Deposition of platinum catalyst by plasma sputtering for fuel cells: 3D simulation and experiments

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Abstract

Plasma sputtering is one of the most promising methods for reducing the amount of platinum catalyst in porous electrodes for low temperature fuel cells. Here, a simulation of the platinum deposition by radio frequency plasma sputtering has been developed and compared with experimental results to allow optimization of the deposition process. In the simulation, the transport of sputtered atoms through the argon plasma is obtained using a 3D Monte Carlo model called SPaTinG (Sputtered Particles Transport in Gas). The Yamamura formula provides the Pt sputtering yield on the target, and the initial energy distribution of sputtered atoms is given by the Thompson distribution. A 1D hybrid model is used to estimate the mean energy of argon ions impinging onto the platinum target. Experimentally, platinum is deposited on silicon in two plasma sputtering chambers with different geometries. The deposition rate is measured by Rutherford backscattering spectroscopy. The angular distribution of the Pt atoms ejected from the target surface and the condensation coefficient of the Pt atoms on silicon are calculated by adjusting the simulated and experimental deposition rates at 0.5 Pa. A good agreement between the simulation and the experiment is observed as a function of the target–substrate distance for the two system geometries at low pressure (0.5 Pa).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Controlled deposition of nanoparticles is an important issue for the plasma-aided nanofabrication of advanced microporous materials [1, 2]. Sputter deposition, an established and widely used method for the growth of thin film, has been recently applied to the growth of nanoparticles. Intensive studies have been conducted to understand the effect of the sputtering parameters, the plasma parameters and the surface potential on the growth of nanoparticles [3–5]. Here, two plasma sputtering systems designed and manufactured for the growth of platinum and/or ruthenium catalytic nanoparticles onto microporous substrates for electrochemical devices (such as low temperature fuel cells) are used [6–10]. The electrochemical performance of these advanced microporous materials strongly depends on the spatial distribution of the nanoparticle diameter [11, 12]. Hence, the deposition profile dependence on the process parameters must be predicted to control the nanoparticle growth over the microporous material area and to optimize the electrochemical activity of the synthesized functional material. In addition, the loss of the catalyst on the reactor walls needs to be quantified and minimized due to the limited availability and high cost of the catalytic materials. Usually, the plasma sputter deposition is
well described with four processes: the ion bombardment of the target, the physical sputtering, the gas phase transport and the resulting atomic deposition.

Amongst the numerous studies on the physics of plasma sputtering, Yamamura [13] deduced analytic expressions of the sputtering yield and its angular dependence for different types of impinging particles and target materials. The initial energy distribution of the ejected particles is well described by the Thompson distribution [14] based on the linear cascade theory. The angular distribution of the sputtered atoms is usually considered to be cos² type [15–17], where ν is between 0 and 2 and depends on the energy and the mass of the impinging ions and of the sputtered atom. The atom transport in the gas phase can be described by an analytical expression assuming a continuous energy loss [18–21]. Alternatively, Monte Carlo methods [22, 23] can be used to calculate the parameters of sputtered atoms impinging onto the substrate. In this case, hard sphere, Lennard–Jones 6-12, Abrahamson or Thomas–Fermi–Dirac interatomic potentials have been used to reproduce collisional transport. The deposited amount of sputtered particles τ on the substrate is defined as the product of the incoming species flux Φ and the condensation coefficient S. Molecular dynamic simulations are usually used to describe the growth of nanoparticles on flat and rough substrates [24] although a few studies have considered micropatterned substrates or open surface areas [25].

This study focuses on the simulation of the four steps involved in the plasma sputter deposition of platinum. For the latter step (atomic deposition), only the condensation phenomenon on silicon is considered and nanoparticle formation and growth in the porous media is not described here. The platinum deposition model is presented and validated by comparing the simulated and the experimental deposition rate of platinum in two different plasma deposition systems called Southern Cross (perpendicular target to substrate mode and helicon plasma) and CataPulsP (facing target to substrate mode and transformer coupled plasma). The homogeneity of the deposition is discussed, as well as the loss of platinum on the system walls which is an issue for decreasing the fabrication cost of electrochemical devices such as microporous fuel cell electrodes [26]. The study is carried out for several target to substrate distances (between 2 and 12 cm) and a range of sputtering gas pressures (between 0.1 and 5 Pa). The simulated flux distribution of sputtered Pt atoms impinging onto the silicon substrates ΦPt is compared with the deposition rates rPt measured by Rutherford backscattering spectroscopy (RBS) and the condensation coefficient S Pt is deduced.

### 2. Numerical model

The simulation of the Pt deposition process consists of four parts:

- energetic bombardment of argon ions on the Pt target,
- ejection of the sputtered particles from the Pt target,
- transport of the Pt sputtered particles through the gas phase,
- condensation of Pt atoms on the substrate.

The mean kinetic energy of argon ions ⟨EAr+⟩ reaching the Pt target is assumed to follow the relation ⟨EAr+⟩ = α(300 + Vp), where 300 corresponds to the target bias, Vp is the plasma potential and α is a constant describing the energy losses by collisions in the plasma sheath near the target surface. The flux of argon ions on the target is assumed to be homogeneous. The argon plasma (including the sheath) is investigated by using a one-dimensional hybrid simulation [27], the ions are treated by Monte Carlo collision techniques and the electrons are considered as a fluid in Boltzmann equilibrium. Finally, α is estimated to be 0.76 for the argon pressure range, which is in agreement with previous results [28].

The properties of the sputtered Pt atoms are obtained using analytical models. On the target surface, the energy distribution of the sputtered Pt atoms is deduced using the Thompson energy distribution fTTHOMPSON while the sputter yield (number of Pt atoms per incident argon ion) is estimated at 0.61 using the Yamamura form at normal incidence.

For the gas phase transport, a classical description of the scattering dynamics using a Monte Carlo sampling procedure and an analytical potential is applied. Our three-dimensional simulation (called SPaTinG for Sputtered Particles Transport in Gas) computes the collisional transport of the Pt atoms travelling through the argon gas between the target and the substrate (or one of the chamber walls). The energy and the spatial distribution of the Pt atoms reaching the substrate are determined.

A total of 5 × 10⁶ Pt atoms (corresponding to 8.2 × 10⁶ impinging argon ions with a sputter yield of 0.61) are randomly sputtered from the target surface. Each atom is injected into the simulation. At the start of a trajectory, one sputtered atom is released from the target surface with initial energy E and ejection angle θ selected from the Thompson distribution fTTHOMPSON and the cosine distribution cos² θ, respectively. The azimuthal angle (in the target plane) is randomly selected in [0, 2π]. The ejection location is randomly implemented on the 25 cm² face of the target which is facing the substrate.

The program calculates the trajectory of the atom from its ejection location, through a series of collisions, to the chamber walls or to the substrate surface. We only consider the Pt–Ar atom elastic interactions where Ar atoms are assumed to be immobile and we neglect the effect of the Pt–Ar inelastic collisions and of the Pt–Pt collisions. The Pt–Ar elastic collision events are modelled by scattering through a Lennard–Jones potential. The mean free path l between successive collisions is randomly generated on the [0, λ(E)] range by the relation: l = λ(E) ln (RAND), where RAND is a random number selected in [0,1]. λ(E) is the energy-dependent mean free path given by the relation: λ(E) = kBT/πrb². T, kB and ρ are the gas temperature, the Boltzmann constant and the gas pressure, respectively. The impact parameter b is uniformly and randomly generated in [0, l max], where l max is the highest impact factor that produces a deflection of less than 2°. Once a Pt–Ar collision has occurred, the polar scattering angle φCM (in the centre of mass) is given by the equations [29, 30]:

\[
ψ_{CM} = π - 2b \int_{r_{max}}^{∞} \frac{dr}{r^2 \sqrt{1 - V(r)/E_j - (b^2/r^2)}},
\]

where
where \( r_{\text{min}} \) is determined from the equation:

\[
r_{\text{min}} = \frac{b^2}{r^2} \left( 1 - \frac{V(r_{\text{min}})}{E_i} \right) - 1 = 0.
\]

\( E_i \) is the kinetic energy of the Pt atom before the Pt–Ar collision. The azimuthal angle (in the centre of mass) is randomly selected in \([0, 2\pi]\) whereas the energy of the Pt atom after the collision is obtained from the theory of elastic binary collisions (conservation of momentum and conservation of kinetic energy during the collision).

A new mean free path corresponding to the new energy is generated according to the above procedure and the Pt atoms travel through the gas phase. When the trajectory of the Pt atom intercepts either the substrate, the target or the reactor walls, a new sputtered atom is generated on the target surface. When the simulation run is completed, the Pt flux density on whole area of the chamber walls is estimated using a linear interpolation up to a total of \(1.5 \times 10^{19}\) argon ions impinging onto the target (i.e. \(9.2 \times 10^{18}\) sputtered atoms). This corresponds to an ion current of 40 mA on the 25 cm\(^2\) Pt target over a period of one minute.

### 3. Experimental setup

Platinum deposition on silicon is performed in two plasma processing chambers, respectively, called Southern Cross and CataPulP as shown in figure 1.

In Southern Cross (figure 1(a)), a low pressure radio frequency (RF) (13.56 MHz) argon plasma is generated by a double saddle antenna which is placed around a 15 cm diameter glass tube attached to the top of a diffusion chamber. During the experiment, the argon pressure \(P\) and the argon flow \(Q\) are fixed at 0.5 Pa and 60 sccm, respectively. The Pt target (50 \(\times\) 50 \(\times\) 0.1 mm\(^3\)) is vertically fixed on a ceramic support in the diffusion chamber, 10 cm below the helicon source. Two different substrate holders are used for the study. A 72 mm in diameter circular substrate is positioned perpendicularly to the Pt target. This substrate is fixed on a holder which can be moved vertically. The horizontal distance \(d\) between the centre of the Pt target centre and the substrate is fixed at 5 and 10 cm for this study. A horizontal semi-annular substrate holder with different radius \(R\) (5 and 10 cm) has been specially built for this study to measure the angular flux distribution of the Pt atoms ejected from the target. This substrate holder and target are centred in the same horizontal plane and 13 pieces of silicon (10 \(\times\) 10 \(\times\) 1 mm\(^2\)) are attached at regular intervals onto the semi-annulus (figure 1(a)).

In CataPulP (figure 1(b)), the plasma source is the deposition chamber and the geometry is different. The argon plasma is ignited using an external planar antenna (also known as a transformer coupled plasma antenna) connected to a (13.56 MHz) RF power generator. The substrate is placed on a movable 25 cm\(^2\) square substrate holder and is parallel to the Pt target (50 \(\times\) 50 \(\times\) 0.1 mm\(^3\)). The distance \(D\) between the target and the substrate is between 3 and 12 cm. The argon pressure is adjusted between 0.5 and 5 Pa by using a valve placed between the pumping system and the deposition chamber.

![Figure 1. Schematic of Southern Cross (a) and CataPulP (b), the two plasma sputtering apparatus.](image)

| Table 1. Experimental setup and synthesis conditions for the two plasma apparatus. |
|------------------------------------|----------------|----------------|
| Experimental parameters | Southern Cross | CataPulP |
| Argon flow \(Q\) (sccm) | 60 | 5 |
| Argon ion current \(I_{\text{Ar+}}\) (mA) | 40 | 30 |
| Deposition time \(t\) (min) | 30 | — |
| Vertical distance \(d\) (cm) | 5 and 10 | — |
| Radius \(R\) (cm) | 5 and 10 | — |
| Horizontal distance \(D\) (cm) | — | 4 \(\rightarrow\) 12 |
| Argon pressure \(P\) (Pa) | 0.5 | 0.5 \(\rightarrow\) 7 |

For both plasma sputtering systems, the dc bias \(V_{\text{Pt}}\) applied to the target is fixed at -300 V. The input RF power is adjusted during the deposition to keep a constant target current \(I_{\text{Ar+}}\) of 40 mA on the 25 cm\(^2\) target (i.e. \(1.5 \times 10^{19}\) ions min\(^{-1}\)). The injected power is about 300 W and 600 W in CataPulP and Southern Cross, respectively. The experimental setup and the synthesis conditions are listed in table 1. Langmuir probe measurements are carried out to determine the plasma potential \(V_{\text{p}}\), the electron density \(n_e\) and the electron temperature \(T_e\). Typical values are \(V_{\text{p}} = 15\) V, \(n_e = 10^{13}\) cm\(^{-3}\) and \(T_e = 4\) eV near the Pt target at 0.5 Pa for the two sputtering systems. After a deposition time \(t\) of 30 min, the amount of platinum (expressed in unit of \(10^{15}\) atoms cm\(^{-2}\)) deposited on each piece of silicon is measured \(ex \; situ\) by RBS. A 2 MeV \(\alpha\) particle beam is directed onto one piece of Pt covered silicon.
and $\alpha$ particles are backscattered after colliding with a Pt or a Si atom. The backscattered $\alpha$ particles have an energy distribution that reflects the substrate composition [31] and the amount of platinum deposited in 30 min can be deduced.

4. Simulation and experimental results

Figure 2 displays the flux of Pt atoms $\Phi_{Pt}$ impinging onto two 3D cylinders surrounding the Pt target for a cosine angular distribution with $\nu = 1$ and for an argon ion flux of $1.5 \times 10^{19} \text{ min}^{-1}$ on the $25 \text{ cm}^2$ target. The circular and the semi-annulus substrate holder of Southern Cross are placed on the bottom and on the circular walls of the 3D cylinder (inner diameter of $20 \text{ cm}$ and height of $20 \text{ cm}$) in figure 2(a), respectively. The wall of the 3D cylinder in figure 2(b) directly reproduces the CataPulP wall. The $5 \times 5 \text{ cm}^2$ substrate holder is positioned in the centre of the 3D cylinder and in front of the target. For better clarity, only half of the cylindrical wall and half of the bottom wall are displayed. The top wall is not displayed.

As can be seen in figure 2(a), most of the $9.2 \times 10^{18} \text{ Pt} \text{ atoms}$ sputtered during 1 min strike the walls facing the target: the cylinder wall (59.3%) and the bottom wall (10.4%). Less than 5% of the platinum reaches the circular substrate holder placed on the bottom wall. The maximum flux is about $100 \times 10^{15} \text{ atoms cm}^{-2} \text{ min}^{-1}$ on the circular wall in front of the Pt target where the semi-annular substrate holder is fixed. In figure 2(b), only 42.7% and 11% of the sputtered atoms reach the cylinder and the bottom walls, respectively (maximum flux is about $70 \times 10^{15} \text{ atoms cm}^{-2} \text{ min}^{-1}$) because the substrate intercepts a relative large number of Pt atoms: 14.7% with a mean density flux close to $400 \times 10^{15} \text{ atoms cm}^{-2} \text{ min}^{-1}$.

In both reactors, around 20% of sputtered Pt atoms come back to the surface of target. Hence, about 95% and 85% of the platinum is lost on the system walls and on the target in the Southern Cross and the CataPulP systems, respectively.

The $\nu$ exponent of the cosine angular distribution and the condensation coefficient $S_{Pt}$ are combined to adjust the simulated deposition rate to the experimental deposition rate (expressed in $10^{15}$ atoms cm$^{-2}$ min$^{-1}$) on the semi-annular substrate of Southern Cross. Firstly, Pt deposition is performed at 0.5 Pa on pieces of silicon stuck on the semi-annulus substrate placed at 5 and 10 cm from the centre of the Pt target. Figure 3 shows the experimental Pt deposition rates for $R = 5 \text{ cm}$ (+) and for $10 \text{ cm}$ (c) as a function of the angle on the horizontal plane between the target normal and the direction towards the substrates. Both depositions have an inverted bell shape with a maximum rate of about $100 \times 10^{15} \text{ atoms cm}^{-2} \text{ min}^{-1}$ and $23 \times 10^{15} \text{ atoms cm}^{-2} \text{ min}^{-1}$ at 0°, respectively. Assuming a density of the Pt film of $6.619 \times 10^{22} \text{ atoms cm}^{-3}$, these values correspond to 15.1 and 4.5 nm min$^{-1}$, respectively. Secondly, the deposition rates $\tau_{Pt/Si}$ simulated along the semi-annulus substrate for three $(\nu, S_{Pt})$ combinations [(0.5,0.43), (0.8,0.33) and (1.0,24)] are shown in figure 3 for comparison with experimental results. Good agreement is observed for $\nu = 0.8$ and $S_{Pt} = 0.33$ for both target–substrate distances. Consequently, a cosine distribution with a $\nu$ exponent of 0.8 and a condensation coefficient $S_{Pt}$ of 0.33 are used in simulations presented here. This $\nu$ value is consistent with the value generally used in the
both positions along the target–substrate holder in Southern Cross, defined as \( r_\perp \) (\( \perp \)) and \( r_\parallel \) (\( \parallel \)).

The simulated curves fit the experimental data accurately for distances: 5 cm (\( \bullet \), --- ) and 10 cm (\( \bullet \bullet \), ——). In contrast, the deposition rates are obtained for two horizontal target–substrate distances: 5 cm (\( \star \), - - - - ) and 10 cm (\( \star \star \), ——). The deposition rates are not provided in the literature. However, this value is not far from the condensation coefficient of palladium on silicon which has been estimated at 0.4 in previous experiments [32].

Figure 4 displays the experimental (symbols) and simulated (dashed and solid lines) deposition rates \( \tau_{Pt} \) along the two axes of the circular substrate holder in Southern Cross, defined as \( r_\perp \) (\( \perp \)) and \( r_\parallel \) (\( \parallel \)).

The simulated curves fit the experimental data accurately for both positions along the \( r_\parallel \) parallel axis (figure 4(a)) and the \( r_\perp \) perpendicular axis (figure 4(b)) shown in figure 2(a). In figure 4(b), the deposition rate curves are symmetric with respect to the origin where the deposition rate is the maximum, i.e. \( 15 \times 10^{15} \) and \( 12 \times 10^{15} \) atoms cm\(^{-2} \) min\(^{-1} \) for a distance \( d = 5 \) cm and 10 cm, respectively.

The deposition rates decrease to \( 11 \times 10^{15} \) atoms cm\(^{-2} \) and \( 10 \times 10^{15} \) atoms cm\(^{-2} \) at the edge of the substrate holder for 5 cm and 10 cm distance, respectively. In contrast, the deposition rate continuously decreases with increasing \( r_\perp \) from 40 and 16 \( \times 10^{15} \) atoms cm\(^{-2} \) at a respective distance of 5 and 10 cm to \( 9 \times 10^{15} \) atoms cm\(^{-2} \), in figure 4(a). In this perpendicular target to substrate mode, the platinum deposition is strongly nonuniform (especially for \( d = 5 \) cm). By applying a rotation of the circular substrate holder, the mean deposition rate is close to \( 15 \times 10^{15} \) atoms cm\(^{-2} \) min\(^{-1} \) and the homogeneity decreases to 17% for this latter distance. Assuming that the platinum shapes are spherical nanoparticles, the catalytic surface area of the deposition varies by 11.3% (the surface area \( S \) and the volume \( V \) of a sphere are related by \( S = 4.84V^{\frac{2}{3}} \)).

This contributes to the inhomogeneous electrical performance of fuel cell electrode covered by platinum catalyst in this plasma sputtering geometry.

To further validate the model, the Pt deposition rate \( \tau_{Pt} \) is studied as a function of the target–substrate distance \( D \) in CataPulP. Platinum is deposited on a silicon sample placed in the centre of the square substrate holder of CataPulP. The target–substrate distance \( D \) is changed from 4 to 12 cm whereas the argon pressure \( P \) is kept constant at 0.5 Pa. Figure 5 displays the experimental deposition rate (diamonds) obtained from RBS analysis and the simulated rate (squares) performed between 2.5 and 11.5 cm. The graph shows that the simulation also agrees very well with the experiment in this second reactor.

In addition, both curves are well fitted by an exponential curve (line) with a characteristic length of 3.5 cm: the squares of the correlation coefficients \( R^2 \) are 0.991 and 0.998 for the experimental and the simulated data, respectively. Similarly, quite high correlation coefficients (0.85 and 0.99, respectively) are obtained with the inverse square fitting curve (dashed line) expressed in the form \( D^{-n} \) with \( n = 2 \). This suggests that for a target–substrate distance greater than 5 cm, a spherical expansion of the sputtered Pt atoms from the target is a good approximation. Below 5 cm, the simulated deposition rate is lower than that described by the inverse square fitting curve. This may be the result of the large Pt target size compared with the target–substrate distance (extended source of Pt atoms) and of the cosine angular distribution of the ejected Pt atoms (anisotropic distribution), whose respective effects are more important at a low target–substrate distance (around four Pt–Ar collisions occurs for \( D = 5 \) cm and \( P = 0.5 \) Pa in the SpaTinG simulation).

Figure 6 displays the experimental deposition rate \( \tau_{Pt} \) (diamonds) in CataPulP as a function of the argon pressure.
5. Conclusion

The platinum deposition by plasma sputtering in two reactor geometries is simulated using numerical and analytical models. The angular distribution of the Pt atoms ejected from the target surface and the condensation coefficient of Pt atoms on silicon (cos^0.8 and S_p = 0.33, respectively) have been estimated by comparing simulated atoms fluxes and experimental deposition rates. The simulated deposition rate is in agreement with the experimental results in the two plasma processing chambers at very low pressure (0.5 Pa) but overestimates the deposition rate at higher pressure.

This study yields data relevant for the estimation of an accurate catalyst content, integrated over a fuel cell electrode, for the manufacturing of efficient and homogeneous fuel cell electrodes and for the long-term development of plasma sputter reactors where the platinum loss on the system walls is minimized.

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References