the best fit parameters. Normal (thermal) diffusion in a porous medium should occur for  $q \rightarrow 1$  and  $\lambda = 2$  [17, 19]. Hence, it can be concluded that the present penetration of platinum into the diffusion layer is not of a thermal nature. The combination of a high Pt atom kinetic energy combined with the low energy ( $E_{Ar^+}^s = eV_p = 15$  eV) argon ion bombardment of the substrate during deposition is expected to play a role in the deviation from thermal diffusion [12, 14, 15, 10]. It is also important to note that a penetration depth of  $2 \mu\text{m}$  is reached for the first time whereas previous works reported Pt depths less than  $100$  nm [2, 3, 4, 5, 6, 7, 8]. Figure 7 shows the temporal evolution of the concentration profiles. It is interesting to note that even at early times, the Pt is already incorporated into the carbon cloth. With increasing time, the density of the Pt increases but the profile appears to remain the same.

SEM micrographs of porous carbon gas diffusion layer are shown in Figure 8 and the sizes of the outermost carbon particles (those observed near the surface) are in the range  $30 - 50$  nm (Figure 8a). After Pt deposition, the carbon particles seem uniformly coated and their dimensions appear to be increased (Figure 8b). A zoom on carbon particles shows that carbon is coated by Pt nano-clusters with a size of  $3.5$  nm (Figure 8c). All visible particles seen in Figure 8b display Pt nano-clusters implying that Pt atoms grow as nano-clusters along the diffusion path on the surface of the connected carbon particles. Thus the recorded Pt depth profile is composed of Pt nano-clusters presumably of decreasing size with increasing depth. Finding the size distribution along the depth profile is a challenging experimental work. Unfortunately, none of the present, more sophisticated, microscopy or scattering (X-ray or neutron) is able to reach the submicron resolution necessary for displaying such information.

So combined SEM and RBS measurements suggest that Pt atoms arriving with a relatively high kinetic energy undergo multiple ballistic scattering on the surface of the complex inner channels of the porous carbon cloth, and that a local nucleation takes place leading to the observed Pt nanoclusters

These two important results, Pt depth profile and the observation of nano-clusters with size less than  $4$  nm are of primary importance for fuel cell electrode design and efficiency. Catalytic reactions are surface phenomena, thus only surface atoms of catalyst are effective and nano-cluster with size below  $4$  nm have almost all atoms as surface atoms. When this is the case, all atoms of the cluster can be involved in a catalytic

reaction. The Pt concentration decreasing from electrode surface (in contact with the proton exchange membrane) towards the inner part of the electrode is interesting for use in fuel cells. Indeed, at low current density all the catalyst is effective, while at high current density only the outermost part is used in the reactions due to competition between reaction rates and reactant flux at the catalysts.

Preliminary fuel cell tests have been conducted with the plasma sputtering prepared electrodes and compared with commercial E-TEK (Pt content  $0.35 \text{ mg cm}^{-2}$ ) and are plotted in Figure 9. The two fuel cells have similar behaviour except at high current density where the potential of the plasma sputtering system drops rapidly above  $1000 \text{ mA.cm}^{-2}$ . There are a number of possible reasons for this which merit some discussion. The first is that there is some poisoning of the deposition by impurities sputtered from the surrounds of the Pt target. Future experiments will be conducted with an improved design for the target aimed at eliminating any possible sputtering of unwanted material. Secondly, the size of the pores between the surface coated particles may well decrease with increasing deposition of Pt resulting in a consequent decrease in the flow of reactants and a decrease in the efficiency of the fuel cell. If this be the case then a different route should be followed unless there is some optimum depth of deposition less than the 2 micrometres cited in our present experiments. Thirdly, the Pt load on the electrode may be insufficient to achieve the power efficiency obtained with the E-TEK electrode. In that a better result could be achieved by increasing the sputtering time or sputtering rate. At this present early stage all explanations are speculative but we are conducting additional experiments with different Pt loads and a variety of plasma conditions.

Nevertheless, we have already achieved with our initial experiments a quite respectable power density as high as  $400 \text{ mW.cm}^{-2}$  which has to be compared with the  $600 \text{ mW.cm}^{-2}$  for the commercial E-TEK electrode. Considering the efficiency per weight of catalyst, the plasma prepared electrode becomes  $5 \text{ W.mg}^{-1}$  compared to  $1.7 \text{ W.mg}^{-1}$  for the commercial E-TEK electrode. Next set of experiments are scheduled to give deeper insights into relation between Pt contents and penetration with fuel cell performances.

In conclusion, a low pressure high density inductive plasma sputtering deposition system has been built for depositing catalysts onto porous substrates. For the first time fuel cell electrodes displaying both a low Pt content and a concentration gradient extending as deep as  $2 \mu\text{m}$  into the diffusion layer have been fabricated. The Pt layer has been found to consist of nano-clusters with a maximum size of 4 nm. The depth concentration profile of Pt atoms into the porous substrate has been recovered and attributed to the interaction of energetic plasma species with the substrate combined with hyperthermal Pt kinetic energy during deposition. The efficiency of fuel cell electrodes fabricated using plasma sputtering deposition has been observed at low Pt content due to the optimum location and distribution of the Pt in the surface layer of

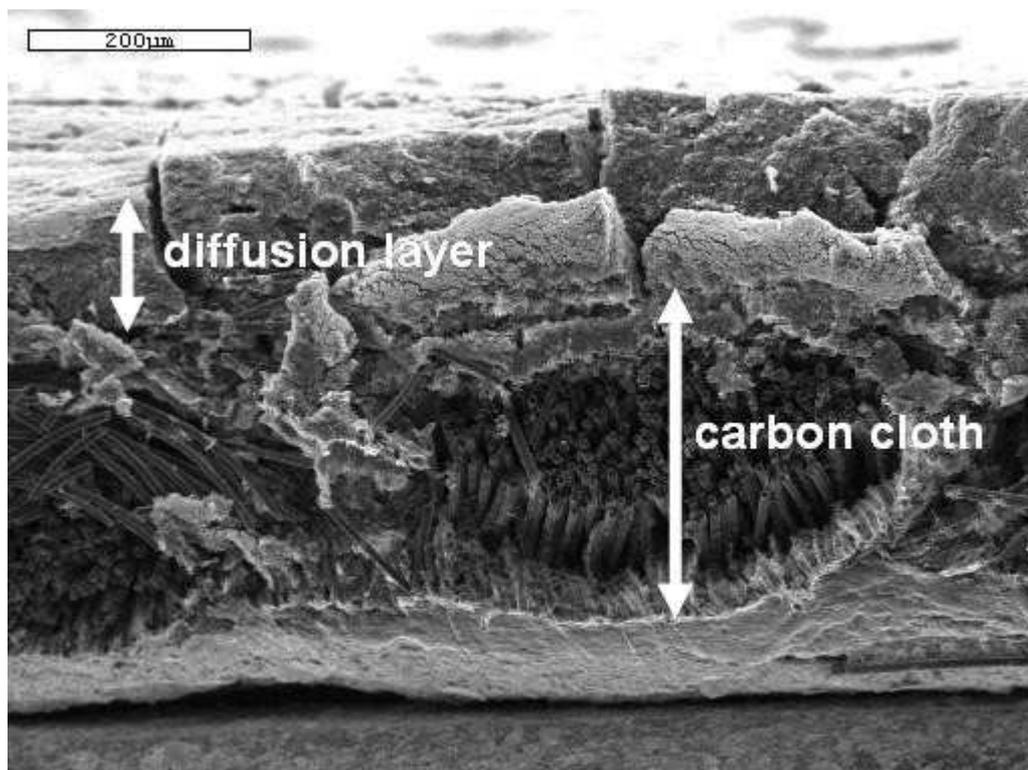
the electrode.

## Acknowledgments

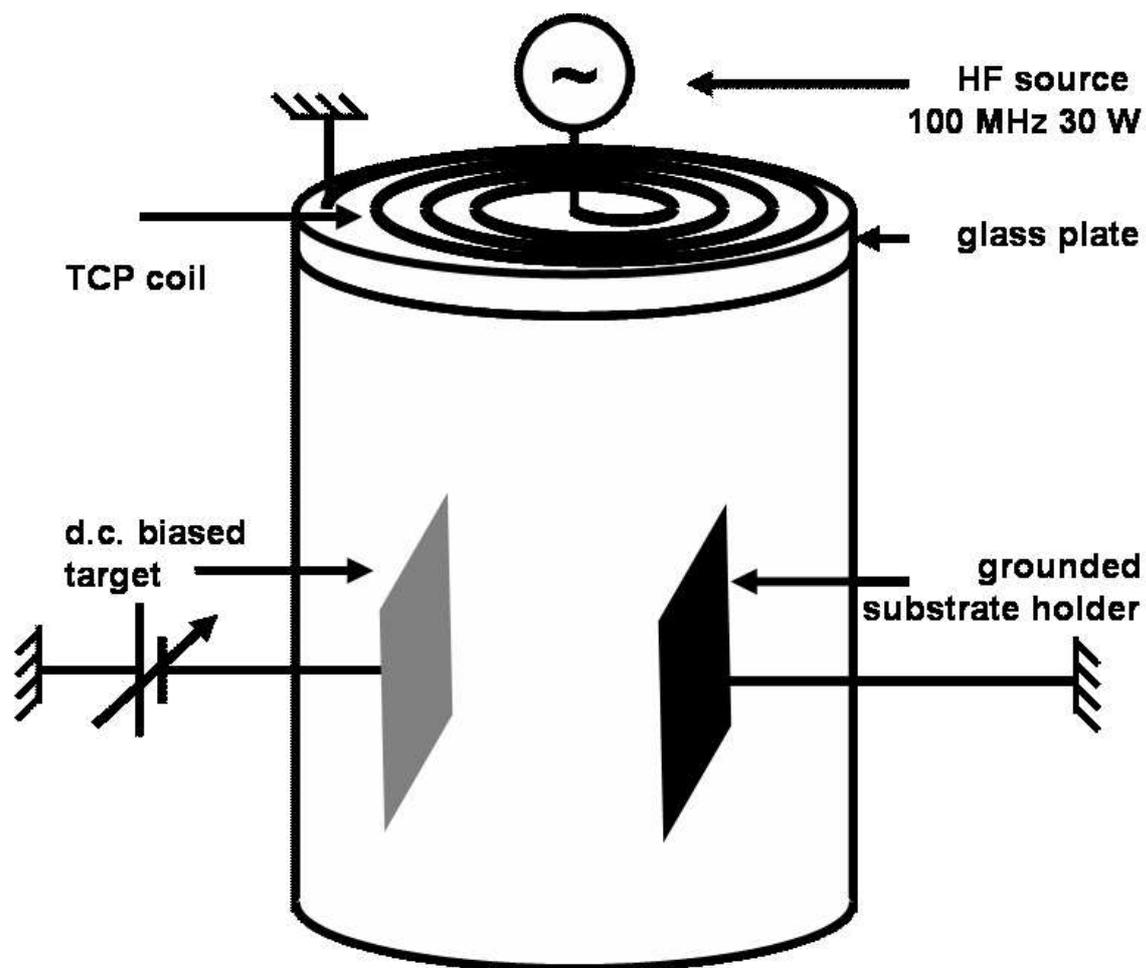
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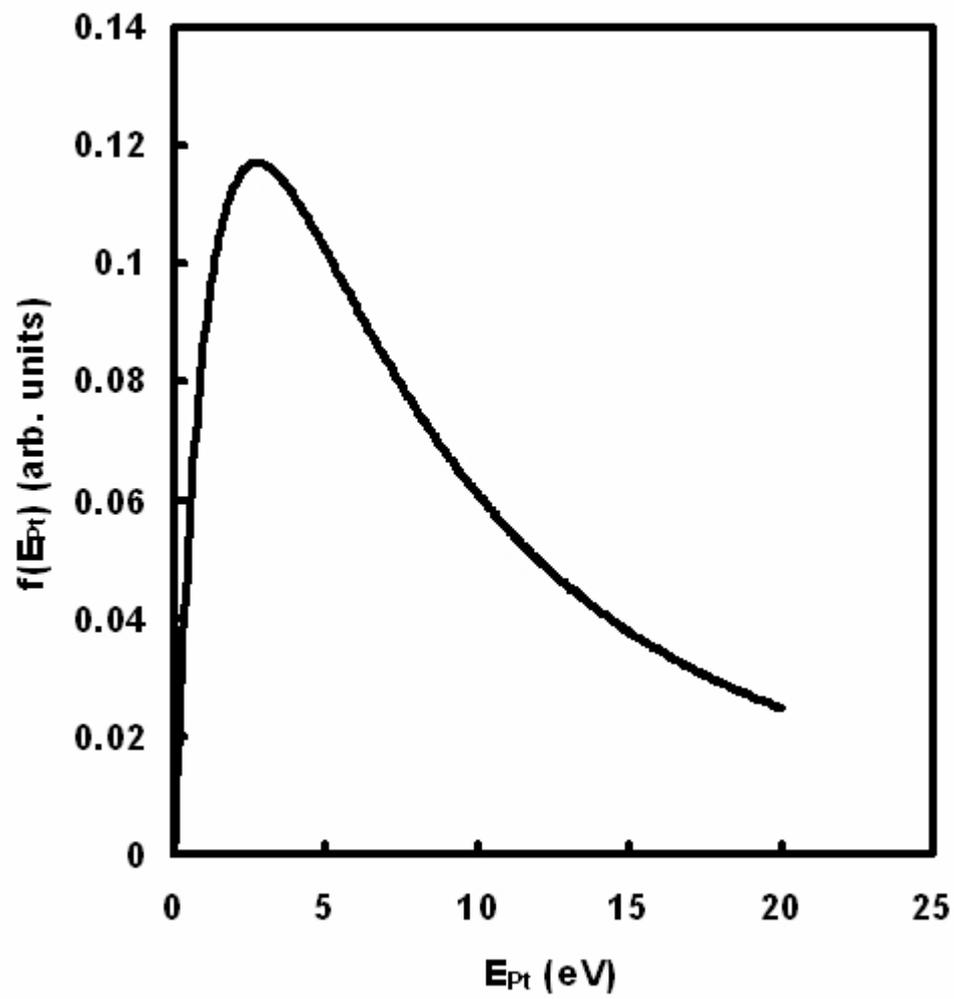
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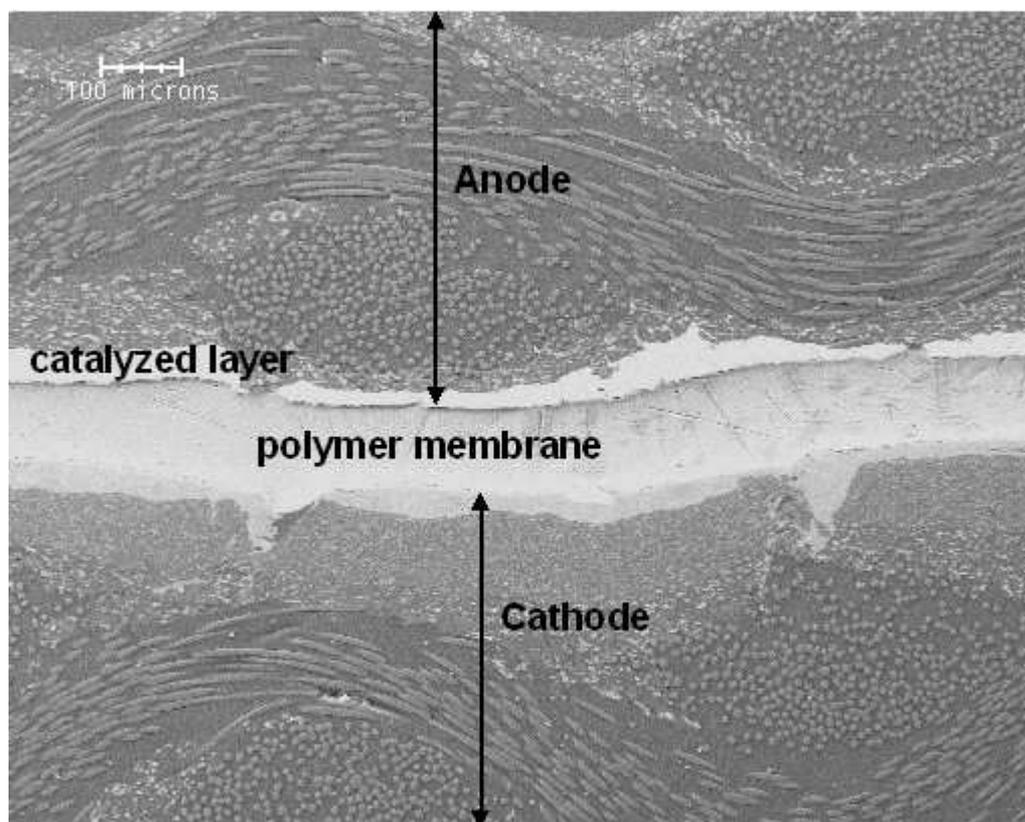
**Figure 1.** SEM micrographs of a uncatalyzed PEMFC electrode



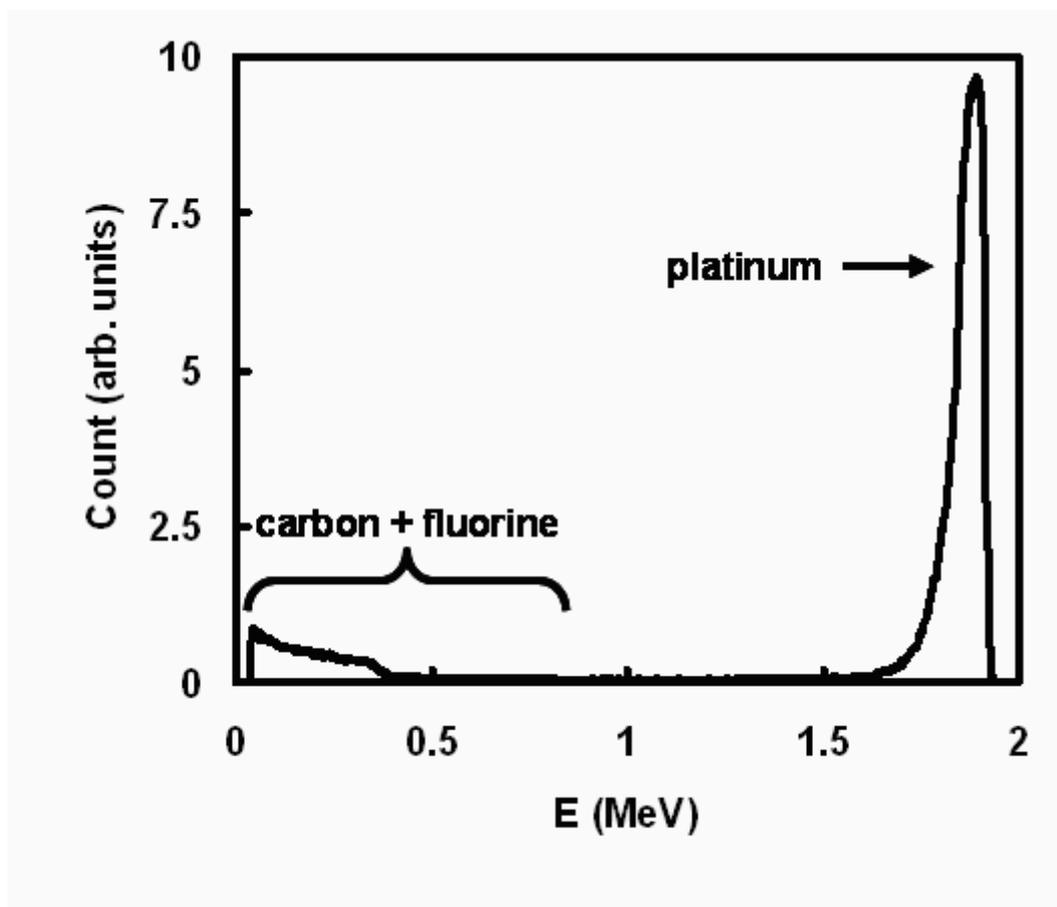
**Figure 2.** Experimental setup of the inductive high density plasma sputtering deposition chamber



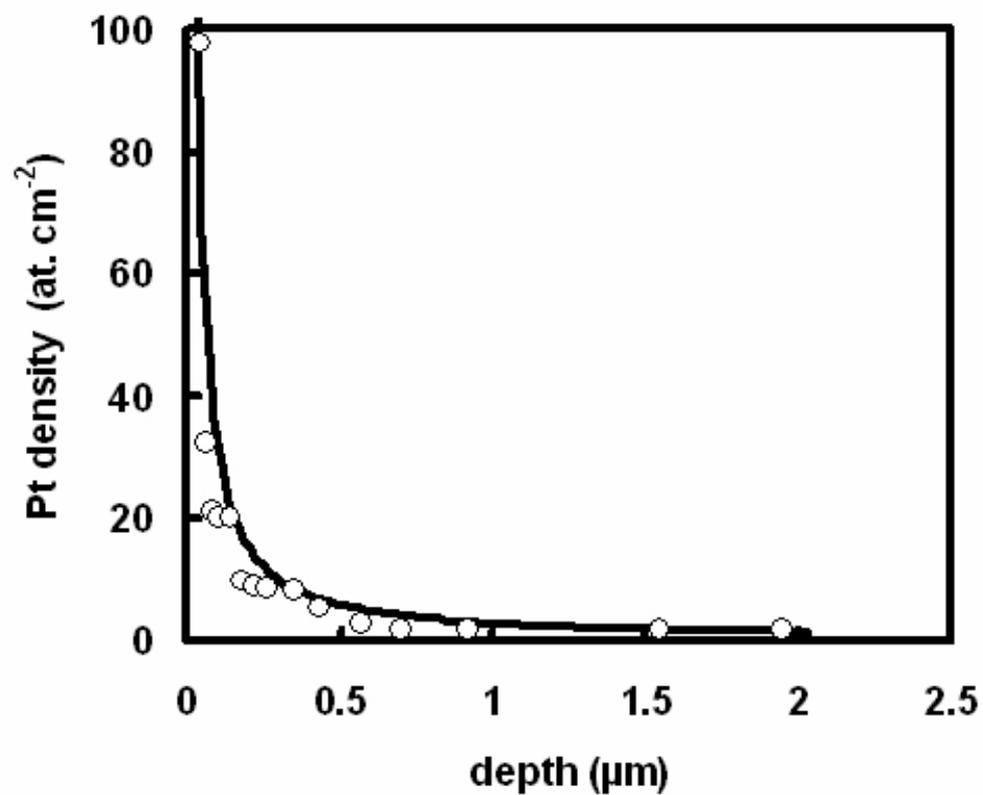
**Figure 3.** Thompson energy distribution function of sputtered Pt atoms at the substrate location. Ar pressure is  $5 \cdot 10^{-3}$  mbar,  $V_b = -300$  V, target-substrate distance was 4.5 cm.



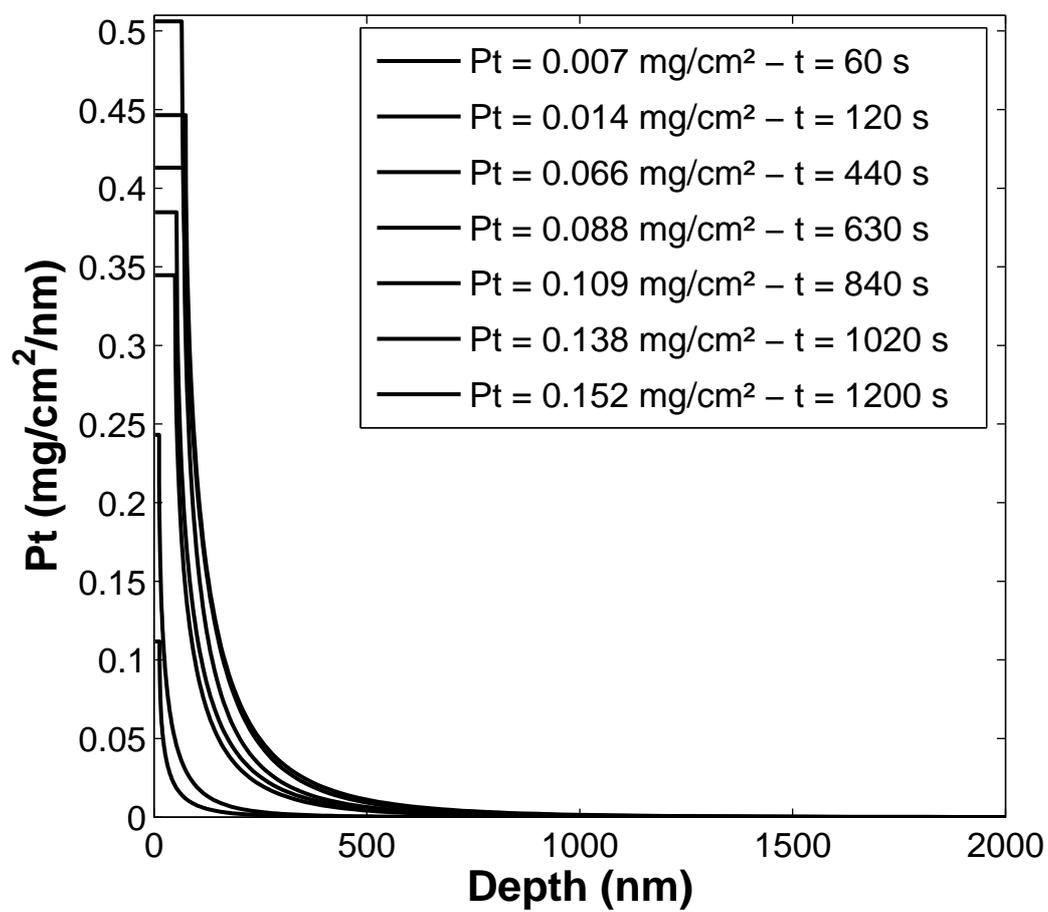
**Figure 4.** Schematics of a PEMFC electrode membrane assembly



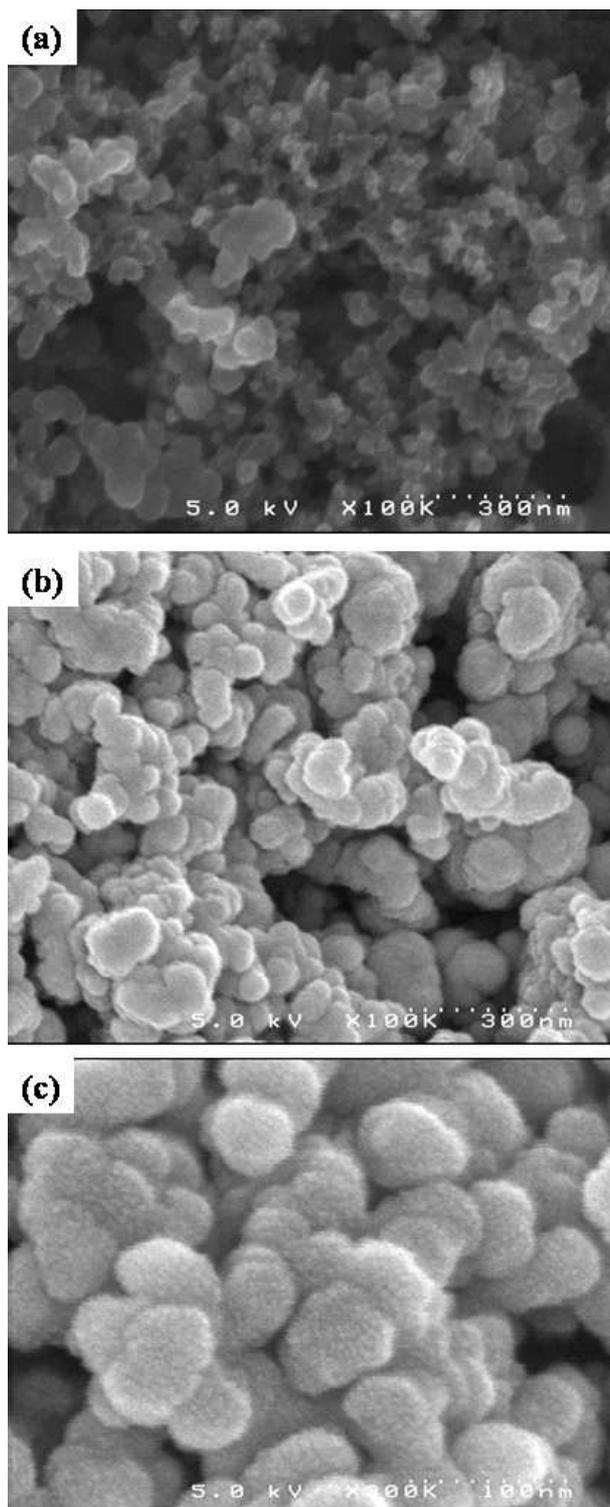
**Figure 5.** A RBS spectrum of Pt atom deposited into porous carbon diffusion layer by plasma sputtering at  $P=5 \cdot 10^{-3}$  mbar,  $V_b = -300$  V,  $t=20$  min.



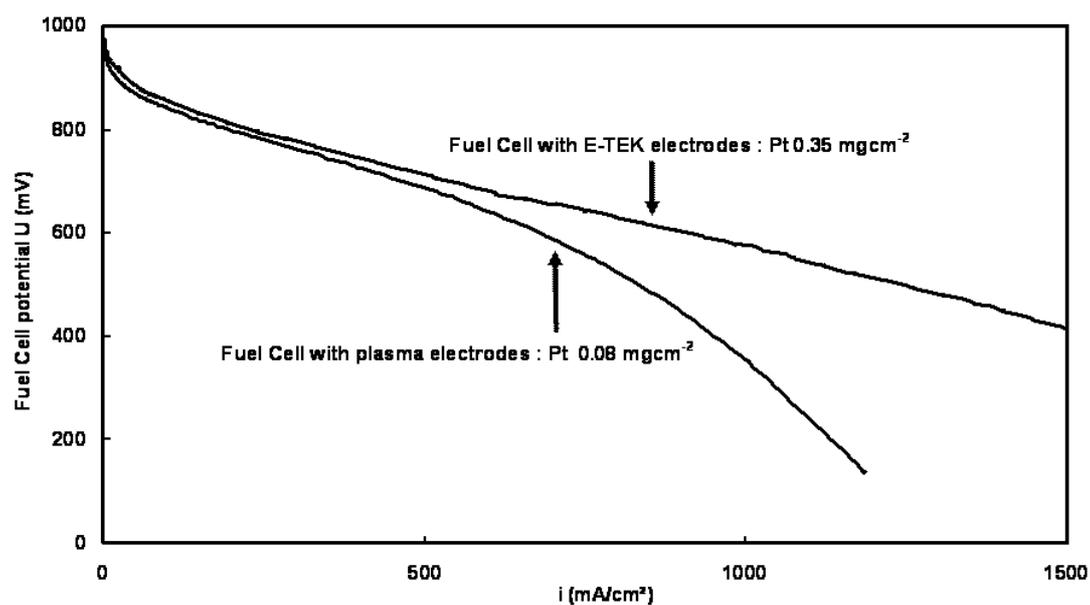
**Figure 6.** Depth profile of Pt deposited by plasma sputtering at  $P=5 \cdot 10^{-3}$  mbar,  $V_b = -300$  V,  $t=20$  min. The solid line is the generalized stretched gaussian function fitting.



**Figure 7.** Depth profiles of successive Pt deposition in porous carbon. Deposited quantities increase from bottom to top of the figure



**Figure 8.** SEM micrographs of diffusion layer (a) before Pt deposition (b) after Pt deposition (c) a zoom on a Pt coated carbon particle : the Pt clusters are clearly visible with a mean cluster size around 3.5 nm



**Figure 9.** Current-Voltage curves of two fuel cells built with a plasma catalysed electrode ( $2 \mu\text{m}$  active layer of  $0.08 \text{ mg}\cdot\text{cm}^{-2}$  Pt content) and with a commercial E-TEK build with standard electrodes ( $50 \mu\text{m}$  active layer of  $0.35 \text{ mg}\cdot\text{cm}^{-2}$  Pt content).