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Short communication

A fully spray-coated fuel cell membrane electrode assembly using Aquivion ionomer with a graphene oxide/cerium oxide interlayer

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HIGHLIGHTS

- A fully sprayed multilayer membrane-electrode assembly with Aquivion is produced.
- GDL fibers, protruding through the MPL are identified by confocal microscopy.
- A 200 nm thin GO/CeO_2 interlayer reduces H_2-crossover and electrical shorts.

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ABSTRACT

A novel multilayer membrane electrode assembly (MEA) for polymer electrolyte membrane fuel cells (PEMFCs) is fabricated in this work, within a single spray-coating device. For the first time, direct membrane deposition is used to fabricate a PEMFC by spraying the short-side-chain ionomer Aquivion directly onto the gas diffusion electrodes. The fully sprayed MEA, with an Aquivion membrane 10 μm in thickness, achieved a high power density of 1.6 W/cm^2 for H_2/air operation at 300 kPa_{abs}. This is one of the highest reported values for thin composite membranes operated in H_2/air atmosphere. By the means of confocal laser scanning microscopy, individual carbon fibers from the gas diffusion layer are identified to penetrate through the micro porous layer (MPL), likely causing a low electrical cell resistance in the range of 150 Ω cm^2 through the thin sprayed membranes. By spraying a 200 nm graphene oxide/cerium oxide (GO/CeO_2) interlayer between two layers of Aquivion ionomer, the impact of the electrical short is eliminated and the hydrogen crossover current density is reduced to about 1 mA/cm^2. The peak power density of the interlayer-containing MEA drops only by 10% compared to a pure Aquivion membrane of similar thickness.

1. Introduction

In conventional polymer electrolyte membrane fuel cells (PEMFCs) a free-standing ionomer membrane such as Nafion is used to provide mechanical support to the cell, and is used as a substrate for deposition of the anode and cathode gas diffusion electrodes [1]. Direct membrane deposition (DMD) has recently been utilized as a novel alternative membrane electrode assembly (MEA) manufacturing process. In DMD, an ionomer material such

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as Nafion is inkjet-printed [2–4], sprayed [5] or drop-casted [6] from dispersion directly onto one or both of the electrodes. This technique has been used to fabricate very thin membranes down to about 10–12 μm and the resulting MEAs displayed record fuel cell power densities [2].

Whilst Nafion has been by far the most commercially successful ionomer over the decades, alternatives with superior conductivity or materials properties are being developed. Over the past years, industry has focused on the modification of perfluorinated sulfonic acid (PFSA) ionomers to improve cell performance. Solvicore commercialized a modified version of a perfluorinated sulfonic acid (PFSA) with shorter side chains under the trademark "Aquivion" [7]. In comparison to Nafion, Aquivion possesses a short side chain (SSC), leading to higher polymer crystallinity and an increased glass transition temperature of ~140 °C. Water uptake is also improved, leading to improved proton conductivity, especially at low relative humidity and higher temperatures [8]. Similar activities were reported by 3 M, developing SSC-ionomers with EWs as low as 580 [9], as well as other low EW ionomers, based on multi-acid side chains [10]. As such, the application of SSC ionomers is also promising for the development of next-generation DMD fuel cells.

In the work of Klingele et al. electrical shorts in the range of 120 mΩ cm^2 were observed in DMD-based PEMFCs, despite observation of low hydrogen crossover current densities of ~2 mA/cm^2 [2]. The cause of these electrical shorts has remained unclear up until now. In this work, we characterize the substrate surfaces in more detail, revealing small gas diffusion layer imperfections, which are the likely cause of this type of process failure. After identification, this issue is resolved by utilization of a thin electrically insulating interlayer, comprising a graphene oxide (GO) and cerium oxide (CeO_2) nanoparticle composite.

The proton conducting properties of GO are now relatively well known, and have been reported previously by Bayer et al. [11]. Thin GO layers have also been reported to prevent methanol crossover in direct methanol fuel cell (DMFC) applications [12]. Lue et al. applied 1–10 μm thick GO layers onto commercial Nafion membranes for DMFCs by the use of spin-coating [13]. Lin et al. laminated a 1 μm thick, free-standing GO sheet onto a Nafion membrane for DMFCs [14]. However, the application of GO interlayers has not been widely explored for PEMFCs. A recent patent from 'Johnson Matthey Fuel Cells' on multilayer membranes with a GO interlayer for fuel cell applications demonstrates the industrial interest for this type of GO/ionomer multilayer fuel cell membrane [15].

Cerium oxide is a highly relevant additive for fuel cell membranes due to its extremely efficient radical scavenging properties [16,17]. Even at very small weight percentages in the range of 1 wt %, the stability of fuel cell membranes towards chemical degradation can be extended by a factor of 7 [18]. In DMD-based fuel cells, the beneficial impact of CeO_2-decorated polymer nanofibers as membrane reinforcement has been recently shown [19]. Thus, based on the experience from literature, the use of a bifunctional interlayer composed of GO and CeO_2 nanoparticles was pursued in this work. With this it is possible to provide membrane degradation stability, low hydrogen crossover and good electrical insulation by maintaining reasonable electrochemical performance of the composite membrane.

2. Methods

2.1. MEA fabrication

Gas diffusion layers (GDLs) were chosen specifically for their crack-free surfaces (Freudenberg H23C8, 5 cm^2) and used for MEA fabrication. The catalyst ink was composed of 159.82 mg Pt/C (Tanaka Kikinyoku Kogzo K. K., 46.2 wt% Pt) which was wetted in 869 ml of deionized water. Subsequently 194 ml of 24 wt% Aquivion dispersion (D83-24B) and 7821 ml of ethanol were added to the mixture. This resulted in a final CL-ionomer content of 25 wt % (solids). The ink was stirred overnight and then ultrasonicated for 30 min (SMT Ultrasonic Homogenizer UH-600). A spray-coating device (Nordson K. K., C-3J) was used for the deposition of the catalyst layers (CLs), ionomer, and interlayer. For the CL, a spray head speed of 33 mm/s was used. The catalyst loading and the interlayer deposition was determined by weighing the sample with a high-precision scale (Mettler-Toledo XP2U, precision: ±0.1 μg). A moderate Pt-loading of 0.3 mg/cm^2 was used for both anode and cathode. The CL on the GDL/MPL substrate was hot-pressed at 132 °C for 3 min with a force of 0.3 kN (Sinto Digital Press CZPT-10). Subsequent hot-pressing of the gas diffusion electrode, as well as the membrane surface significantly improved the surface homogeneity of the membrane as can be seen in the confocal laser microscopy images in the supplementary information Figs. S1) & S2).

Ionomer membrane deposition was performed with identical spray-coater scan settings as used for the CL deposition. The ionomer ink used for the membrane consisted of a mixture of 2 mg D83-24B Aquivion dispersion and 8 mg ethanol, corresponding to 4.8 wt% Aquivion solids in dispersion. The ionomer loadings for the 10 and 20 μm membranes were 1.2 and 2.5 mg/cm^2, respectively, determined gravimetrically. The Aquivion membrane surfaces were hot-pressed under the same conditions as used for the CL.

The GO/CeO_2 dispersion was composed of 25 ml ethanol, 2.5 ml GO dispersion in water (5 mg/ml, Graphene Supermarket) and 2.5 ml of CeO_2 (25 nm nanoparticles, Sigma-Aldrich) dispersion in water (5 mg/ml), corresponding to a mass ratio of 1:1. Interlayer

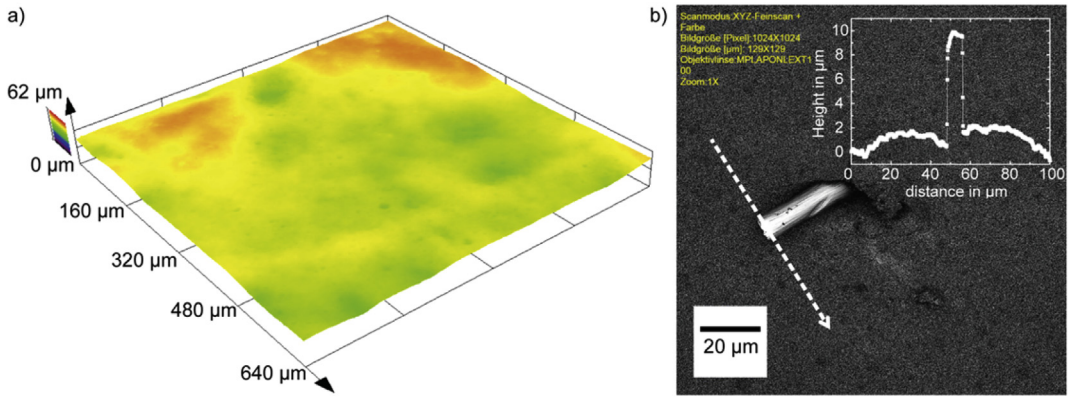

Fig. 1. Confocal laser microscope images. a) 20× magnification image of the crack-free gas diffusion layer (GDL) surface. b) Microscopic image (100× magnification) of a GDL fiber penetrating through the surface of the micro porous layer (MPL). The graph (inset) shows the z-profile along the path of the white dashed arrow.