



Ultra-low-loading pulsed-laser-deposited platinum catalyst films for polymer electrolyte membrane fuel cells



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HIGHLIGHTS

- Ultra-low loading (0.18–7.44 $\mu\text{g cm}^{-2}$) Pt catalyst for PEMFC was deposited by PLD.
- Power density 59.36 mW cm^{-2} at 1.24 $\mu\text{g cm}^{-2}$ of Pt on Nafion membrane was obtained.
- Power density 106.36 mW cm^{-2} at 1.24 $\mu\text{g cm}^{-2}$ of Pt on gas-diffusion layer obtained.
- Power density 188.44 mW cm^{-2} at 7.44 $\mu\text{g cm}^{-2}$ of Pt on gas-diffusion layer obtained.

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ABSTRACT

In this work experimental results are presented and analyzed for catalytic platinum films of ultra-low thickness of 0.09–3.47 nm and Pt loading of 0.18–7.44 $\mu\text{g cm}^{-2}$ deposited using the PLD method with an ArF excimer laser ($\lambda = 193$ nm) at room temperature. For Pt deposited on the surface of the Nafion[®] membrane (electrolyte), in a fuel cell with PLD Pt working as oxygen cathode the peak power density is obtained equal to 59.36 mW cm^{-2} for the Pt loading of 1.24 $\mu\text{g cm}^{-2}$. In the case of Pt deposition on the gas-diffusion layer (as cathode), a much higher maximum power density of 106.36 mW cm^{-2} at the same loading and a maximum of 188.44 mW cm^{-2} at the 7.44 $\mu\text{g cm}^{-2}$ loading is observed. Experiments are also presented of Nafion[®] modification before the deposition of Pt on the Nafion[®], in which the surface of the membranes is enlarged by bombarding with Ar ions from a plasma generator of RF 13.56 MHz. The electrochemical activity of the elements prepared by PLD is assessed in a $\text{H}_2/\text{Pt}/\text{Nafion}^{\text{®}}/\text{Pt}/\text{O}_2$ PEMFC. The structure and morphology of the surface layers is examined by AFM and SEM microscopy.

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1. Introduction

This work concerns fuel cells with ion conducting polymer membranes (PEMFC). The most important advantage of PEMFC is low temperature operation below 100 °C and the possibility of miniaturization, allowing their utilization in portable electronic equipment. The electrodes used in PEMFC are usually in the form of porous carbonized paper or of carbon fibre cloth impregnated from one side with a suspension of carbon in Teflon[®]. Between the electrodes there is an ion conducting membrane in the form of a thin polymer foil, most often Nafion[®]. Both sides of the membrane are covered with a platinum based catalyst and pressed on both

sides to the electrodes to obtain a good electric connection between the catalyst and the electrode and a large contact surface between the catalyst and the electrolyte [1].

In traditional implementations, thin films of catalyst are deposited on both sides of the polymer membrane as nanoparticles of platinum, unsupported or supported on an inert, conducting support for the cathode, and platinum–ruthenium for the anode [2–5]. Most often the catalyst films are applied from a suspension (a mixture of the catalyst and Nafion emulsion) by painting, sputtering, or similar application technique [3,6–9]. The amount of metal deposited that way usually ranges from 0.1 mg cm^{-2} in the case of hydrogen anodes to 4–6 mg cm^{-2} or more in the case of methanol anodes. Such an approach is not optimal, because its low effectiveness of catalyst utilization results in the increased cost of the fuel cell. The technical objective of this work was a substantial reduction of the quantity of Pt used without reducing the utility life

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time of the cell as well as its efficiency [4,6,10–16]. One of the main directions of research on fuel cells is the application of plasma deposition methods allowing the deposition of catalyst films of even nanometric thickness [5,13,17–22,28] sometimes with designed molecular structure [19]. Sputtering [17–20,24,26] and also e-beam evaporation [31] have been used to deposit the catalyst films. If the catalyst is deposited as a thin film, it is important to accurately choose its thickness, which determines the type and amount of loss from active material placement as well as polarization losses in the cell [5]. The catalysts can be deposited directly on the Nafion membrane forming the cell electrolyte [5,8,20,23] or on the carbon-fibre gas-diffusion layer [13,18,19,24,25]. Attempts were also reported of simultaneous deposition of elements, like platinum and carbon, to obtain more efficient catalytic films [26]. Plasma deposition techniques were also used in conjunction with other methods, when thin films of catalyst were deposited on the catalyst layers formed by traditional methods (ink printing) [13]. Since the catalyst utilization in the fuel cell is determined mainly by the contact surface area of the catalyst with the Nafion electrolyte, the reduction of the thickness of the metal layer by an order of magnitude thanks to the use of plasma techniques can result in an improvement of the catalyst utilization and reduction of the fuel cells cost. Thus, plasma techniques allow improvement of the cell power per the mass unit of the catalyst [17]. Polarization curves presented by Schwanitz et al. [27] showed that to achieve the effectiveness of hydrogen oxidation at the level comparable to the commercial E-TEK electrode with $500 \mu\text{g cm}^{-2}$ of platinum it is sufficient to deposit a $3 \mu\text{g cm}^{-2}$ film of Pt. It was also observed that the increase of the effective loading of the Pt to $25 \mu\text{g cm}^{-2}$ significantly improved the durability of the anode. The electrodes with catalyst films deposited by plasma techniques proved themselves equally as oxygen-reducing cathodes [5,13,18,19,23,24,26,30] as well as hydrogen-oxidizing anodes [27]. Since the reaction of hydrogen oxidation in the cell is much more efficient than the reaction of oxygen reduction, it is not possible to compare directly the cells, in which the experimental electrode was the anode, to those, in which it was the cathode. In the case of the oxygen-reducing cathode the optimal amount of platinum was about $100 \mu\text{g cm}^{-2}$ [5,19,24]. Increasing the amount of platinum usually reduces the porosity of the deposited metal layer, which has a negative effect on the transport of the reagents and the products of the reaction [5]. However, much in this respect depends on the structure of the support used for sputtering. As apparent from the work of the 3M company [32], sputtering even considerable amounts of Pt ($150 \mu\text{g cm}^{-2}$) on a regular, nanostructured layer of crystalline, organic whiskers led to a cathode catalyst layer exhibiting absolute performance on par with a higher-loaded traditional PEMFC cathode. The initial problem of the 3M's nanostructured thin film (NSTF) electrodes was insufficient proton conduction in the film because ionomer was not introduced in the layer between the catalytic metal and the PEM [33]. This underlines the importance of designing an effective three-phase boundary in these catalyst layer fabrication techniques.

The method used in this work of pulsed laser deposition (PLD) of catalyst films in high vacuum conditions with an ArF laser allows precise control of the thickness and of the physicochemical structure of the fabricated films. The deposition in conditions of high vacuum also assures a high chemical purity of the films.

The research objective of the present work was the determination of the effects of the PLD process parameters on the physicochemical and electrochemical properties of the catalyst films deposited on off-the-shelf PEM fuel cell components. An important aspect of the work was to investigate if the laser deposition method would allow reducing the utilized amount of the noble metal, while

maintaining the efficiency of the cell or at least to increase the cell power obtained from a mass unit of the metal.

2. Experimental details

2.1. Pulsed laser deposition of platinum

The investigated catalyst was deposited by the pulsed laser ablation method using a Lambda Physik excimer laser LPX 305i at $\lambda = 193$, $E_L \leq 0.7$ J, $\tau \sim 15$ – 20 ns. Because of the low Nafion degradation temperature, the laser radiation fluency on the surface of the target disc did not exceed 14 J cm^{-2} . The pumping system allowed achieving an oil-free vacuum of $5.0 \cdot 10^{-5}$ mbar. The system included a 13.56 MHz RF plasma generator from the ENI Company and a gas dosing system for O_2 , N_2 , Ar and CH_4 . The catalyst was deposited from a $20 \times 20 \times 2$ mm platinum (99.99%at.) target. The thickness of the deposited Pt films was controlled by changing the number of the laser pulses. Because of differences in the roughness of the surfaces, on which the catalyst was deposited, we have introduced further in this work the concept of the effective thickness of the catalyst representing the thickness of the catalyst deposited on a polished silicon wafer with the same number of laser pulses.

In the first part of the investigation the catalyst films were deposited directly on the Nafion membranes. In order to increase the active area of the catalyst-electrolyte interface, some membranes were treated in 13.56 MHz argon plasma [2]. The modification process was conducted for different periods of time and RF generator power. The pressure in the experimental chamber was held during the modification process between $2.7 \cdot 10^{-2}$ and $9.0 \cdot 10^{-3}$ mbar. In an alternating electric field argon is ionized, which gives source to a stream of ions, electrons and UV radiation. The energy of ions used for the modification of the membranes depended mainly on the vacuum chamber pressure, on the geometry of the gas injection into the chamber, and on the gas flow. Depending on the conditions, the energy of ions could vary from a few tens to a few hundreds of electronvolts. The amount of energy transferred by the Ar^+ ions to a unit of the Nafion membrane surface is subject to large fluctuations and is difficult to estimate. The energy of the UV radiation in the present system was at least three times lower than the energy of the generated Ar^+ ions. Because the UV energy is emitted in the full solid angle, its contribution to the Nafion properties modification could be ignored, as was proven by Ramdutt et al. [2].

In the second part of investigations the Pt catalyst films were deposited directly on the gas-diffusion layer of the cathode structure. It was expected that the diffusion layer extending in three dimensions would assure a larger contact surface of Pt and the electrolyte and better transport conditions for the fuel and the oxidant compared to the deposition of the catalyst on the flat surface of Nafion.

2.2. Preparation of materials for the fuel cell

Platinum deposited by the PLD method was the cathode catalyst of the fuel cell. For the anode, a layer of platinum black (E-TEK, a division of De Nora North America Inc., Somerset, NJ, USA) was used, applied by painting [7] on the opposite side of the Nafion membrane (Nafion[®] 117, DuPont, USA). The anode ink was prepared in an ultrasonic mixer by mixing the platinum black powder with a 5% alcohol suspension of Nafion (Ion Power, USA) and double-distilled water. The composition of the ink was adjusted so as to obtain a volume ratio of 1:1 of the metal to solid Nafion in the dried catalyst layer. The fabricated membrane-electrode assembly (MEA) was mounted in house-designed fuel cell hardware. Carbon cloth

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