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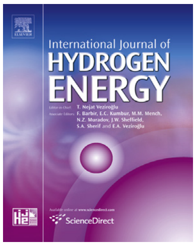

Nanostructured Pd barrier for low methanol crossover DMFC

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ABSTRACT

This work reports the successful fabrication of Pd nanostructured proton conducting-fluid blocking barriers on standard perfluorosulfonic acid membranes, able to reduce considerably methanol crossover in Direct Methanol Fuel Cells. The barrier nanostructure and grafting to the underlying membrane was optimized by fine-tuning the deposition conditions. A reduction in methanol crossover up to 50% was achieved, increasing significantly the fuel cell efficiency, admitting a slight power density reduction with respect to a reference cell. The developed barriers hindered methanol transport through the membrane as well as water transport, therefore membrane dehydration can be observed at low current density, if operating conditions are not suitably modified.

1. Introduction

Direct methanol fuel cells (DMFCs) are a promising technology for portable and small stationary applications, due to the advantages of a liquid and readily-available fuel [1]. At the moment DMFCs are studied in a wide and growing number of research projects for portable and small stationary power supply, a short-term application, where cost and technical requirements are close to be achieved. To be competitive in portable applications and in general to improve DMFC performance, some technical challenges that strongly reduce efficiency and power density have to be overcome, with a particular reference to the low rate of methanol oxidation kinetics on the anode and the methanol crossover through the polymeric membrane [2]. Methanol crossover occurs due to the inability of the commonly used proton-conducting polymeric membranes to prevent methanol from permeating their structure; diffusion and electro-osmotic drag are the primary driving forces for methanol transport through the proton-conducting polymeric membrane [3,4]. Methanol reacts with platinum catalyst sites on the cathode, leading to a mixed potential on the cathode and a lower oxygen availability for the electro–chemical reaction [5,6].

Methanol crossover in DMFCs has been recently studied both experimentally and theoretically [2–6]; different reports confirm that methanol diffusion is generally the dominant contribution. Research activities to reduce crossover are focussing on membrane formulation and other types of

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methanol permeation barriers. A number of techniques has been reported recently. One of them is to modify proton-conducting electrolyte membranes based on Nafion™. Antonucci et al. [7] prepared a Nafion-silica composite electrolyte membrane and a Nafion-zirconium phosphate composite membrane [8], both of which had lower methanol permeation than Nafion. DMFCs including these membranes could be operated at a high temperature of 140–150 °C. Uchida et al. [9] dispersed Pt nanocrystal particles in Nafion117™ to suppress methanol permeation. Jia et al. [10] modified Nafion117™ by impregnating the membrane with poly(1-methylpyrrole) by "*in-situ*" polymerization. Although the methanol crossover was decreased in their modified membrane, its conductivity became lower. On the other hand, Peled et al. [11] developed a novel low-cost nanoporous proton-conducting membrane consisting of high-surface-area inorganic powders such as silica, and polymer binders like polyvinylidene fluoride (PVDF).

In general, the experimental results showed that this kind of membranes are characterized by a lower methanol crossover but also by an important reduction in proton conductivity. An alternative approach consists in modifying the features of the anodic transport layer; however, reduction is still limited to less than 50% [12]. Another recent and innovative approach is to produce barriers to prevent methanol crossover by means of a methanol-impermeable proton conducting (MIPC) layer. Thin films of Pd and Pd alloys look as promising candidates in this respect since hydrogen in palladium behaves like a proton [13], so this kind of metal or alloy membranes may be considered as a proton exchange membrane. Although the cell with the Pd-sputtered membrane exhibited superior performance, the repeated hydride formation in the Pd thin layer during the continuous operation of the cell may lead to hydrogen embrittlement in the Pd thin layer, due to $\alpha \rightarrow \beta$ phase transition at low temperatures (<150 °C). This, in turn, can cause the mechanical delamination of the Pd layers from the surface of the membrane. This problem is known in other fields of application and several solutions have been proposed, mainly alloying Pd with Ag (30 wt%), Cu (40 wt%) and Au (5 wt%). Alloys of Pd–Ag [14] and Pd–Cu [15] sputtered on standard Nafion have been tested. Pd–Ag shows a higher proton conductivity than Pd–Cu [16].

Even though they are very promising, these works failed to obtain a complete blockage of methanol crossover. This is mainly attributed to the high density of wide cracks (200–300 nm) present on the reported films. It is believed that the cracks were caused by the residual stress between the sputtering layer and the Nafion polymer membrane during the sputtering process. Since sputtering is generally carried out under medium vacuum conditions (1–10^{-3} mbar), the polymer substrate might become completely dry without moisture, thus shrinking. When samples are exposed to ambient air they re-absorb water moisture, leading to expansion. In the meantime, the sputtered metal layer is insensitive to the environmental condition; thus, its volume would remain more or less the same after the sputtering process. Therefore, a mismatch might be caused between the expanded polymer substrate and the metal barrier, leading to the thin layer cracking. The other fundamental issue in using the sputtering technique is its limited capacity of depositing films with a controlled porosity and nanostructure, thus limiting the possible strategies to solve the problem.

This work aims to demonstrate that the Pulsed Laser Deposition technique (PLD) is able to solve these issues and to produce Pd barriers with controlled characteristics on a standard membrane even at pressures of several Pascal. The preliminary results of materials characterization and fuel cell testing are reported and discussed.

2. Experimental

2.1. *Preparation of the samples*

Nafion117™ membranes were procured from Quintech. Each Nafion117™ membrane was successively boiled for 30′ in 5% H_2O_2, deionized (DI) water, 1 M H_2SO_4, and DI water. After this wet conditioning, the membrane was dried in air overnight. Upon mounting on the 2″ PLD substrate holder, a wet tissue was placed in between the conditioned membrane and the holder in order to keep hydrated the membrane during the PLD deposition. Palladium barrier films were deposited at room temperature on the membrane by ablating a Pd target with a ns-pulsed laser (Nd:YAG by Continuum, $\lambda = 266$ nm, $f_p = 10$ Hz, pulse duration ≈ 6 ns) in vacuum. The fluence on the target was 2 $J\cdot cm^{-2}$ and the background gas (He, purity 99,9999%) pressure was varied from 1 Pa to 400 Pa. Deposition distance was varied between 3 and 7 cm, but optimal results, shown here, were achieved at 3 cm. The number of laser pulses was varied in order to obtain the desired film thickness. Off-axis deposition and substrate rotation were implemented in order to obtain an uniform deposition on the 2″ active area. More specifically, the off axis position was adjusted in order to have a radial thickness uniformity in the order of 10–20%, depending on the other deposition parameters, most significantly the background gas pressure.

2.2. *Instruments and methods*

Scanning Electron Microscopy (SEM) images were acquired on deposited barriers and some tested samples by a Zeiss SUPRA 40 Field-Emission SEM equipped with a pole piece mounted solid-state Back Scattered Electrons (BSE) detector. Structural characterization was performed via XRD analysis, which was carried out using a PANalytical X'Pert PRO x-ray diffractometer in θ/2θ configuration, with a solid state X'Celerator detector. Spectra were collected using Cu K_α (1.54 A°) radiation. Atomic Force Microscope images were acquired with a Thermomicroscope Autoprobe CP Research in non-contact mode.

The collection of dynamic mechanical analysis (DMA) data was executed by means of a TA Instruments DMA Q800 instrument using the film/fiber tension clamp. The temperature spectra were determined by subjecting a rectangular dry film sample of ca. 25 (height) mm × 6 (width) mm × 0.2 (thickness) mm to an oscillatory sinusoidal tensile deformation with an amplitude of 4 mm at 1 Hz and with a 0.05 N preload force. The temperature range spanned from −10–180 °C, and was