



Membrane patterned by pulsed laser micromachining for proton exchange membrane fuel cell with sputtered ultra-low catalyst loadings



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HIGHLIGHTS

- Stainless steel molds for pressing process were made by laser machining.
- Molds were used to structure proton exchange membranes.
- Proton exchange membranes are nano- and micro-patterned on their cathode side.
- Patterned AMEs were tested and compared in same conditions with ultra-low Pt loading.
- An increase in performance of a factor 3.6 was found for one patterned AME.

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ABSTRACT

Proton exchange membranes were nano- and micro-patterned on their cathode side by pressing them against stainless steel molds previously irradiated by a Ti:Sapphire femtosecond laser. The membranes were associated to ultra-low loaded thin catalytic layers ($25 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$) prepared by plasma magnetron sputtering. The Pt catalyst was sputtered either on the membrane or on the porous electrode. The fuel cell performance in dry conditions were found to be highly dependent on the morphology of the membrane surface. When nanometric ripples covered by a Pt catalyst were introduced on the surface of the membrane, the fuel cell outperformed the conventional one with a flat membrane. By combining nano- and micro-patterns (nanometric ripples and $11\text{--}24 \mu\text{m}$ deep craters), the performance of the cells was clearly enhanced. The maximum power density achieved by the fuel cell was multiplied by a factor of 3.6 (at 50°C and 3 bar): 438 mW cm^{-2} vs 122 mW cm^{-2} . This improvement is due to high catalyst utilization with a high membrane conductivity. When Pt is sputtered on the porous electrode (and not on the membrane), the contribution of the patterned membrane to the fuel cell efficiency was less significant, except in the presence of nanometric ripples. This result suggests that the patterning of the membrane must be consistent with the way the catalyst is synthesized, on the membrane or on the porous electrode.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) are attracting increasing research interest as they have a great potential as clean-energy power sources for portable, transportation and stationary

applications owing to their high power densities, low temperature operation and zero greenhouse-gas emissions. The membrane electrode assembly (MEA) is the main component of the PEMFC. It consists of a proton exchange membrane (PEM), two catalytic layers and two gas diffusion layers (GDL). Nafion membranes are the most popular electrolytes due to their excellent proton conductivity, their mechanical and their chemical stability. The catalytic layer where proton, electronic, and fuel transfers occur is still the subject of intense research. These components are typically

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fabricated individually and then pressed together at high pressure and high temperature. While significant progress has been achieved in recent decades, the high cost of PEMFCs (materials and fabrication process) is one of the main obstacles preventing their commercial application. One of the approaches to overcome the cost issue is to reduce the most widely used electrocatalyst, platinum (Pt), to maximize the surface area of the Pt catalyst and to enhance its use without sacrificing cell performance. This will help to minimize the fuel cell size and the amount of materials required to build an efficient fuel cell. The use of sputter deposition can reduce the catalyst loading by increasing the increase its mass activity [1–6], but performance is still reduced in terms of area specific power density (expressed in mW cm^{-2}). When the Pt thin film is formed on the membrane by sputtering (a fuel cell architecture called catalyst coated membrane, CCM), the fuel cell reaches about half the power density of a commercial MEA (about 0.5 W cm^{-2} against 1 W cm^{-2}) with one-twentieth of the platinum loading on the cathode side (typically $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ against $400 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$), which increases the mass specific power density by a factor of 10 (typically 25 W mg^{-1} against 2.5 W mg^{-1}).

To improve the performance of fuel cells in which the membrane is Pt-coated by sputtering, one approach is to optimize the interface between the membrane and the catalytic layer of the cathode, where the sluggish oxygen reduction reaction (ORR) occurs. This interface should be built in such a way that electrons, protons and the gas molecules can have easy access to the catalytic sites. For example, the Pt catalyst must be deposited on a support that allows a good interaction with the Nafion ionomer, encouraging proton access to the Pt catalyst sites and not disturbing the diffusion of the gaseous species. In addition, the MEA must exhibit excellent bonding between the electrodes and the membrane to minimize electrical losses, while ensuring high mechanical strength to promote durability. One strategy to satisfy such conditions is to tailor the morphology of the catalyst layer-Nafion interface by promoting a high contact area between the catalyst and the membrane, which may facilitate proton migration (high proton conductivity), and access to the catalyst, decrease interfacial resistance and even enhance the water retention capability of the membrane. This concept can be realized by the direct sputter deposition of Pt catalyst particles on nano/micro-scale structures previously formed on the membrane surface.

Recent studies seem to indicate that the patterning of PEM enhances the fuel cell performance, especially with the use of different techniques to generate a surface - patterning structure. These include surface roughening by abrasion [7], by the introduction of a rough transition Nafion thin film [8,9], by plasma treatments [10–14] and by the use of (optic, electronic) lithography [15–21]. One of the first attempts to pattern the surface of a Nafion membrane was made in 2002 by O'Hayre et al. [7] who abraded the membrane by using SiC sandpaper to obtain fine and coarse roughening. This textured surface disrupted the sputtered platinum film. It was found that fuel cell performance was extremely sensitive to membrane texture [7]. However, some SiC impurities can be present on the surface of the membrane after abrasion which can disturb the electrochemical reactions. Wang et al. [9] introduced a rough Nafion thin film between the catalyst layer and the membrane using the spray technique to fabricate a direct methanol fuel cell. The rough interface reduced the contact resistance and expanded the reaction region of MEA, significantly improving of the fuel cell performance. In addition, the modified structure also exhibited a better durability due to the enhancement of interaction between electrode and membrane compared to the normal CCM structure. The membrane was also treated by argon ions and plasma to enlarge the effective area of the electrode/cathode interfaces. Cho et al. [12,13] demonstrated that the roughness and

hydrophobicity of the membrane surface increased with increasing argon ion density, which is favored for a high-performance PEMFC. In fuel cell tests, one MEA based on a roughened Nafion[®] membrane exhibited a maximum power density, which was two times higher than that of the single cell employing an untreated Nafion[®] 115 membrane. Kim et al. [14] used less expensive atmospheric-pressure glow plasma in a gas mixture of He/H₂ to etch the Nafion surfaces very efficiently. By using SiC abrasion, by the introduction of the rough thin film of Nafion or by subjecting the membrane to plasma/ion bombardment, no regular or ordered patterns are formed and the surface of the membrane resembles a creased paper, especially when abrasion is used.

In order to obtain ordered patterns on the membrane and thus a better understand the influence of pattern dimensions on the fuel cell activity, different patterning techniques using lithography were introduced in the mid-2000s. For most of these techniques, master molds having regular and ordered patterns on their surface are required. These patterns are then transferred to the membrane by hot pressing or by casting. The molds are previously fabricated by coupling lithography to produce a patterned mask and plasma etching. For example, Aizawa et al. [15,16] fabricated ordered hole structures on the polished side of an Si wafer using optical lithography and the Bosh etching process before casting the ionomer solution over the Si mold to form an ordered micro pillar-array patterned Nafion membrane. With this technique, they were able to control the pillar widths and heights. Each pillar had micrometric dimensions, the same average width of about $2 \mu\text{m}$ and different average heights of about 3, 6 and $10 \mu\text{m}$. To reduce these dimensions, one dimensional nanometric SiO₂ grating molds were formed by Taylor et al. [17] using the electron beam lithography technique. Identical techniques were used by Yildirim et al. [18] to form molds consisting of a one dimension grating (channel width $19 \mu\text{m}$ and distance between two features $25 \mu\text{m}$), but the transfer of the patterns to the membrane was achieved by hot pressing (also called hot embossing). This transfer technique has been also used to transfer patterns from two micrometric stainless steel meshes on both sides of a Nafion N115 membrane [19]. To avoid the need for a mold, Omosebi et al. [20,21] demonstrated the patterning of per-sulfonic Nafion membranes using electron beam lithography coupled with dry etching. Lithography was used to define the pattern structure on the membrane (and not on the mold) whereas a plasma based on a mixture of O₂ and CHF₃ gas allowed the direct etching of the membrane through a germanium mask. Although optical or electronic lithography can be used to form ordered patterns on the membrane surface, some studies claim that these methods have certain limitations such as high cost and a complicated fabrication method. Chi et al. [22] developed a process to form $1 \mu\text{m}$ surface patterned Nafion films by using different types of ZnO nanorods as templates. They obtained a 59% increase in the power density in a PEMFC when using the surface-patterned MEA with the highest surface area. Li et al. [23] introduced mesopores to Nafion membranes via a soft template method using either non-ionic block copolymer or a colloidal silica mediated self-assembly technique. With the second technique, the highly ordered and periodic mesoporous Nafion significantly enhanced the water retention capability and had a higher proton conductivity particularly at reduced relative humidity as compared with the pristine Nafion. In addition, Zhou et al. [24] used liquid precursors to form micro-patterned PEM with micrometric features by using soft lithographic/micromolding techniques. They used patterned sacrificial templates made from poly(cyanomethyl-acrylate) films which were patterned by soft-lithography techniques using a PPPE mold. Finally, Wang et al. [25] developed a novel MEA in which both the cathode and the membrane were incorporated in a porous PTFE matrix.

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