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Polydopamine as a promising candidate for the design of high performance and corrosion-tolerant polymer electrolyte fuel cell electrodes

Hongtao Long [c], Doriane Del Frari [c], Arnaud Martin [c], Joffrey Didierjean [c], Vincent Ball [a, b], Marc Michel [c, *], Hicham Ibn El Ahrach [c]

[a] *Unité INSERM 1121, Faculté de médecine, 11 rue Humann, 67085 Strasbourg Cedex, France*

[b] *Université de Strasbourg, Faculté de Chirurgie Dentaire, 8 rue Sainte Elisabeth, 67000 Strasbourg, France*

[c] *Luxembourg Institute of Science and Technology (LIST), Materials and Research Technology (MRT), 5 Avenue des Hauts-Fourneaux, L-4362 Esch/Alzette, Luxembourg*

HIGHLIGHTS

- Incorporation of polydopamine (PDA) into PEMFCs electrode architectures.
- PDA promotes the proton conductivity and protects electrodes against corrosion.
- PEMFC shows a power density of 780 mW cm^{-2}.
- Pt utilization is one order of magnitude higher than for standard electrodes.

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ABSTRACT

Carbon materials such as carbon black or nanotubes suffer from degradation when subjected to harsh conditions occurring in a Polymer Electrolyte Membrane Fuel Cells (PEMFCs) electrode. Hence, nowadays it is more and more important to search for alternative support materials. The present work shows the results for the incorporation of alternative materials into PEMFCs electrode architectures. Commercially available Multi-Walled NanoTubes (MWNTs) are used as a support for Pt nanoparticles in combination with Polydopamine (PDA). The role of MWNTs is to confer a high electronic conductivity and help to form a porous network. On the other side the role of polydopamine is both to promote the proton conductivity similarly to ionomers such as Nafion and to protect the MWNTs against corrosion. The fuel cell polarization test shows a maximum power density of 780 mW cm^{-2} and a Pt utilization of 6051 mW mg$^{-1}_{(Pt)}$. The Pt utilization reached in this work is almost three times higher than for Pt/MWNTs electrodes containing the same Pt loading. Beside this, it is also shown for the first time that PDA serves as protective layer against carbon corrosion.

1. Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are considered as promising clean energy converters for future applications such as stationary, portable, and automotive applications [1,2]. However, their market launch is far for being ready due to the high cost of the membrane and the catalyst. Indeed, the price is related to the amount of noble metal, which is mostly platinum. In order to circumvent this problem, the use of carbon decorated with Pt nanoparticles along with the use of Nafion® as a proton conductive media has already proven that it is possible to reduce the loading of Pt (from 4 mg$_{(Pt)}$ cm^{-2} to 0.5 mg$_{(Pt)}$ cm^{-2} in the electrode layer) [3] allowing to enhance the Pt utilization. Note that in conventional Membrane Electrode Assemblies (MEAs) only 10% of the available Pt is accessible for the catalysis [4]. Consequently, one of the most important challenges in PEMFC research is to decrease the Pt loading in accordance with a high Pt utilization.

It is well established that the Pt utilization is typically linked to

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* Corresponding author.
E-mail address: marc.michel@list.lu (M. Michel).

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the Triple-Phase Boundary (TPB) which corresponds to the unit of reactant, electrolyte and the catalyst and which is responsible for the performance in terms of power densities of a PEMFC [5]. In order to effectively use the catalyst, the TPB (located in the MEAs), has to find the right la balance between the electronic and the ionic conducting media, allowing a continuous pathway of the electrons to the electrode and the protons to the electrolyte. Moreover, the porosity of the catalyst environment must allow the reactants and the products of the reaction to easily diffuse through these TPBs. Hence, an optimization of these interfaces can be obtained thanks to the fine tuning at the nanoscale level of the electrode structure. Up to now, plethora of methods were developed such as ink-jet printing [6,7], sputtering [8], and others [9] allowing to optimize the electrode assembly at a low platinum level.

For example, Taylor et al. [6] applied an inkjet-based printing technique able to design PEMFC electrodes layers directly deposited onto a Nafion® membrane. In this work, the anode made of commercial 20% Pt/C catalysts with a loading of 0.021 $mg_{(Pt)}$ cm^{-2} yielded a Pt utilization of about 17 600 mW $mg^{-1}_{(Pt)}$ in a H_2/O_2 fuel cell. In comparison O'Hayre et al. [10] designed MEAs consisting of sputtered Pt films on both sides of a Nafion® membrane whose thicknesses were around 5 nm and yielding 60% of the power output of a commercial MEA. Nevertheless, such methods require ultra high vacuum conditions, costly and appropriate equipments. Moreover the limited Pt deposition into only two dimensions and the lack of uniformity of sputter coating over a large surface area constitute the main drawback of such a deposition method.

Recently, a versatile technique was applied for the development of fuel cell electrodes: the “layer-by-layer” (LBL) assembly [11–13] developed by Gero Decher [14]. This technique consists in alternately adsorbing oppositely charged polyelectrolytes on substrates by dipping or spraying [11,12]. Very high performance of Pt utilization was obtained with this dipping technique and values of Pt utilization as high as 3400 mW $mg^{-1}_{(Pt)}$ were reached. Nevertheless the dipping LBL remains still time consuming and not suitable for in-line process [15]. Izquierdo et al. demonstrated that the spraying method can replace the dipping method allowing to speed-up the LBL assembly by a factor of about 100 [16]. By comparing dipping with spraying methods, these authors observed that spraying can be of asset for designing homogeneous films exhibiting a reduced roughness. Moreover, Izquierdo et al. suggested that the rinsing step could be skipped between each spraying deposition step thanks to the drainage occurring during spraying. In previous work, we showed that the sprayed LBL technique is suitable for the fabrication of hydrogen fuel cell MEAs containing different catalysts [17]. Here, the amount of Pt used was almost two times lower than for standard carbon supported Pt catalyst MEAs. More recently [18], we used an approach inspired from our previous work in order to manufacture “fast prepared” electrodes based on the sprayed LBL assembly of oxide particles under heat treatment. We proved that such a process can accelerate the manufacturing even more thanks to the drying step when one layer is sprayed onto the membrane. In this case, no drain of the excess solvent occurs, which could flush away the precious catalyst. The idea behind concerns the fact that we were able to both increase the porosity in the multilayer structure and to limit any material loss in a fast manner making this method extendable to an in-line fabrication process of MEAs. Moreover, high values of Pt utilization were obtained (the Pt utilization for the multilayer MEA was 1468 mW $mg^{-1}_{(Pt)}$.

Another crucial factor affecting PEMFC performances concerns in particular the catalyst support such as for example carbon black or carbon nanotubes. These materials suffer from degradation when subjected to the harsh conditions occurring in a polymer electrolyte membrane fuel cells (PEMFCs) electrode. Hence, nowadays it is more and more important to search for support materials able to withstand such hard conditions. In this work we propose to build electrodes made of carbon nanotubes and polydopamine. PDA has been widely studied and emerged as a highly versatile bio-inspired coating for the development of efficient adhesive primers [19]. Moreover, PDA presents several advantages such as:

i) the strong binding between PDA and Pt precursor thanks to the presence of catechol and amino groups [20],
ii) the $\pi-\pi$ interaction between PDA precursors (in particular dopamine) and graphitized carbon structures such as carbon nanotubes [21],
iii) the hydrophilicity of PDA and the controllable thickness of PDA films deposited onto carbon nanotubes [22].

Carbon nanotubes are well known for their excellent electric conductivity and high surface area which are essential for good Pt electrocatalytic activities. Carbon nanotubes have been reported to form interconnected conducting networks [23]. This feature tends to increases the contact between loaded Pt catalyst and the electrolyte. Moreover the simultaneous presence of hydrophilic catechol and amine groups in an electrode could be suitable to increase the probability of having excellent proton conductivity. Consequently, we are strongly convinced that carbon nanotubes decorated with Pt nanoparticles and wrapped with PDA could be an interesting structure able to enhance both electric and proton conductivities and protect the carbon material from oxidation usually occurring in the PEMFC harsh conditions. Indeed, standard carbon supports, such as carbon black for example, tend to corrode in environments of high water content, acidic pH, elevated temperatures (50–90 °C), high potential (0.6–1.2 V), and high oxygen content. Moreover, the presence of platinum also accelerates the carbon corrosion [24]. As a result, the support material is degraded and the performance of the cell strongly decreases leading to a total collapse of the electrode structure. Based on our previous observations [25], we fabricated here a novel electrocatalytic active $(Pt/MWNTs\text{-}PDA)_{50}$ multilayered nanocomposite film via spray deposition. The size and the distribution of Pt nanoparticles were investigated by transmission electron microscopy (TEM). X-ray Photoelectron Spectroscopy (XPS) was performed in order to prove the presence of PDA in the film. Electrochemical analyses were also made on the films to measure the electrochemical surface areas with and without PDA as well as the stability of the electrodes against oxidation. Polarization curves were also performed to measure the performance of the multilayered electrodes with and without the presence of PDA. In this article, we show that Pt/MWNTs-PDA are very promising candidates yielding high power densities. Moreover, this work clearly highlights the fact that PDA is able to both improve the performance of PEMFC and to protect the electrode against oxidation.

2. Experimental

All materials were used in this study as received from Sigma-Aldrich. Multi-walled carbon nanotubes MWNTs (ref. 698849), and Nafion 117 solution (5% Nafion® 1100 in a mixture of lower aliphatic alcohols and water) were also purchased from Sigma-Aldrich.

Commercially available carbon supported Pt catalyst (20 wt.-% Pt on Vulcan XC-72, Johnson Matthey, Pt/CB) was used as reference.

2.1. Functionalization of MWNTs with Pt

100 mg multi-walled carbon nanotubes (MWNTs) in 20 ml ethylene glycol (EG) were stirred under sonication for 10 min,