# Nano architecture MEA for next generation fuel cell

J. Schneider, G. Picard and M.F. Seye
Nanometrix Inc., 329 West, rue de la Commune, suite 200, Montréal (Québec), Canada H2Y 2E1, juanschneider@nanometrix.com

## ABSTRACT

A new method for mass production of Membrane Electrode Assembly Fuel Cell (MEAFC) is presented. The Schneider-Picard (SP) method for industrial monolayer and ultra-thin film deposition has shown a great effectiveness for the production with nano scale architecture for fuel cells. Today, MEA's are built in such a way that no control is possible at the nano scale. Nanometrix process opens a new way showing the importance on the PEM performance of the effective triple contact line made by the contact between the colloidal Nafion, the platinum nano particles and the hydrogen gas access for high efficient catalytic reaction with ultra-low platinum loading.

Nanometrix industrial monolayer allows designing the catalytic reaction surfaces. Similar performance was obtained even after reducing the platinum loading by 100X. Furthermore, platinum-carbon chunks were substituted by the Carbon Nanotubes coated with platinum. Doing so, we were able to verify that the catalytic performance was extremely dependent on the spatial organization of the nano reactors. Platinum-PEM triple contact line and gas access are all important factors that are adjusted with the SP method to web process fuel cell MEA's with innovative nano materials and architecture, deployable now.

***Keywords:*** nanotechnology, fuel cells, web, monolayer, platinum-CNT, catalyst, membrane electrode assembly

## 1 INTRODUCTION

Nanometrix was founded based on a new process for surface architecture at the nanoscale and up. This novel approach was a cherished idea since 1930's when another great inventor, physicist and Nobel Prize winner, developed, at the General Electric's facilities, the first monolayer characterisation tool, the Langmuir method. Mrs. Blodgett added shortly later the transferring principle, forming together the well known Langmuir-Blodgett technique. But, this process never achieved its most important goal: bring monolayers and their properties to the industry. This situation seemed to us like a dam without a turbine.

The SP method was invented to respond to this basic problem. Doing so, many sectors may now benefit from 50 years of fundamental research in the field of monolayers, worldwide.

Energy is one of the most important fields of application. Fuel cells are interfacial devices for catalytic reactions and monolayers are 2D interfacial architectures as well. It was natural for us to see the potential breakthrough.

A monolayer is an assembly of elements stacked side-by-side in an organized manner. So far, four sectors are already in development for specific applications. One of these sectors is the fuel cell electrode. The SP method was proof tested for making continuous high speed production of Membrane Electrode Assembly (MEA) and is described here.

Today, MEA's are built in such a way that no control is possible at the nano scale [1]. Slurries containing colloidal Nafion and carbon chunks (Figure 1) supporting platinum nano dots attached to their surfaces are mixed and "printed" on both sides of a proton exchange membrane (PEM). Performance and costs are the main drivers in MEA's business. Unfortunately, this way of handling nano dots hasn't shown any major improvement.

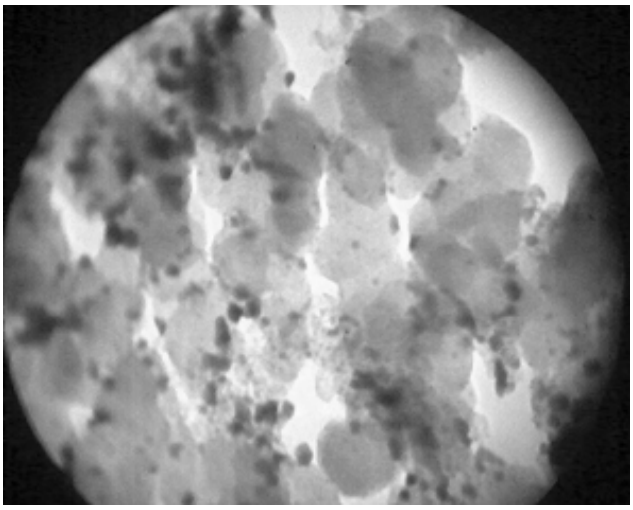

Figure 1: TEM image of carbon-platinum colloidal chunks.

Nanometrix MEA assemblies were bench tested and compared to commercially available MEA's with 0.1 $mg/cm^2$ as well as with a 0.3 $mg/cm^2$ of platinum load on each side of the proton exchange membrane.

Our coatings have shown significant catalytic performance. Similar power densities have been obtained with less than 10X platinum than a commercially available membrane with 0.3 mg/cm$^2$ of platinum loading.

Therefore, we first explain the basic ideas behind the SP method. This is followed by examples of MEAFC and their behavior. A discussion concludes this document with the future trends and new architecture design for catalytic surfaces.

## 2 NANOMETRIX FUNDAMENTALS

Nanometrix presents in this document a breakthrough technology, a new thin film generator concept to make monolayers and engineered surfaces at the nanometric scale, suitable for a vast myriad of applications, and more specifically to the fuel cell energy production. Energy is an important human concern and our approach is showing preliminary encouraging results for the industrial fabrication of Polymer Electrolyte Fuel Cells (PEFC).

In order to avoid confusion with the terminology, a monolayer is defined as a one layer thick assembly of elements. More than 20 different materials in nature and properties have been tested in our present industrial production tool. From nano diamonds to polymers, ceramics and CNT's have been tested successfully obtaining amorphous as well as tightly packed polycrystalline monolayers and ultra thin films. Multilayers have also been fabricated with similar and heterogeneous colloids, clusters, molecules and polymers of different kind. Particles from one nanometer up to colloids of a tenth of a micron have been assembled on flexible and rigid substrates.

Certainly that MEA's are not a straightforward and simple surface structure. This is a functional structure where, spatial organization, environment, humidity, pressure, temperature, gas flow and conductivity have to work simultaneously in a proper manner. This is a complex assembly of heterogeneous materials.

Structural-functional relations and interdependency have been studied by many R&D groups, testing different recipes, most of them from a macroscopic empirical approach. Others have been working through a more theoretical view combining, surface architecture and composition to maximize performance.

The SP method has shown great flexibility in handling the platinum, carbon, Nafion and membrane at once. The process has achieved single pass multilayer as well as the possibility to use a transfer membrane before application of the electrode on both sides of the proton exchange membrane. Multilayer structures have been also produced. Up to three complex assembly layers having a combination of Nafion colloids, platinum and carbon chunks for each layer, one on top of the other, have been produced showing no technical limitations for complex multilayer assembly.

## 3 THE TRIPLE CONTACT LINE: "THE THIN LINE OF EFFICIENCY"

Hydrogen gas is made of a pairs of atoms. The diatomic molecule is separated in two atoms at the surface of the platinum dot. Afterward, the atoms are separated into elementary charges at the triple contact line made with platinum, Nafion and hydrogen gas. Positive charges migrate through Nafion leaving the negative charges to find their path in a conductor, the carbon chunks so far.

With today's fuel cell configuration, a simple mathematical model applied to calculate for a 0.1 mg/cm$^2$ platinum loading, we obtain a total contact line length in the range of about 50 linear km/cm$^2$! This could mean that the catalytic loading (grams/cm$^2$) should be refined to be the parameter to characterize MEA performance. In fact, for a monolayer of nano platinum particles with for instance 10 nm diameter, arranged side by side in contact with a PEM, we obtain roughly the same linear contact length for the same unit surface. An experiment performed with cm$^2$ platinum vacuum deposition [2] validates our approach. Indeed, with the SP method, no vacuum is needed and the process runs at a speed of m$^2$ per minute with our present machine.

As mentioned before, Nanometrix technology is capable of producing MEA's with a performance matching commercially available membranes.

Our first target was to produce a MEA monolayer assembly. This was achieved with different carbon-platinum particles. Secondly, carbon platinum chunks where treated to reduce their average size. After treatment, the particles showed an average diameter of 100 nm. Nafion colloids and platinum nano dots were observed by TEM. Their diameter had a polydisperse size distribution with a mean value of 20 nm in diameter for the first one and 5 nm for the platinum.

It is interesting to point out that at this coating thickness, Nanometrix MEA's looked transparent enough to be able to read through it showing the small amount of platinum used. Figure 2 shows a commercially available 0.3 mg/cm$^2$ platinum load membrane compare to Nanometrix MEA's. Commercially available coated membranes have no light coming through the coated membrane.

Nafion colloids were entrapped in between the carbon chunks carrying the platinum nano dots and the Nafion membrane. The amount of Nafion colloids was tailored for better performance and minimum material needed. We wanted to expose as much as possible the catalytic

reaction sites to the Nafion barrier with less intermediate material.

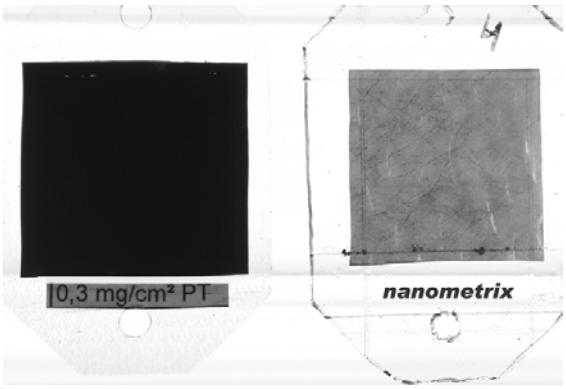


Figure 2: Nanometrix light transmission photography comparison to a commercially available MEA.

Nafion colloids were entrapped in between the carbon chunks carrying the platinum nano dots and the Nafion membrane. The amount of Nafion colloids was tailored for better performance and minimum material needed. We wanted to expose as much as possible the catalytic reaction sites to the Nafion barrier with less intermediate material. Performance was still there. Indeed, compared to a commercially available membrane with a loading of 0.1 mg/cm$^2$ of platinum, our assembly showed similar performance with almost 100X less platinum.

In the market, integrators are looking for membranes with higher energy density. Then, our next milestone was to produce a membrane with power performance comparable to a commercially available membrane, in the range of 0.3 mg/cm$^2$ of platinum. The results are showing almost the same behaviour but with substantially better performance. Indeed, 10X less platinum were needed showing great potential and performance with Nanometrix approach. Figure 3 present these results.

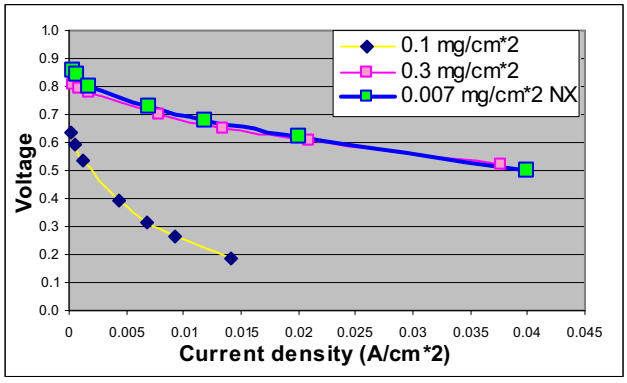


Figure 3: Polarization curves of three different platinum loadings. Nanometrix membrane load is 0.007 mg/ cm$^2$. It matches the 0.3 mg/cm$^2$ commercially available MEA's under the same conditions in our PEM test cell.

## 3 MONOLAYERS VS. SLURRY FILM

The slurry film presents several problems:

*Diffusion*: from one side, hydrogen and oxygen have to diffuse through fine pores. Diffusion being proportional to the fourth power of pore size, the **bigger the particles** are, the better the diffusion.

*Electric contact*: electrons must travel from the platinum to carbon chunks, and then from chunks to chunks up to the electrode. The **smaller the particles** are, the better the contacts.

The proton must travel from the platinum-Nafion-hydrogen triple contact line to Nafion colloid ionic channels to other ionic channels up to the Nafion membrane. The **smaller the particles** are, the better the proton conduction.

*Flooding*: water vapour produced should evacuate at the cathode against in coming oxygen and nitrogen. To avoid flooding, the **bigger the particles** are, the better the gas diffusion.

Fluid dynamics supports these points. Most of the concepts presented above are related to practical facts in many domains of physics and chemistry, and not only on the fuel cell technology.

It is evident that the requests go in opposite directions forcing the industry to fabricate electrodes through the difficult task of well balancing conditions using macroscopic tools. Therefore, all efforts of the present fuel cell industry are concentrated to find the optimum combination. It is possible to foresee that a monolayer of pure platinum colloids would have no problems with the hydrodynamic flow, more particularly with:

- Diffusion
- Electric contact
- Ionic channels
- Water flooding

The platinum surface and triple point are access free. The efficiency is therefore improved since the in and out flows do not have major restriction. It is expected that the yield with monolayer of platinum colloids will be at least an order of magnitude higher than the slurry film. The total mass of platinum onto the membrane should be in the order of the micrograms per square centimetre.

Due to the near molecular size of platinum nanodots, it is probable that such a monolayer on the Nafion membrane would need a performing larger structure like Carbon Nanodots. Its surface to volume ratio interfaces well Nafion and electrodes.

## 4 CARBON NANO TUBES

Carbon Nano Tubes (CNT) are of great performance. Extremely strong, flexible and with high conductivity, it seems to be a material of great potential for the fuel cell application. Several research groups have shown interest on the possibilities with carbon nano tubes (CNT) as platinum colloids support and charge carriers [3-5].

Further research guided us to see how nanotubes could be handled by our process. The SP Method showed easiness in handling this novel material. CNT's were pre treated by a new method for platinum dots adsorption on the surface of CNT's. This new catalytic material is under study and performance tests. Further data will be presented on the poster about recent results with platinum-CNT's.

Figure 4 is a TEM picture of CNT's mat with platinum nano dots on their surface. Our first approach was to deposit the CNT-platinum assembly in the same way that carbon chunks were deposited on Nafion membrane.

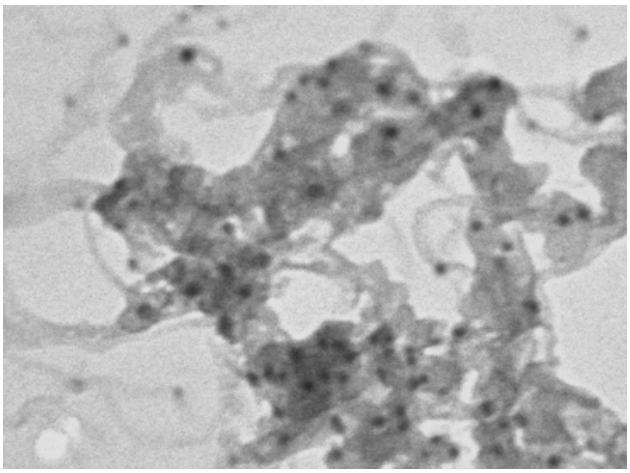

Figure 4: TEM image of platinum-CNT's mat.

## 5 COATED GDL's

Further development has been done with the gas diffusion layer (GDL) [6]. GDL can be also treated to be the receiving substrate where the catalytic reaction will take place. This eliminates the need of carbon chunks or other electric contact material. Platinum monolayers, combined with Nafion colloids are laid down and attached to the GDL closest fibers to the Nafion membrane. This approach is also currently tested in our facilities.

## 6 CONCLUSION

The Schneider-Picard method is a breakthrough technology. It is showing encouraging results in different domains of application. This technology can handle commercially available material used by the present fuel cell industry. New materials like CNT's have been successfully pre treated to carry platinum colloids becoming a possible substitution for the carbon chunks. Further development is in progress to improve efficiency and doing so, improving performance at the lowest cost possible.

The method has shown great versatility as well as ease of use, making the near future promising for significant advancements in the fuel cell industry.

## REFERENCES


[1] V. Mehta and J. S. Cooper, Review and analysis of PEM fuel cell design and manufacturing, Journal of Power Sources 114, 2003, pages 32-53

[2] R. O'Hayre, S.-J. Lee, S.-W. Cha and F. B. Prinz, A sharp peak in the performance of sputtered platinum fuel cells at ultra-low platinum loading, Journal of Power Sources 109, 2002, pages 483-493

[3] Z. Liu, X. Lin, J. Y. Lee, W. Zhang, M. Han and L. M. Gan, Preparation and Characterisation of Platinum-Based Electrocatalysts on Multiwalled Carbon Nanotubes for Proton Exchange Membrane Fuel Cells, Langmuir 18, 2002, pages 4054-4060

[4] C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, and Y. Yan, Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes, Nano Letters Vol.4, No.2, 2004, pages 345-348

[5] W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zhou, G. Sun and Q. Xin, Preparation and Characterization of Multiwalled Carbon Nanotube-Supported Platinum for Cathode Catalysts of Direct Methanol Fuel Cells, J. Phys. Chem. B 107, 2003, pages 6292-6299

[6] E. Antolini, Recent developments in polymer electrolyte fuel cell electrodes, Journal of Applied Electrochemistry 34, 2004, pages 563-576