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Plasma assisted diffusion in porous materials: Experiments, modeling and applications

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Abstract. Plasma sputtering deposition of platinum on porous substrates is a relevant way for building high performance catalytic thin films. The knowledge and control of platinum density adsorbed in the porous medium, during deposition, are of primary importance. We show that the experimental concentration depth profiles originate from a superdiffusion phenomenon. Moreover experimental results are well described by a classical porous-fractal diffusion model, for which diffusion coefficient is also time-dependent, even if such a model does not include the proper physical mechanisms.

Introduction

Fuel cell electrodes are typical catalytic layers. It was demonstrated that realizing it using plasma sputtering deposition results in highly efficient fuel cell operation [1,5]. Basically, electrodes are built as randomly stacked conducting carbon spheres with 30 to 100 nm size (Fig. 1a). This staking

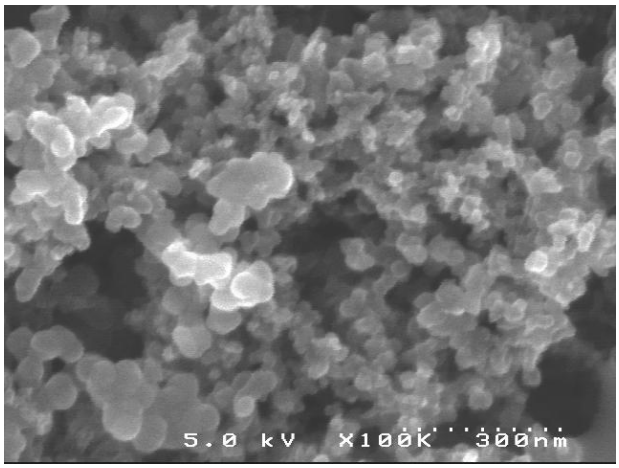


Fig.1: Scanning Electron Microscopy picture of porous carbon layer made of random stacking of carbon spheres

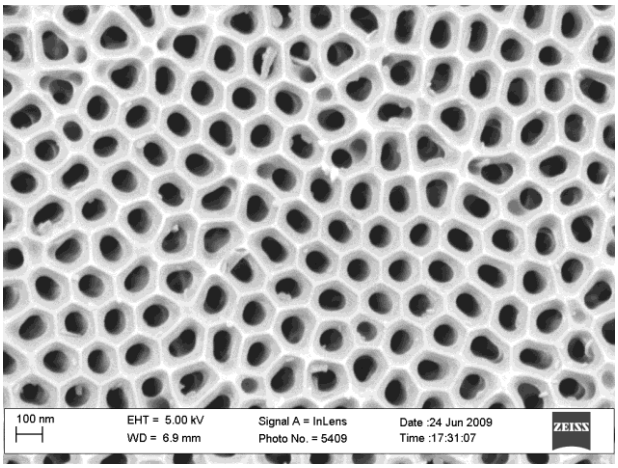


Fig. 2: Scanning Electron Microscopy picture of a AAO template.

leads to a porosity of 50-60 %. The layer thickness is 20-50 µm. This layer, called active layer, is supported on a Gas Diffusion Layer made of a carbon cloth or paper. The catalyst, e.g. platinum, is deposited using plasma sputtering deposition. In that case, a biased platinum target is sputtered by the ions (argon, here) created in the plasma. The platinum vapor is thus transported to the porous carbon layer onto which platinum atoms stick after travelling in the pores to some extent. As a comparison we are using another kind of porous medium with a better defined structure: Anodic Aluminum Oxide (AAO) template (Fig 2). While the former case exhibits a disorder medium, this AAO template is an ordered structure made of a 2D quasi-hexagonal array of cylindrical holes. In

the present study, the hole diameter is 90 nm with a 4.0 10^9 cm^{-2} density. This leads to a porosity (void density) of 25 % (Fig. 2). The AA0 are 60 µm thick. The experimental depth profiles are measured using Rutherford Backscattering Spectroscopy (RBS) [1,2,6,7]. As shown in Fig. 3, they take the form of stretched Gaussian functions [1,2,6,7], as:

$$\rho(z,t) = Z_1(t) \qquad -z_0(t) < z \leq 0$$
$$\rho(z,t) = Z_1(t)\exp\left[-\frac{z^{2+\theta}}{Z_2(t)}\right] \qquad z > 0. \qquad (1)$$

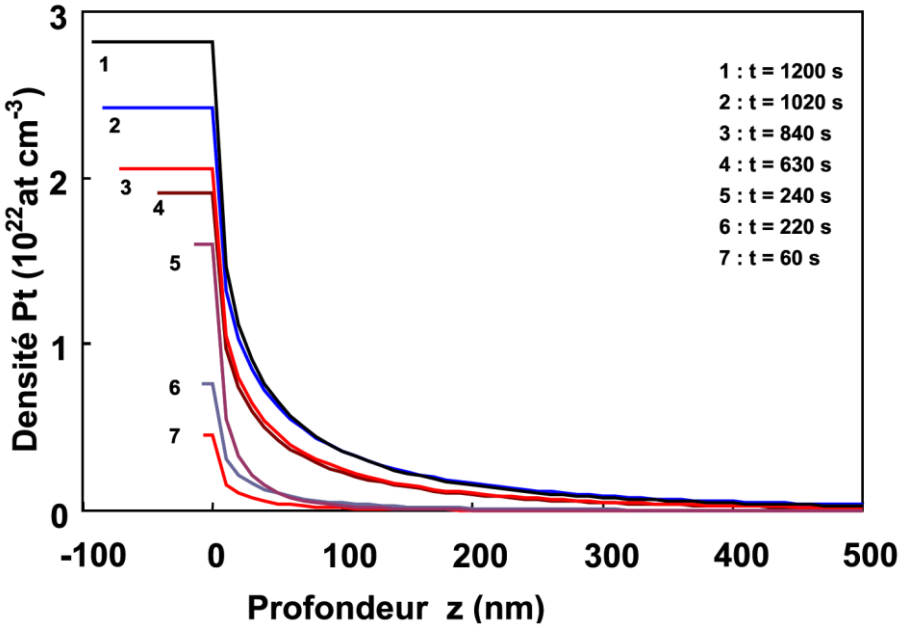


Fig. 3: Concentration profile of deposited platinum into porous carbon of Fig. 1a. The concentration profile in AAO template has a similar shape.

For which $Z_1(t)$ and $Z_2(t)$ are the power law functions: $Z_1(t) \propto t^m$ and $Z_1(t) \propto t^p$. The parameter θ describe the porous medium, $z_0(t)$ is the height of a possible growing overlayer.

Modeling

These profile functions are in fact solutions of a porous diffusion equation [8-12], we have modified for including a power law time dependence of the diffusion equation [6], while it is already dependent on the space variable *z* [11,12]:

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial z}\left(K_0 \frac{t^\gamma}{z^\theta}\frac{\partial\rho}{\partial z}\right). \qquad (2)$$

For which the space and time dependent diffusion coefficient takes the form: $K(z,t) = K_0 \frac{t^\gamma}{z^\theta}$. This allows for taking into account the position and time evolutions of transport-diffusion-adsorption processes inside the pores. The time evolution of the overlayer at $z \leq 0$ is also taken into account by a time dependent boundary condition on the flux:

$$K_0 \frac{t^\gamma}{z^\theta}\frac{\partial\rho}{\partial z} \propto t^\varepsilon, z = 0 \qquad . \qquad (3)$$

Moreover the flux at $z = -\infty$ is constant, mimicking the experimental behavior of the sputtering source.

It is advantageous to search for a self-similar solution in the form:

$$\rho(z,t) = t^{\beta} f\left(\frac{z}{t^{\alpha}}\right). \quad (4)$$

And thus exponents are defined by: $\alpha = \frac{1+\gamma}{2+\theta}$ and $\alpha + \beta = 1 + \varepsilon$ [6].

The parameter θ is a measure of the diffusion ability of the media: if $\theta > 0$, it means that the medium is slowing down the diffusion (subdiffusion) while $\theta < 0$ means the diffusion is facilitated (superdiffusion). In the experiments, θ is ranging from -1.0 and -1.8 depending on plasma deposition conditions and materials. Parameters α, β, θ are rather depending on plasma conditions while ε, γ are depending on the actual porous medium [6]. Solutions of equations (2) and (3) are:

$$\rho(z,t) \propto t^{\beta} \exp\left[-\frac{(1+\gamma)z^{2+\theta}}{(2+\theta)^2 K_0 t^{1+\gamma}}\right] \quad (5)$$

Because $\alpha = p/2+\theta$ and $\beta = m$, when comparing equations (1) and (5) and taking into account the $Z_1(t)$ and $Z_2(t)$ power law expressions, it becomes possible to find the relations between experimental parameters m, p, θ and the "diffusion" exponents $\gamma = p-1$ and $\varepsilon = p/2+\theta+m-2$. So the concentration profiles in the porous layers are fully determined.

Discussion

Three kinds of deposition have been carried out: 2 on random porous carbon using two different plasma conditions and one using the AAO template, at successive deposition times. Deduced m, p, θ, α, β, γ, ε values are gathered in Table 1.

Table 1: Exponents of stretched Gaussian functions m,p, self-similar α, β and diffusion ε, γ for three different deposition conditions

Conditions	m	p	θ	α	β	γ	ε
C1	0.4	0.2	-1.5	0.4	0.4	-0.6	-0.2
C2	0.25	0.25	-1.33	0.5	0.25	-0.75	-0.25
AAO	0.75	1.25	-1.66	3.75	0.75	0.25	4.0

Differences between C1 and C2 only originate from deposition conditions: the kinetic energy of platinum atoms and argon ion flux impinging the porous layer are larger in the case of C1, carbon layers being identical. On the contrary the AAO condition shows a different substrate while deposition condition is identical to the C1 case.

C1 and C2 are leading to negative values of γ and ε, which, on one hand, means that diffusion is decreasing due to pore filling, at least in the upper part. The Pt flow at the boundary z = 0 is decreasing due to a growing overlayer, which in turn, is limiting the Pt access to the pores. On the

contrary, for deposition on AAO, the γ and ε becomes positive, which indicates that diffusion is somewhat enhanced despite pore narrowing. This can be explained by the fact the deposited platinum on surface between pores can serves as a reservoir for diffusion inside the pores [7]. Indeed, when considering the time evolution of platinum mass inside the pores ($z>0$), it evolves following a power law faster than linearity. At the same time, the mass on the topmost surface between pores follows a power law evolution slower than linearity. This two effects lead to a total mass evolving exactly linearly with time, in agreement with measured constant deposition rates.

Differences between porous carbon layer and AAO template are both porosity and tortuosity. For C1 and C2 substrate the porosity is high while the tortuosity is also high due to the sphere stacking. On the contrary, for AAO the porosity is lower and there is no tortuosity for straight holes. So despite lower porosity AAO template favors Pt diffusion along pore wall. This can be explained by the lack of AAO tortuosity favors the platinum transport inside the cylindrical pore whereas in the sphere stacking the access inside the pore is limited despite a greater porosity. This provides a limit for treating transport in porous media using diffusion equations, for which the real geometry of the porous medium and the microscopic processes, as transport-adsorption coupling, are not taken into account. Complementary studies using molecular dynamics simulations [13] and modeling using transport-diffusion equation combined with adsorption laws are currently conducted [14-16].

Conclusions

Experimental and modeling studies show that atom diffusion in a porous, tortuous or not, medium leads to reconsidering the diffusion equation with adding a power law time dependence (t^{γ}) in addition to the usual porous space dependence (z^{θ}). Concentration profile exponents as well as self-similarity exponents are dependent on plasma deposition conditions while “diffusion” exponents are function of the porous geometry. Moreover, it is expected that tortuosity plays a major role in guiding the inside diffusion and thus the maximum reached depth.

The present diffusion model is able to reproduce experimental results of atom diffusion. In all cases, superdiffusion occurs in plasma assisted deposition. The diffusion is slowed down in sphere stacking and enhanced in cylindrical pores. Despite this overall qualitative agreement, it seems necessary to build a model that more precisely relies on microscopic physical processes.

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