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Atmospheric Plasma Deposition: A new pathway in the design of Conducting Polymer-based Anodes for Hydrogen Fuel Cells

Marc Michel[1], Jérôme Bour[1], Julien Petersen[1], Claire Arnoult[1], Frank Ettingshausen[2], Christina Roth[2] and David Ruch[1]

[1]*Centre de Recherche Public Henri Tudor, Department of Advanced Materials and Structures, Esch-sur-Alzette, L-4002, Luxembourg*

[2]*Institute for Materials Science, TU Darmstadt, D-64287 Darmstadt, Germany*

Abstract

In this study, we explored thin films of nanofibrous functionalized conducting plasma Polyaniline (pPANI) with platinum deposited by an atmospheric plasma deposition process for the potential design of anodes for hydrogen fuel cell applications. We observed that the incorporation of such a polymer, characterized by both electronic and ionic conductivity, associated with a catalyst in a 3D porous network, could lead to an increased probability of the three-phase contact to occur. In this context, aniline was mixed with functionalized platinum nanoparticles and used as the precursor. The role of these functionalized nanoparticles was not only to act as the catalyst for fuel cell purposes, but also as nucleation sites promoting the formation of the nanofibrous pPANI thin film during the plasma polymerization. The morphology of the thin film was analyzed by scanning electron microscopy and the efficiency, in terms of energy conversion, was assessed in a single fuel cell test bench.

Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are being considered as promising candidates for a number of commercial applications including their use in portable electronic devices and automobiles. One of the key challenges facing the widespread commercialization of PEM fuel cells is their high cost. The cost is largely associated with expensive materials such as a noble metal catalyst, and inefficiencies in their utilization due to a weak control on the so called triple phase boundary (TPB) [1], which is located in the membrane electrode assembly (MEA). To effectively utilize the catalyst, these regions, corresponding to the interfacial areas between the reactant, electrolyte and catalyst, must balance the ionic and electronic conducting media, allowing continuous pathways of the protons to the electrolyte and electrons to the electrode. These media influence the hydrophilic and hydrophobic properties of the composite material bringing a design challenge at the nanometer scale due the necessary integration of disparate materials.

In this context, it has been shown elsewhere that electrodes fabricated by incorporating a polymer, characterized by both ionic and electronic conductivity, in a so called Layer-by-Layer (LbL)[2] architecture can give a significant boost to the fuel cell performance, whereas less catalyst is employed. [3-10] Despite very promising results, this method of preparation can only be done in a batch process.

Inspired by these works, this paper aims at designing a new generation of multilayered anodes using Atmospheric Plasma Polymerization, which has become a promising technology for in-line processing. Plasma polymerization is a versatile technique for the deposition of plasma polymer films with functional properties suitable for a wide range of applications such as protective coatings, biomedical materials, electronic and optical devices or adhesion promoters. [11-13] For example, plasma-induced polymerization has been extensively used for the preparation of conducting polymeric thin films including polyaniline (PANI). In

particular, Tiwari et al. have shown that nanofibrers of conducting polyaniline (PANI) thin film can be obtained and they explored its application in the fabrication of NO_2 gas sensor. [14]

It is now well-established that plasma polymers are different from those fabricated by conventional wet synthetic methods: they are usually branched, highly cross-linked, insoluble, pinhole-free, and adhere well to most substrates.

Nevertheless, plasma-polymerization is mostly performed at low pressure, limiting its application to batch processes. In addition, low pressure plasma technology requires the use of costly vacuum pumping systems. [15]

Among various atmospheric pressure plasmas, dielectric barrier discharges (DBDs) [16] have received a lot of attention due to the easy formation of a stable discharge and their scalability. These discharges are usually generated in the space between two parallel electrodes, at least one of these being covered with a dielectric layer. [17-18]

The functionality of the plasma deposited layer is mainly determined by the nature of the used vapour precursors or monomers. [19] These precursors or monomers, which lead to the coating formation, are diluted in a carrier gas, which is usually helium, argon, or nitrogen.

In this study, we explored nanofibrous pPANI thin films deposited using the atmospheric pressure dielectric barrier discharge process for the design of potential anodes for hydrogen fuel cell applications. We expect that the incorporation of such a polymer, characterized with electronic and ionic conductivity and associated with a catalyst in a 3D porous network could lead to an increased probability of the three-phase contact to occur. In this background aniline was mixed with functionalized platinum nanoparticles and used as the precursor. The role of these functionalized nanoparticles was not only to act as a catalyst for fuel cell purposes, but also as nucleation sites promoting the formation of the nanofibrous pPANI thin film during the plasma polymerization. The morphology of the thin film was analyzed by scanning

electron microscopy and the efficiency, in terms of energy conversion, was evaluated in a commercial single fuel cell test bench.

To our knowledge, this paper is the first showing that electrodes for fuel cells can be manufactured by a sequential atmospheric pressure dielectric barrier discharge process of aniline and functionalized platinum.

Experimental section

Materials

Hexylamine, sodium borohydride ($NaBH_4$) 99%, 4-Aminothiophenol (mercaptoaniline), Aniline, and platinum (IV) chloride ($PtCl_4$) 99.99% were obtained from Aldrich and used as received. $PtCl_4$ was stored in a dessicator under vacuum.

Functionalization of Platinum nanoparticles

The synthesis and the functionalization of platinum nanoparticles were strongly inspired by a previous work. [20] Briefly, 150 mg $PtCl_4$ was dissolved in 35 mL of hexylamine in a 200 mL flask leading to the formation of an orange solution (solution 1). Then, 165 mg of 4-Aminothiophenol was dissolved in 15 mL of a methanol/hexylamine solution (50/50) (solution 2). Finally, 150 mg of $NaBH_4$ was dissolved in 20 mL of a water/methanol solution (50/50). 10 mL of hexylamine was added after complete dissolution of sodium borohydride (solution 3). Solution 3 was then poured into solution 1 under vigorous stirring at room temperature. The reaction mixture turned brown within a few seconds. After 30 s, solution 2 was added to the mixture. After 5 min, 100 mL of Milli-Q water was added. The resulting solution was then stirred for 20 min before being transferred into a separatory funnel. Just after phase separation, the water was removed and the organic phase was repeatedly washed with the same amount of water (100 mL). The volume of the dark brown organic phase was reduced to ca. 1-2 mL by rotary evaporation at 30 °C and transferred into a centrifuge tube

with 0.1 g of 4-Aminothiophenol dissolved in 7.5 mL of ethanol. After this solution was stirred overnight, a black solid residue was recovered by centrifugation. The supernatant presumably contained unreacted 4-Aminothiophenol and platinum complexes. The precipitate was washed with pure ethanol and centrifuged again. The fraction yielded to a dark brown solution, which remained stable for several weeks.

Plasma polymerization

In this study, the precursor used for the plasma polymerization consisted of 5 mL of functionalized platinum solution mixed with 5 mL of aniline (adjusted at pH=2).

The DBD discharge was generated between an earthed bottom aluminium plate and two high-voltage aluminium top plates protected by a 3.25-mm-thick glass plate. The gap between the electrodes was set to 2 mm.

A commercial Nafion 117 membrane was used as the substrate and was positioned at the bottom electrode. The precursor was atomized by a TSI 3076 system at a constant atomization pressure of 2.10^5 Pa and injected into the gas before entering the plasma zone. The carrier gas composition, which was set by mass flow controllers, consisted of a N_2/O_2 (97/3 vol. %) mixture with a gas flow of 20 $L.min^{-1}$. The gas mixture containing the precursor aerosol was injected into the plasma through a slit between the two top electrodes. The experiment was carried out at atmospheric pressure and at room temperature. During the experiment, the top electrode block moved over the sample at a constant speed (4 $m.min^{-1}$) and in a range of 380 mm. The plasma coating consisted of 100 passes and lasted 10 min leading to the formation of a greenish film on the Nafion 117 membrane. For the coating process, plasma discharges were generated by an AC power supply with variable frequency. The frequency was set to 1.5 kHz and the voltage was a pseudo sinusoid as a function of time. Power was kept constant

during the experiment and was set to 500 W, which corresponded to a power density (over the electrodes) close to 0.8 $W.cm^{-2}$.

Characterization Techniques

Materials characterization

The chemical structure of the coatings was evaluated by FTIR spectroscopy using a Bruker Optics Tensor 27 spectrometer. UV-Visible investigations were obtained by using a Perkin Elmer lambda 35 Spectrophotometer.

The pPANI-Pt fibers were investigated by X-ray powder diffraction using a diffractometer STOE STADI-P with Germanium monochromated $Cu_{K\alpha}$ radiation (λ= 1.54060 A) and a position-sensitive detector with 40° aperture. Average particle sizes are estimated by the Scherrer equation.

In addition, transmission electron microscopy (TEM) was employed to measure the Pt particle size and the particle distribution. A JEOL 3010 high resolution electron microscope equipped with LaB_6 filament and an acceleration voltage of 300 kV was used for the measurements. A small amount of the platinum dispersion was placed on a holey-carbon film covered Cu grid and left to evaporate.

The platinum loading on the pPANI was obtained by thermogravimetric analysis (TGA) with a Netzsch STA 490 under synthetic air (Linde(R), 80% N_2, 20% O_2) atmosphere from 30 to 1000 °C with a heating rate of 5 °C min^{-1}.

The morphology of the LBL films was checked by scanning electron microscopy (SEM) using a JEOL JSM 6340 field-emission gun scanning electron microscope. The MEA was cut into tiny pieces and deposited onto a SEM holder before being observed.

Fuel cell testing

The MEA was tested in a single cell fuel cell test bench using a commercial cell hardware (Electrochem. Inc.) and was conditioned over night, until a steady state current was reached at a potential of 0.6 V. In hydrogen operation, 150 ml min^{-1} H_2 (N 5.0, Linde) are loaded with water in a humidifier (T=70 °C) and fed into the fuel cell anode. As cathode feed, high-purity oxygen was supplied (N 4.5, Linde) at 75 ml min^{-1} to the fuel cell pre-heated to 80 °C. Current–voltage curves were obtained galvanostatically using an operated fuel cell test bench.

Results and discussion

Functionalization and characterization of Platinum nanoparticles

A major point for the design of the MEA by plasma polymerization was the control of the particles size after their functionalization with mercaptoaniline. It was expected in this work that the use of a mixture of aniline and functionalized platinum particles could help to promote the formation of aniline plasma polymer thanks to nucleation processes occurring during the coating. This functionalization was based on the reduction of platinum salt by a reducing agent ($NaBH_4$) in the presence of mercaptoaniline. [20] The synthesis described here used hexylamine as the intermediate capping agent. The final capping agent was introduced in the reaction mixture directly after reduction of the platinum salt. The rapid addition of mercaptoaniline after platinum reduction was consequently required in order to avoid irreversible particle flocculation phenomena.

Infrared spectroscopy was performed on the functionalized nanoparticles solution in order to check the presence of mercaptoaniline surrounding platinum nanoparticles (Figure 1).

Absorption peaks above 3000 cm^{-1} are attributed to N-H stretching modes whereas the peak located at 1612 cm^{-1} is characteristic of NH_2 deformation. The C-N stretching mode is located at 1272 cm^{-1}. The aromatic ring exhibits vibrations at 1578 and 1480 cm^{-1} corresponding to

aromatic ring stretching modes. Absorption corresponding to C-H bonds appears at 1172 cm^{-1} (in-plane bending modes) and 815 cm^{-1} (C-H wagging vibration).

The morphology of the functionalized platinum was investigated by TEM. On the TEM pictures (Figure 2), one can see the presence of individual particles, suggesting that the functionalization had a positive effect on the dispersion: no aggregation was observed. The good dispersion can be explained by the fact that the presence of mercaptoaniline acted as a powerful capping agent. Note that this dispersion was kept stable for several months. The particles ranged in size from 1 to 4.5 nm with a maximum centred around 3 nm (Figure 3).

Manufacturing of a fuel cell anode using plasma polymerization

The underlying idea was to use the functionalized nanoparticles as nucleation agent able to promote the formation of pPANI. The plasma polymer film was directly deposited onto a commercial Nafion 117 membrane.

As mentioned previously, fuel cell electrodes require three essential properties: they should be electrically conductive, proton conductive and able to trigger a chemical reaction catalyzed by a metal. From the SEM images (Figure 4 A, B), one can see the presence of pPANI-Pt fibers with a diameter range of 50-70 nm. The film that exhibits a total thickness of about 2.5µm, presents a strong interdigitation of pPANI fibers, suggesting a dense 3D porous network. This morphology increases the probability of contacts between the strands, while substantial porosity also offers efficient mass transport. Electrical conductivities were measured on the coated film and were found to be 5. 10^{-3} S. cm^{-1}.

Note that the experiment performed without Pt nanoparticles did not lead to the formation of fibers (Figure 4 C). This point suggests that the presence of functionalized Pt nanoparticles can act as nucleation sites, where pPANI can easily grow during the plasma process.

The amount of Pt contained in the plasma polymer films can be obtained using thermogravimetric analysis (TGA) (data not shown) by completely oxidizing the fibers during analysis. TGA gives a Pt loading of 16 %, which represents 0.09 mg.cm^{-2} of Pt.

The X-ray diffraction (XRD) patterns collected for pPANI-Pt are shown in Figure 5. The diffraction peaks show that Pt nanoparticles are present in the face centered cubic (fcc) structure, as indicated by the characteristic peaks of (111), (200), (220) and (311). The average Pt particle size for pPANI-Pt catalysts was calculated from the broadening of the (220) diffraction peak using the Scherrer equation. The calculated mean Pt particles sizes for pPANI-Pt are 3.4 nm, which is consistent with the TEM observations.

The FTIR spectrum of the pPANI-Pt thin film is presented in Figure 6. The characteristic peaks of emeraldine base form of pPANI were observed in the spectrum at 3260 cm^{-1} (N–H stretching with hydrogen); 3025 cm^{-1} (aromatic C–H stretching); 1532 cm^{-1} (C—C stretching of quinoid rings); 1480 cm^{-1} (C—C stretching vibration of benzenoid rings); and 1290 cm^{-1} (C–N stretching). The absorption band at 1125 cm^{-1} is assigned to N—Q—N bending vibration shift towards the lower wave number that corresponds to the pPANI-Pt emeraldine base. This result further supports the formation of pPANI-Pt using the plasma polymerization technique.

The pPANI-Pt thin film was characterized using a UV–visible spectrophotometer. In the spectrum (Figure 7), the characteristic bands of PANI (emeraldine base) were observed at 310, and 513 nm, due to the π-π^* transition, polaron bands transition, and quinoid unit, respectively. These absorption bands exhibit both excitations of amine nitrogen of the benzenoid segments and imine nitrogen of the quinoid segments of pPANI-Pt. All these features clearly indicate the formation of pPANI by the plasma polymerization.

The performance of the prepared membranes onto the Nafion membrane was tested in PEM fuel cells (Figure 8). The film was used as anode and a standard carbon black (CB) (0.5 mg Pt

per cm^2) based catalyst was used as cathode. H_2 and O_2 are used at the anode and the cathode, respectively. The peak power density of the whole fuel cell was as high as 80 mW cm^{-2}, the obtained value remaining smaller than commercial fuel cells made of carbon black. This limited performance might be due to a low value of conductivity of the pPANI film.

Nevertheless, the Pt utilization, which is considered as one key affecting the practical and commercial prospects of fuel cell technology, can be obtained by dividing the peak power density by the Pt loading. In our case, the Pt utilization was found to be as high as 880 mW/mg_{Pt}, which is a value comparable to those obtained by conventional electrode preparation methods of electrodes. This good value can be attributed to the nanoscale 3D organization of the plasma multilayered film adequate for balancing diverse requirements in the electrodes, and specifically to the significantly improved accessibility of Pt particles at the triple phase boundaries.

Conclusion

In this paper, we demonstrate the potential of atmospheric pressure plasma deposition for the design of conducting polymer-based anodes for hydrogen fuel cells. This work shows that the incorporation of functionalized platinum nanoparticles can act as nucleation sites able to promote the formation of polyaniline fibers during the plasma process. SEM images show that pPANI-Pt electrodes have a strong interdigitation and thus create a dense and extensive 3D network of fibers. This particular morphology increases the probability of contacts between the strands, while substantial porosity also offers promising mass transport. Hence, atmospheric pressure plasma represents an interesting new pathway for creating fast and efficient electrodes for hydrogen fuel cells.

References

[1] R. O'Hayne, D. R. Barnett and F. F. Prinz, J. Electrochem. Soc., 2005, 152, A439–A444

[2] G. Decher, Science, 1997, 277, 1232–1237

[3] T. R. Farhat and P. T. Hammond, Abstr. Pap. Am. Chem. Soc., 2005, 229, U733–U734.

[4] T. R. Farhat and P. T. Hammond, Adv. Funct. Mater., 2006, 16, 433–444.

[5] T. R. Farhat and P. T. Hammond, Chem. Mater., 2006, 18, 41–49.

[6] S. P. Jiang, Z. C. Liu and Z. Q. Tian, Adv. Mater., 2006, 18, 1068-1072.

[7] C. N. Kostelansky, J. J. Pietron, M. S. Chen, W. J. Dressick, K. E. Swider-Lyons, D. E. Ramaker, R. M. Stroud, C. A. Klug, B. S. Zelakiewicz and T. L. Schull, J. Phys. Chem. B, 2006, 110, 21487–21496.

[8] M. Pan, H. L. Tang, S. P. Jiang and Z. C. Liu, J. Electrochem. Soc., 2005, 152, A1081–A1088.

[9] M. Michel, A. Taylor, R. Sekol, P. Podsiadlo, P. Ho, N. Kotov, and L. Thompson, Adv. Mater., 2007, 19, 3859–3864,

[10] M. Michel, F. Ettingshausen, F. Scheiba, A. Wolz and C. Roth, Phys. Chem. Chem. Phys., 2008, 10, 3796–3801.

[11] F. Benitez, E. Martinez, J. Esteve, Thin Solid Films 2000, 377–378, 109-114.

[12] C. Vautrin-Ul, C. Boisse-Laporte, N. Benissad, A. Chausse, P. Leprince, R. Messina, Prog. Org. Coat. 2000, 38, 9–15.

[13] F. Arefi, V. Andre, P. Montazer-Rahmati, J. Amouroux, Pure Appl. Chem. 1992, 64, 715-723.

[14] A.Tiwari,y, R. Kumar, M. Prabaharan, R. R. Pandey, P. Kumari, A. Chaturvedi and A. K. Mishra, Polym. Adv. Technol., 2009, DOI : 10.1002/pat.1470.

[15] R. Y. Korotkov, T. Goff, P. Ricou, Surf. Coat. Technol. 2007, 201, 7207-7215.

[16] G. Borcia, N. M. D. Brown, J. Phys. D: Appl. Phys. 2007, 40, 1927-1936.

[17] J. J.Miasik, A. Hooper, B. C. J. Tofield, Chem. Soc. Faraday Trans. I 1986, 82, 1117-1126.

[18] X. Ma, G. Li, M. Wang, Y. Cheng, R. Bai, H. Chen, , Chem. Euro. J. 2006, 12, 3254-3260.

[19] P. N. Bartlett, S. K. C. Liang, Sens. Actuators B 1989, 20, 287-292.

[20] H. Perez, J. P. Pradeau, P. A. Albouy, J. Perez-Omil, Chem. Mater. 1999, 11, 3460-3463.

Figure caption.

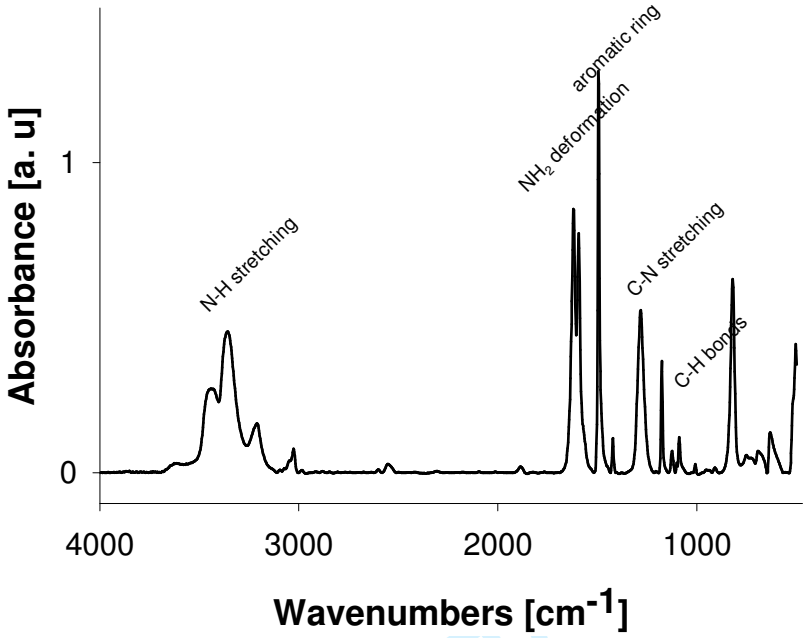


Figure 1. FTIR spectrum of functionalized Platinum nanoparticles with mercaptoaniline.

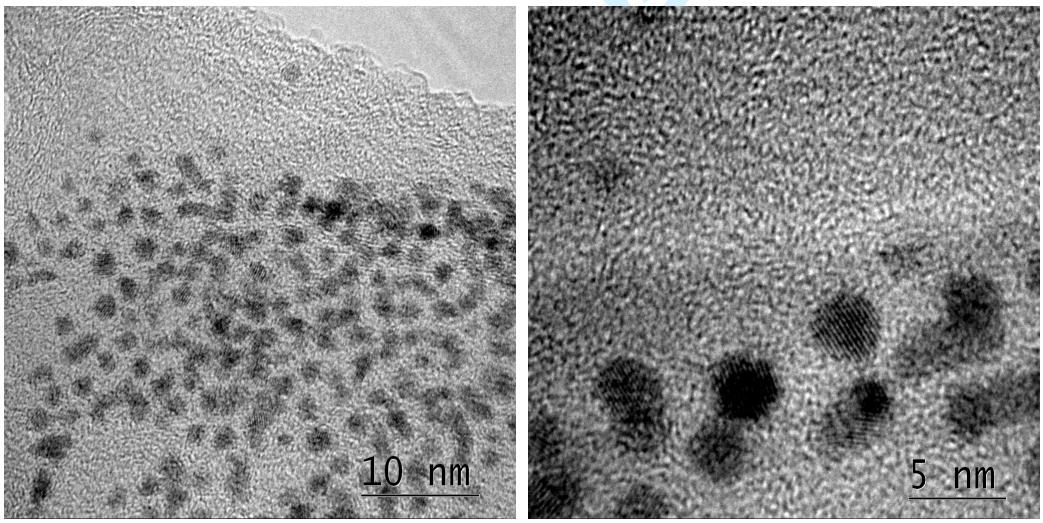


Figure 2. TEM pictures of functionalized Platinum nanoparticles with mercaptoaniline.

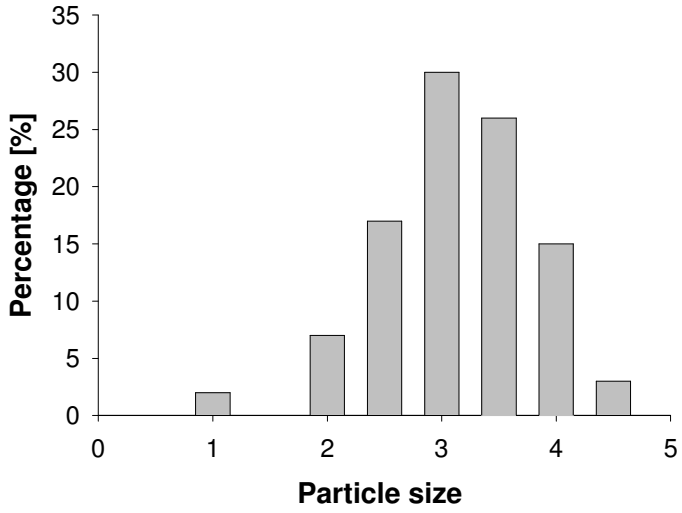


Figure 3. Histogram of functionalized Platinum nanoparticles diameters.

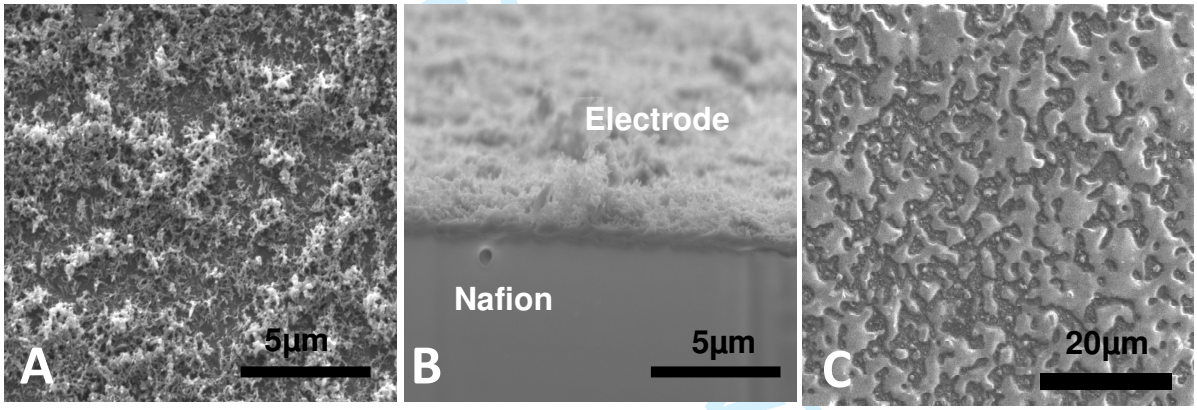


Figure 4. SEM picture of : A) Top-view of pPANI-Pt film coated onto a commercial Nafion 117 membrane; B) Cross-section of pPANI-Pt film coated onto a commercial Nafion 117 membrane; C) pPANI film obtained without Pt.

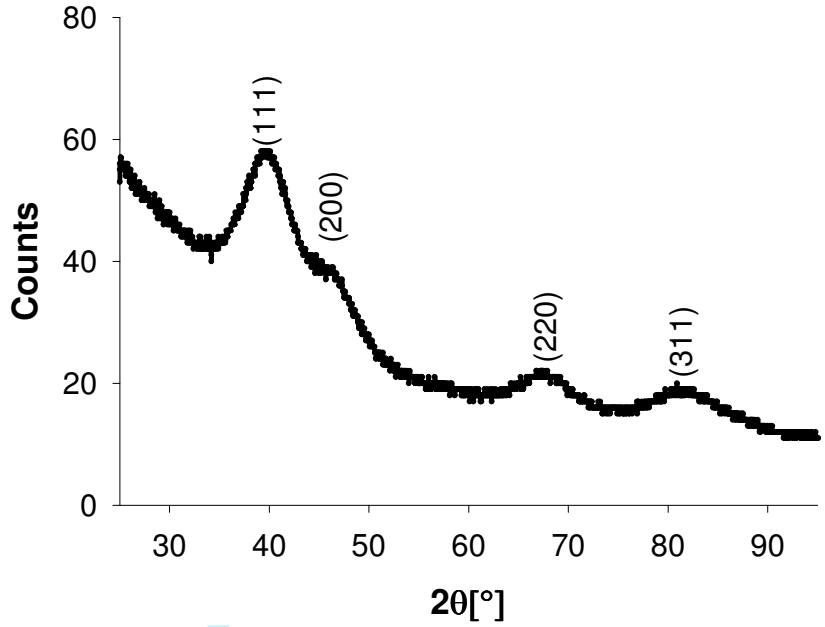


Figure 5. XRD pattern of pPANI-Pt coated onto a commercial Nafion 117 membrane.

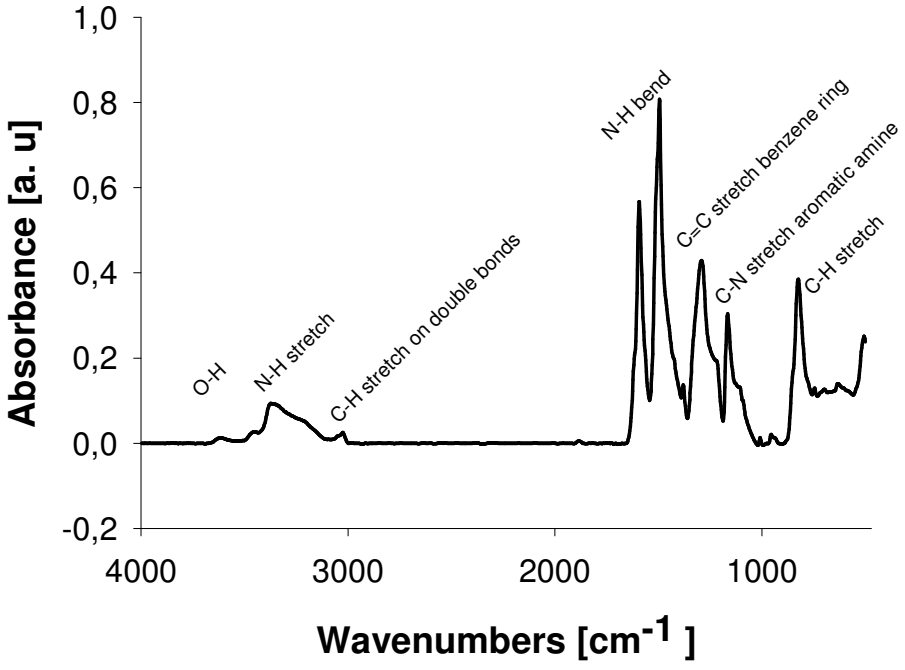


Figure 6. *FTIR spectrum of the coated pPANI-Pt coated onto a Nafion 117 membrane.*

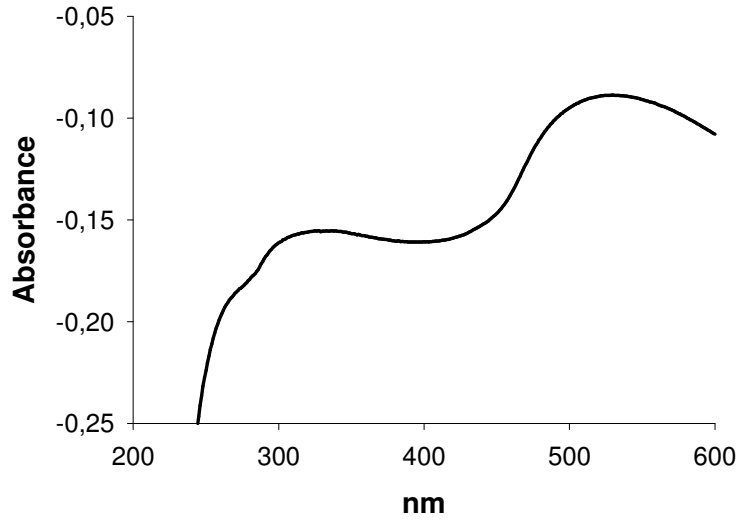


Figure 7. UV-Vis spectrum of pPANI-Pt film coated onto a commercial Nafion 117 membrane.

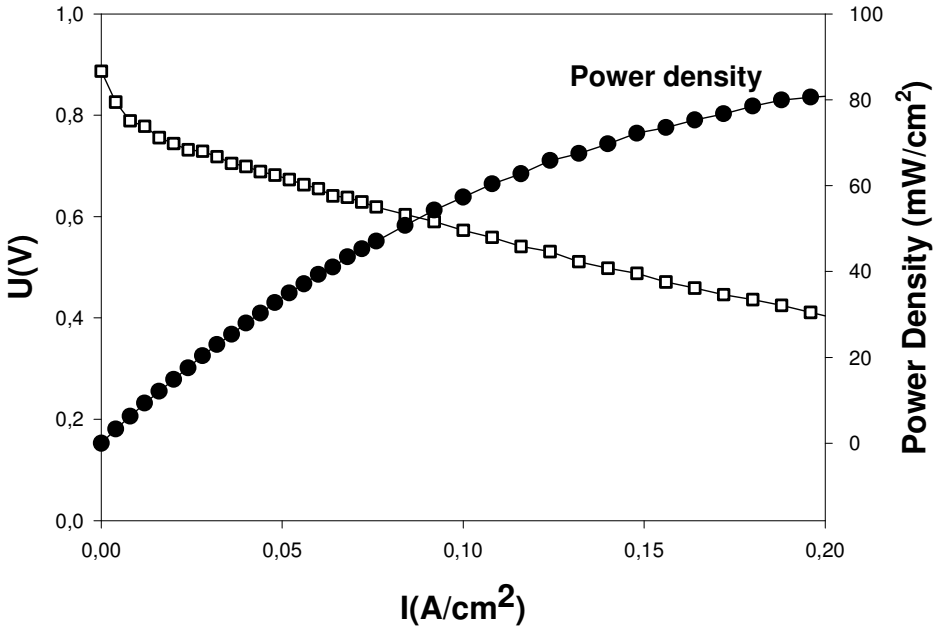
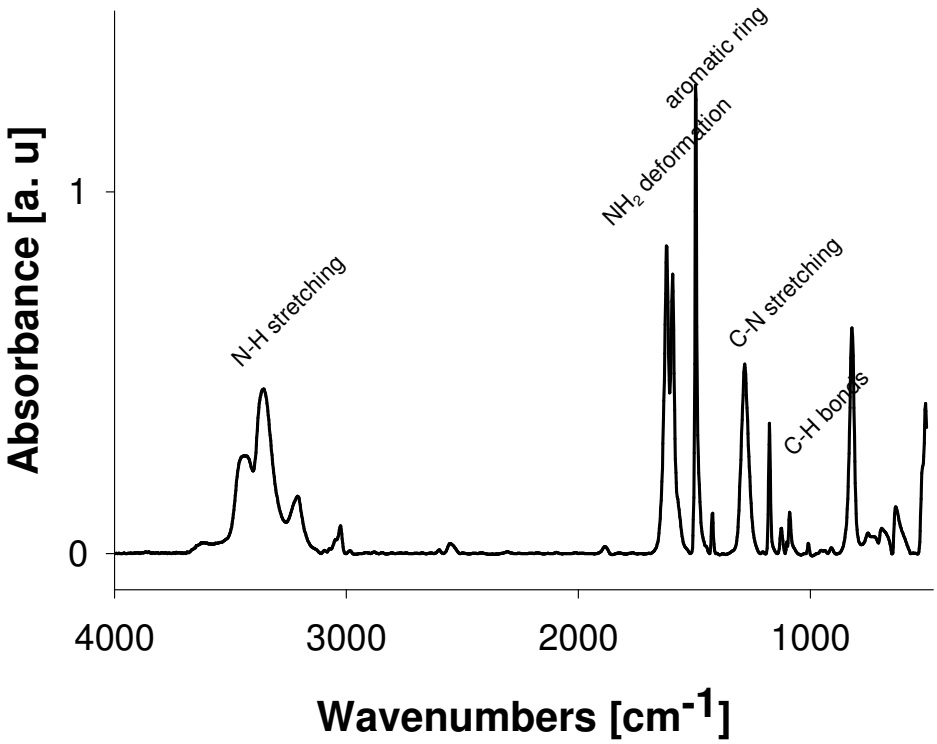


Figure 8. Polarization (□) and power density curve (●) of fuel cell. The fuel cell temperature was 80°C. H_2 and O_2 flows were set at 150 mL. min^{-1} and 75 mL. min^{-1}, respectively.


Absorbance [a. u]
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Wavenumbers [cm-1]
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NH2 deformation
aromatic ring
C-N stretching
C-H bonds

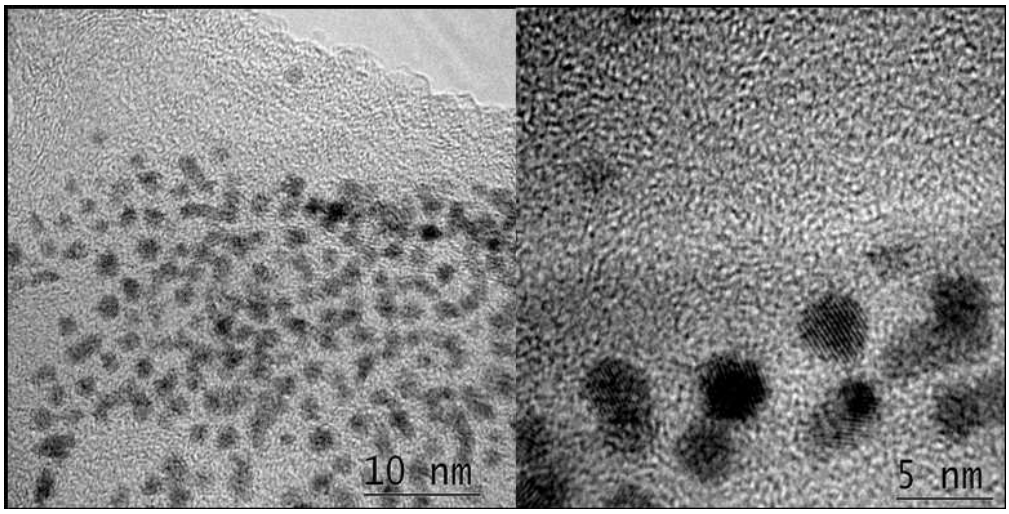

Figure 2. TEM pictures of functionalized Platinum nanoparticles with mercaptoaniline.
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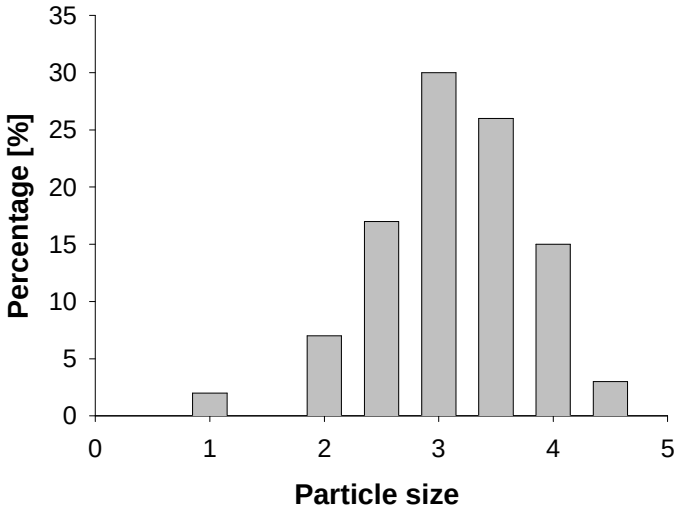

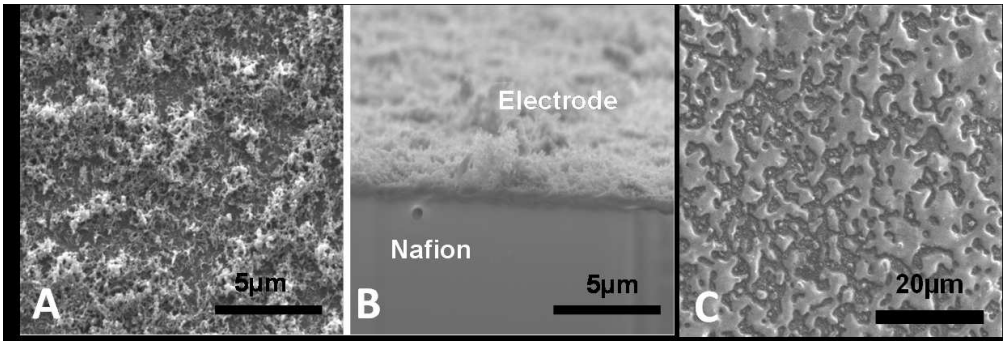

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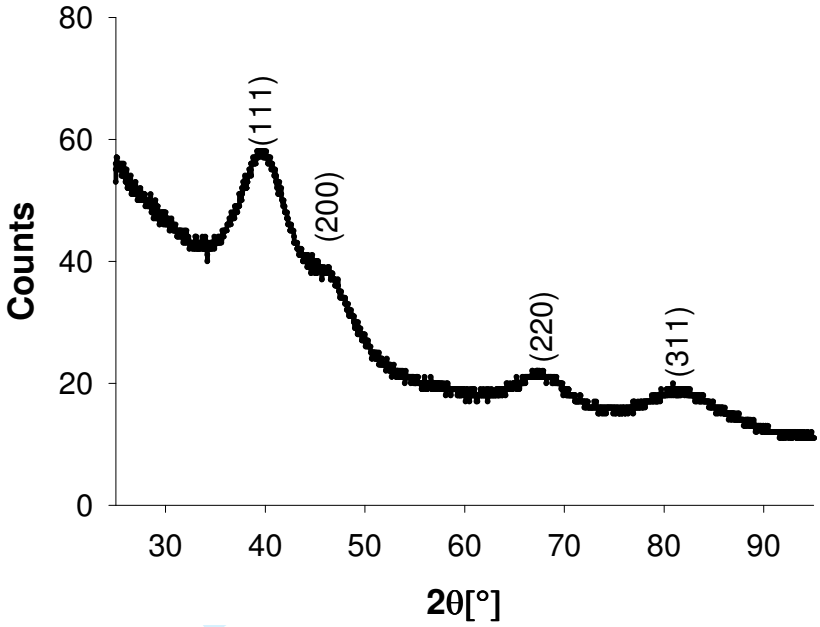
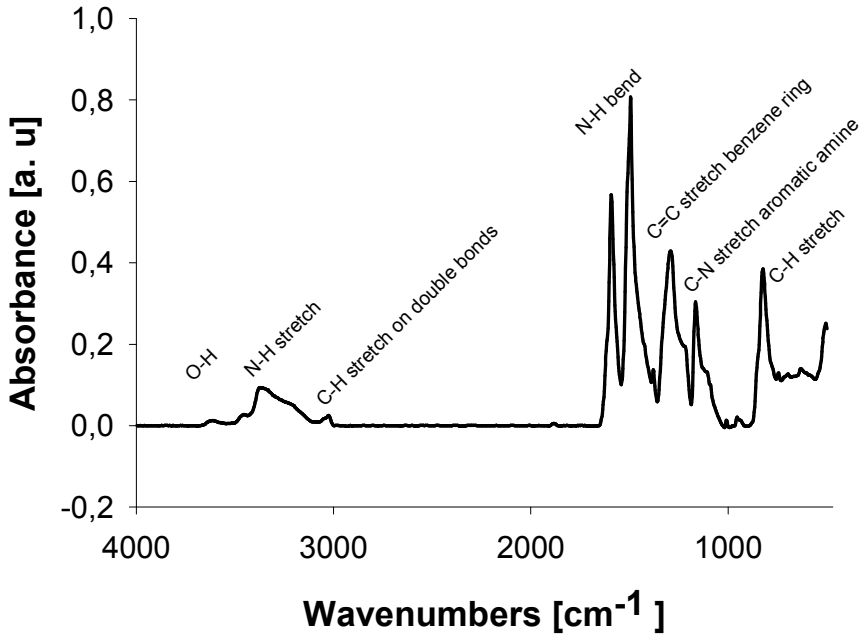
436x146mm (72 x 72 DPI)

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Absorbance [a. u]
4000
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2000
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Wavenumbers [cm-1]
O-H
N-H stretch
C-H stretch on double bonds
N-H bend
C=C stretch benzene ring
C-N stretch aromatic amine
C-H stretch