



# Nanotubes array electrodes by Pt evaporation: Half-cell characterization and PEM fuel cell demonstration



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## ABSTRACT

A self-standing nanotubes (NTs) array electrode is produced by electron beam evaporation of Pt on porous alumina templates. NTs have a mean diameter ranging from 150 to 300 nm, a length of 150 nm and a wall thickness of 20 nm. The ultrathin electrode has a density ranging between  $10^9$  and  $4 \times 10^9$  NTs  $\text{cm}^{-2}_{\text{geo}}$  with a corresponding catalyst loading of  $100 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}_{\text{geo}}$ . The NTs are assembled on a Nafion<sup>®</sup> membrane to obtain a NTs Array based Membrane Electrode Assembly (NTA-MEA) for Polymer Electrolyte Membrane Fuel Cells (PEMFCs) application. Ex-situ half-cell tests are carried out on  $0.5 \text{ cm}^2_{\text{geo}}$  samples to characterize the electrochemical properties of the NTs array electrode. PEMFC tests are also performed on  $17 \text{ cm}^2_{\text{geo}}$  samples to demonstrate the great potential of this architecture as fuel cell cathode under real operating conditions. Comparisons with Pt/C dispersions are made to draw conclusions on the advantage of the NTs array on conventional electrodes in terms of catalyst utilization. The NTs array shows improved catalyst accessibility due to the absence of the porous carbon support. Double current density per catalyst unit surface over Pt/C dispersions is measured at 0.6 V during PEMFC tests under dry  $\text{O}_2$  and air with 30%RH humidification.

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## 1. Introduction

Conventional PEMFC electrodes are made of Pt nanoparticles dispersed in a porous carbon matrix (Pt/C) [1]. These systems show high active surface values ( $50\text{--}100 \text{ m}^2/\text{g}_{\text{Pt}}$ ) due to the small size of the dispersed catalyst particles (3–nm average size) [2], they are effective and easily adaptable to a large scale industrial production. In spite of this, several issues are still connected with this type of electrode. Pt nanoparticles show reduced surface specific activity towards the Oxygen Reduction Reaction (ORR) [3,4]. The durability of a Pt/C electrode is limited by the degradation of the carbon support and by the loss of Pt surface area through the potential-driven dissolution and agglomeration mechanisms [5–7]. The tortuosity of the active layer, related to the presence of the porous carbon support, induces strong limitations to the transport of reactants and products [8].

Huge effort has been recently addressed to the improvement of PEMFC catalyst layers, to overcome the previous issues and boost the ORR reaction at the cathode side. Several works focused on

the development of new supports [9–14] and catalysts [15–17] to achieve higher stability and activity. Nevertheless substantial improvements can hardly be obtained by keeping carbon supported architectures, while they seem to be possible by adopting new self-supported nanostructures [18–23].

In particular self-supported catalyst nanotubes have been indicated as possible ways to approach the high catalyst surface activity of bulky Pt while getting rid of the porous carbon support. These features should eliminate the problems connected with the dissolution and agglomeration typical of dispersed catalyst nanoparticles. The absence of the carbon support should erase the carbon corrosion and should mitigate the mass transport limitations of reactants and products in the active layer.

Recent works have been carried out with the aim to electrochemically characterize the behavior of self-supported catalyst nanotubes [24–29]. These works mainly consist of ex-situ Rotating Disc Electrode (RDE) experiments during which a pure electrocatalyst is in direct contact with the acid electrolyte solution. In this experimental arrangement, nanotubes are usually dispersed without forming an ordered array and are not included in a real electrode structure.

Catalyst surface activity towards Oxygen Reduction Reaction (ORR) is usually evaluated at 0.9 V vs RHE. A 3–4 fold improvement

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in surface activity over Pt/C dispersions is usually reported for these materials underlining excellent catalytic properties for such a kind of nanotubular structures.

In this frame RDE experiments are extremely useful to define the catalytic properties of a pure electrocatalyst, but they do not allow drawing conclusions on its behavior when part of a gas diffusion electrode assembled with a PFSA ionomer membrane. Furthermore, during PEMFC operation the catalyst is in direct contact with gas phase, the demanded current density is normally higher than during RDE experiments and the operating voltage is lower than 0.9 V.

Actually, when current is increasingly demanded, the operating point of a PEMFC shifts out of the active region of the polarization curve. In this situation, mass transport phenomena become progressively more important and the electrode mass transport losses might become predominant over the charge transfer losses. Testing catalyst nanotubes in a real electrode arrangement under conditions more similar to a real fuel cell operation would spread clarity on the effective benefit of this innovative support-free electrode structure. In this view, the test of directional arrays, instead of randomly dispersed nanotubes, is of particular interest since it might improve mass transport in the fuel cell active layer.

Directional electrode architectures have been successfully presented in the literature, where aligned arrays of carbon nanotubes have been successfully used as supporting catalyst structure [30,31]. This structure allows for a better utilization of the electrodes catalyst even though it keeps a carbon supporting structure.

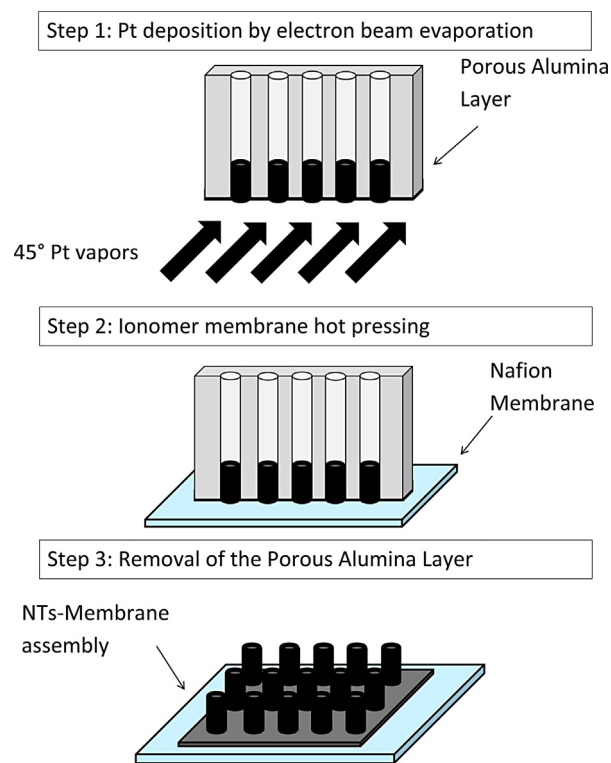
In this work we present the production, the electrochemical half-cell characterization and the fuel cell test of an innovative membrane electrode assembly based on an array of self-supported Pt nanotubes.

The interest of such a new architecture as cathode of a fuel cell during real operation is demonstrated. Considerations about the advantage of the nanotubes array as fuel cell cathode in comparison to Pt/C dispersions in terms of catalyst utilization are drawn. To the authors' knowledge, the test of a Membrane Electrode Assembly based on an ordered Array of support-less catalyst Nanotubes (NTA-MEA) during PEMFC operation represents a novelty and helps in spreading clarity on the effectiveness of NTs for fuel cell energy conversion.

## 2. Experimental

### 2.1. Nanotubes array and MEA fabrication

The Pt-NTs array is produced by deposition of a controlled thin layer of Pt onto sacrificial templates of porous Anodic Aluminum Oxide (AAO, Anopore 47<sup>®</sup> by Whatman Ltd., diameter: 47 mm, thickness: 60  $\mu\text{m}$ , average pore size: 200 nm) [32,33]. The deposition is carried out by Electron Beam Evaporation (EBE) using a commercial evaporator (MEB 550S, PLASSYS SA) by optimizing an available methodology [34]. During the deposition process, the AAO template is mounted on the rotating stage of the evaporator load lock chamber in face-down position. An energy intensive beam of electrons is directed towards the Pt target which is located in the evaporator's process chamber, below the AAO sample. The Pt target is consequently warmed up by the electron beam up to the evaporation temperature, Pt vapors are therefore released and redeposit on the rotating AAO template. The process takes place under vacuum pressure ( $1.5 \times 10^{-6}$  Torr) and the Pt vapors are therefore collimated. The rotating speed of the turning stage was  $15^\circ \text{s}^{-1}$  and the incidence angle between the collimated Pt vapors and the AAO sample was set at  $45^\circ$  by tilting the rotating stage. A Pt amount of 75 nm estimated on a horizontal surface is evaporated with a speed rate of  $0.25 \text{ nm s}^{-1}$ . This resulted in a 20 nm thick Pt layer on the tilted



**Fig. 1.** Schematic drawing of the 3 steps fabrication process of the NTs array based membrane electrode assembly (NTA-MEA).

surface of the porous AAO layer, which corresponds to a loading of  $100 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}_{\text{geo}}$ .

The Pt coated AAO template was stuck onto a Nafion<sup>®</sup> HP membrane (thickness: 20  $\mu\text{m}$ ) by hot pressing at  $135^\circ \text{C}$  for 10 min with a pressure of  $340 \text{ N cm}^{-2}$ , by putting the Pt-covered side in contact with the polymer layer. This step allows achieving a full adhesion of the AAO/Nafion<sup>®</sup> membrane assembly is immersed into NaOH [1 M] for 1 h to dissolve the AAO template. As a consequence, an array of free-standing Pt NTs is left on the Nafion<sup>®</sup> electrolyte membrane forming a NTs array based Membrane Electrode Assembly (NTA-MEA) for PEMFC use. After fabrication, the NTA-MEA is rinsed in ultrapure water (Millipore<sup>®</sup> grade) to wash away possible impurities resulting from the AAO etching. The assembly is subsequently immersed into  $\text{HNO}_3$  [1 M] for 1 h in order to re-acidify the membrane and to remove any eventual metallic cations and organic impurities. A new cleaning in ultrapure water (Millipore<sup>®</sup> grade) is finally done. This straightforward template-based methodology is schematically shown in Fig. 1 and allows obtaining nanotubes based MEAs in a fast and reproducible way. The adhesion of the NTs array electrode on the Nafion<sup>®</sup> membrane is excellent and the resulting NTA-MEA is ultrathin, flexible and includes no carbon support.

### 2.2. Pt/C dispersion electrodes fabrication

Two conventional Pt/C supported electrodes were fabricated in order to make comparisons with the NTs array electrode. The first electrode (hereon named Pt/C-SE electrode) was fabricated by spraying a catalyst ink (Tanaka 50 wt% onto Vulcan XC72) on a SGL-24BC gas diffusion layer support. The spraying was optimized by subsequent tries until the same ECSA of the NTs array electrode was obtained. The final loading of the Pt/C-SE electrode is  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}_{\text{geo}}$ , the average active layer thickness is less than 1  $\mu\text{m}$  (cross section view available in Fig. S1(a) in the supplementary

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