

Deposition and diffusion of platinum nanoparticles in porous carbon assisted by plasma sputtering

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Abstract

Catalytic nano-clusters of platinum are deposited by high density plasma sputtering into porous carbon gas diffusion layers for low temperature fuel cell electrodes. This plasma process leads to the deposition of catalyst onto the surface of the substrate and assists its diffusion in the carbon layer. In this work, we discuss the influence of the plasma parameters on this diffusion of platinum.

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1. Introduction

The low temperature fuel cell is a promising power source due to its high energy conversion efficiency for portable, transport and stationary applications. Nevertheless, several technical and scientific locks must be solved to compete with traditional power sources. Among them a critical step is to lower catalyst content and adjust consistently the catalyst profile in the so-called gas diffusion layer (GDL) in order to improve the fuel cell efficiency [1]. At the heart of the PEM (see Fig. 1) is the membrane electrode assembly (MEA).

The MEA is sandwiched by two flow field plates. The MEA consists of a dense proton exchange membrane, porous catalytic layers, and porous gas diffusion layers (GDL). Their thicknesses are typically 150, 10 and 50 μm , respectively, but it depends on the fabrication method. These components are fabricated individually and then pressed together at high temperature (140 °C) and pressure (35 kg/cm^2). The interface between the membrane and the electrode is critical. [1].

Part of the optimization of an electrode design is the attempt to correctly distribute the amount of volume in the catalyst layer between the transport media for each of the three phases (electrons, protons and gases) to reduce transports losses. This catalyst layer is either applied to the membrane or into the gas diffusion layer. In either case, the objective is to place the catalyst particles, platinum or platinum alloys in close proximity with the membrane, the carbon particles and the gas fed pores. An effective electrode correctly balances the three transport processes shown in Fig. 2:

- protons from the membrane to the catalyst;
- electrons from the current collector to the catalyst through the gas diffusion layer;
- the reactant and product to and from the catalyst layer and the gas channel.

2. Experiments

Many methods are commonly employed to form catalyst layers: chemical deposition such as colloidal, carbonyl, chemical impregnation from salts. Physical deposition such

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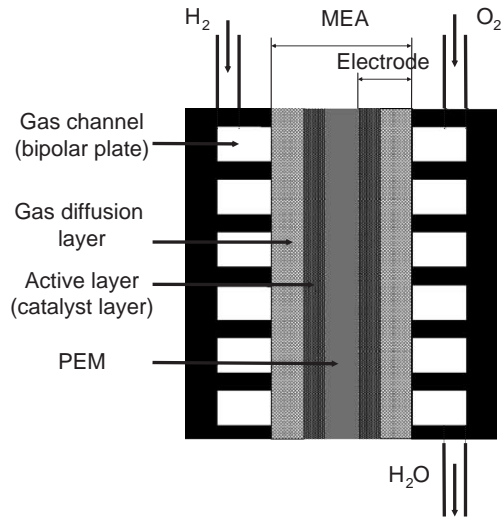


Fig. 1. Schematic of a proton exchange membrane fuel cell.

as sputtering is less often used but is a promising technique due to the control of the catalyst content [2–10]. In this work we used plasma sputtering with a TCP (Transformer Coupled Plasma) antenna. This process consists of a vacuum evaporation process that removes portions of a coating material (the platinum target in our case) and deposits a thin film of the target material into an adjacent porous gas diffusion layer. A low pressure Radio Frequency (RF) inductive plasma sputtering system has been constructed (APRIM VIDE) as displayed in Fig. 3. 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 at an argon pressure of 5×10^{-3} mbar. The excitation antenna is powered by a tunable frequency generator operating for the present experiments at 13.56 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

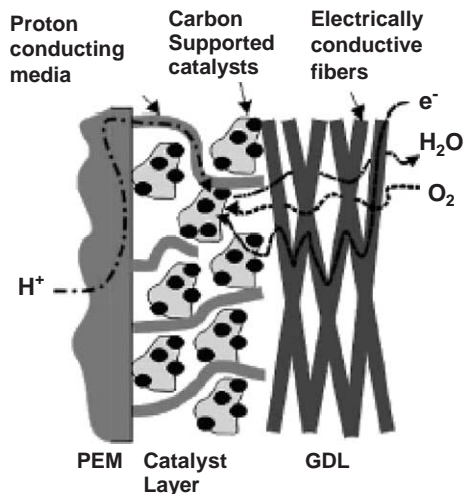


Fig. 2. The three transport processes in a PEM fuel cell.

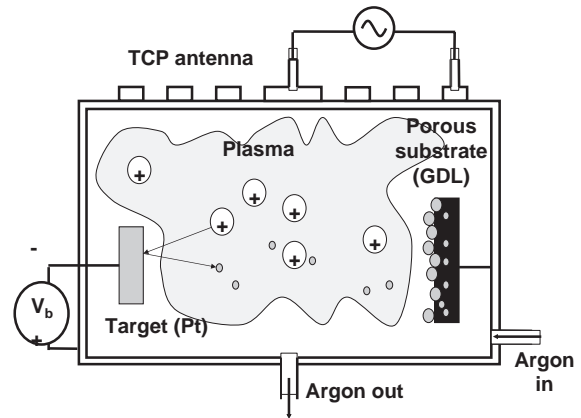


Fig. 3. Schematic of sputtering in argon TCP plasma.

$P_0 = 2.10^{-8}$ mbar could be achieved using a primary/turbomolecular pump combination and during the experiment, an argon flow is fixed to 5 sccm using a mass flow meter.

The uncatalyzed porous gas diffusion layer is thus exposed to a flux of platinum, which then diffuses into gas diffusion layer. This diffusion can be the result of different physical and/or thermal phenomena: (i) local warming of the porous substrate due to ions bombardment, (ii) jump of platinum atoms in the vacuum pores due to its energy gained either during the sputtering process or to the energy brought to the substrate by argon ion bombardment. Substrate is a commercial E-TEK uncatalyzed GDL. Platinum is deposited on a carbon black (80 wt.%) and PTFE (20 wt.%). Mean carbon black particle size is 30 nm. Rutherford Backscattering Spectroscopy measurements were performed to determinate the Pt content depth profile into the electrode diffusion layer. A 2-MeV α beam produced by the Orléans Van de Graaff accelerator is directed onto the Pt catalyzed diffusion layer and α particles are backscattered after colliding with the target. α particle scattered energy depends on the atomic mass and depth of the scattering element.

3. Results and discussion

Fig. 4 show RBS spectra of several successive platinum deposited GDL. The left side of the spectrum, at low backscattering energies, corresponds to carbon and fluorine atoms of the GDL, whereas on the right side, the asymmetrical peak originates from α particles scattered by Pt atoms. The area under the Pt peak is directly related to the number of the platinum atom in the diffusion layer. The tail on the left side of the Pt peak indicates that atoms have diffused into the porous substrate. A program calculating RBS spectrum with arbitrary analytical test depth profile has been written (using Matlab software) and difference with experimental RBS spectrum is minimized until a convenient spectrum is obtained. Fig. 5 reproduces the depth profiles of

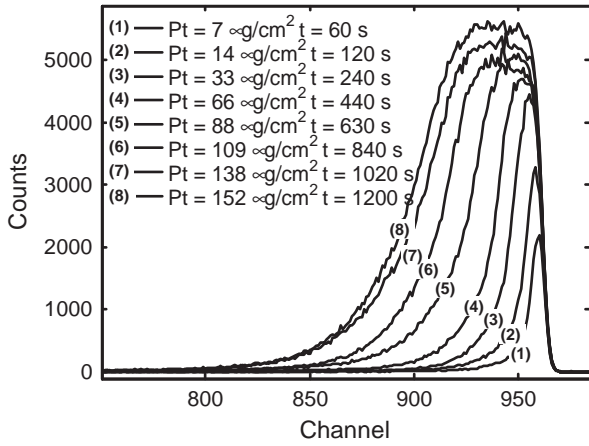


Fig. 4. RBS spectra of a time series of Pt deposition on a commercial E-TEK GDL.

the time sequence of RBS spectra of Fig. 4. The depth profile $C(z)$ is chosen to be a stretched gaussian function issued from nonlinear diffusion equations in fractal media [11–14], i.e.

$$C(z) = A \exp \left[- \left(\frac{z - z_0}{\lambda} \right)^{2+\theta} \right] \quad (1)$$

with z_0 , λ and θ being the fitting parameters. The top surface of the Pt coated carbon particles is seen by RBS as a quasi-homogeneous layer of thickness z_0 . Beyond this depth, the Pt content (density) starts to decrease continuously in the depth of the substrate. λ is an indication of the range of the diffusion. Like for exponential decrease, only a very low content (<5%) has diffused beyond 3λ . θ is a measure of how actual diffusion compares with classical diffusion when $\theta=0$. If $\theta < 0$ then the behaviour is superdiffusive else if $\theta > 0$ it is subdiffusive. In Fig. 5, the resulting $\theta = -1.5$, which means that Ar plasma exposure during Pt deposition induces superdiffusion.

It was found that all these parameters depend on the plasma parameters such as bias potential V_b , input power,

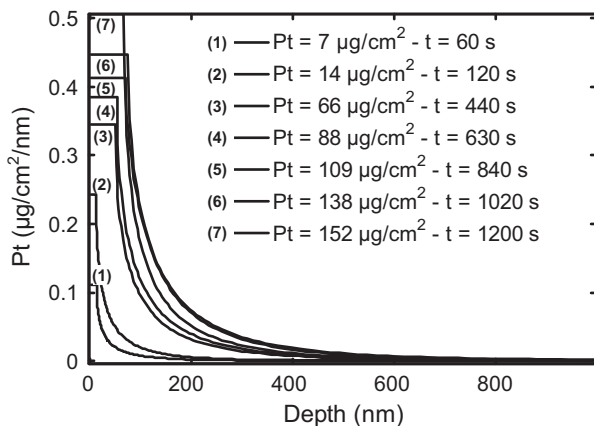


Fig. 5. Resulting depth profiles corresponding to RBS spectra from Fig. 4.

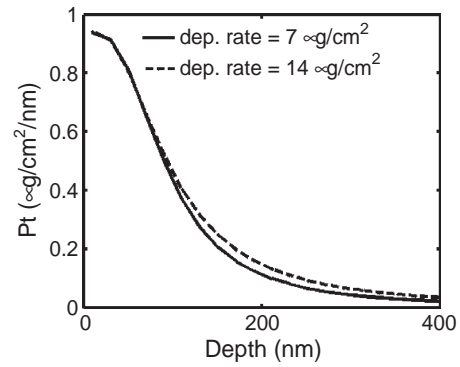


Fig. 6. Pt depth profiles at two different deposition rate.

target to substrate distance. Consequently, not only the porous substrate is responsible for the anomalous diffusion: while maintaining a constant dose of Pt, changing the plasma conditions will affect the diffusion profile, a very interesting and promising result. To illustrate the effect of the plasma on the diffusion process in a porous substrate, Fig. 6 reports on two Pt diffusion profiles for two different deposition rates (15 μg/cm²/min and 7.5 μg/cm²/min).

These are obtained at two different input powers (90 and 200 W) so that the ions and energetic particles and the Pt atoms flux are changed. The deposition time is chosen so as to obtain the same Pt content. Fig. 6 shows that the profile for the lower deposition rate is higher in the range 75–500 nm suggesting that the plasma is assisting the Pt diffusion process into the porous carbon layers. This is very important because fuel cell performances are sensitive to the catalysts location, the control of a non-constant profile being a challenging work [1].

4. Conclusion

In order to improve PEM fuel cell efficiency, the control of the catalyst content and its distribution between the membrane and the gas diffusion layer is required. A low pressure inductive high density plasma sputtering system has been build to deposit platinum into PEMFC gas diffusion layer. It is shown that the plasma parameters modify the platinum diffusion processes. The best fits for the Pt concentration profile are deduced from linear diffusion in fractal porous medium equations. They display superdiffusive behaviour originating from the plasma interaction with substrate during Pt deposition.

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References

- [1] S. Litster, G. McLean, J. Power Sources 130 (2004) 61 (and references therein).
- [2] T.H. Yang, Y.G. Yoon, C.S. Kim, S.H. Kwak, K.H. Yoon, J. Power Sources 106 (2002) 328.
- [3] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, S. Shi, T. Stoner, N. Rana, J. Electrochem. Soc. 149 (2002) A280.
- [4] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, J. Electrochem. Soc. 149 (2002) A862.
- [5] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, S. Shi, N. Rana, S. Grunow, T. Stoner, J. Electrochem. Soc. 149 (2002) A868.
- [6] S.Y. Cha, W.M. Lee, J. Electrochem. Soc. 146 (1999) 4055.
- [7] S. Hira, J. Kim, S. Srinivasan, Electrochem. Acta 42 (1997) 1587.
- [8] S. Mukerjee, S. Srinivasan, A.J. Appleby, Electrochem. Acta 38 (1993) 1661.
- [9] R. OHayre, S.J. Lee, S.W. Cha, F.B. Prinz, J. Power Sources 109 (2002) 483.
- [10] Y.-G. Chun, C.-S. Kim, D.-H. Peck, D.-R. Shin, J. Power Sources 71 (1998) 174.
- [11] L.C. Malacarne, R.S. Mendes, I.T. Pedron, E.K. Lenzi, Phys. Rev., E 63 (2001) 030101(R).
- [12] E.K. Lenzi, M.C. Malacarne, R.S. Mendes, I.T. Pedron, Physica A 319 (2003) 245.
- [13] I.T. Pedron, R.S. Mendes, L.C. Malacarne, E.K. Lenzi, Phys. Rev., E 65 (2002) 041108.
- [14] C. Tsallis, E.K. Lenzi, Chem. Phys. 284 (2002) 341.