



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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H I G H L I G H T S

- 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/CeO₂ interlayer reduces H₂-crossover and electrical shorts.

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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/cm² for H₂/air operation at 300 kPa_{abs}. This is one of the highest reported values for thin composite membranes operated in H₂/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 cm² through the thin sprayed membranes. By spraying a 200 nm graphene oxide/cerium oxide (GO/CeO₂) 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/cm². The peak power density of the interlayer-containing MEA drops only by 10% compared to a pure Aquivion membrane of similar thickness.

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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

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. Solvico 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 $\text{m}\Omega\text{ cm}^2$ 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

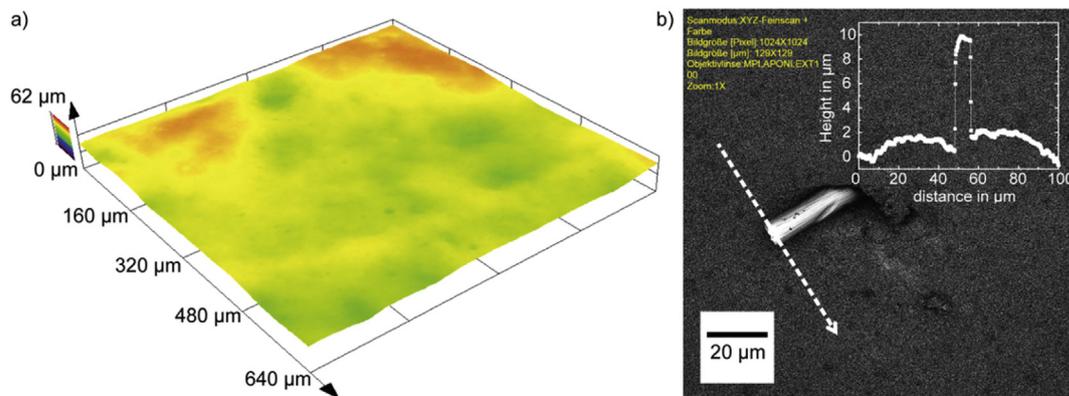


Fig. 1. Confocal laser microscope images. a) 20 \times magnification image of the crack-free gas diffusion layer (GDL) surface. b) Microscopic image (100 \times magnification) of a GDL fiber penetrating through the surface of the micro porous layer (MPL). The graph (inset) shows the z-profile along the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

deposition onto the hot-pressed membrane surface (only on the cathode side GDE) was controlled by weight and adjusted to $10 \mu\text{g}/\text{cm}^2$. No hot-pressing was applied to the GO/CeO₂ interlayer in order to protect the morphology of the very thin layer as well as to avoid thermal reduction of the GO.

Three MEAs were fabricated and characterized with: (1) a pure Aquivion ionomer membrane with $10 \mu\text{m}$ total thickness; (2) a pure Aquivion ionomer membrane with $20 \mu\text{m}$ total thickness; and (3) a multilayer Aquivion ionomer membrane with $20 \mu\text{m}$ total thickness inclusive of a 200 nm GO/CeO₂ interlayer.

2.2. Process control and sample investigation

A confocal laser scanning microscope (Olympus LEXT OLS 4000) was used for imaging all of the substrate surfaces in this work. Cross-sections for scanning electron microscope (SEM) imaging were prepared by fracturing the MEAs in liquid nitrogen. An SEM (Zeiss Auriga 60 Dual Beam) was used to image the MEA cross-sections.

2.3. Fuel cell testing

The fuel cells were tested with a Scribner 850e device using hydrogen and air as reactant gases at fixed flows of 0.25 and 1.0 l/

min. The cell was heated to $80 \text{ }^\circ\text{C}$ and the fuel humidification was set to $95\% \text{ RH}$. The polarization data was acquired with 30 s hold time in the kinetic region ($0\text{--}250 \text{ mA}/\text{cm}^2$), and 5 min over the rest of the polarization curve ($>250 \text{ mA}/\text{cm}^2$), to ensure sufficient stabilization time during the measurement. The cell resistance (high frequency resistance – HFR) was measured by in-situ electrical impedance spectroscopy at a frequency of 3.2 kHz . Linear sweep voltammetry (LSV) was performed with $0.2/0.05 \text{ l/min H}_2/\text{N}_2$ gas flow by sweeping the cell voltage with a potentiostat from open circuit voltage to 0.6 V , in order to determine the hydrogen cross-over current as well as the electrical resistance of the investigated MEAs. The electrical resistance was extracted with a linear fit of the LSV data between 0.4 V and 0.6 V .

3. Results & discussion

3.1. Morphological investigation

A $640 \mu\text{m} \times 640 \mu\text{m}$ section of the MPL surface of the GDL substrate was imaged in 3D using confocal laser microscopy (Fig. 1 a). In contrast to most other commercially available GDLs (e.g. Sigracet 25 BC, see Supplementary Fig. S3) the surface is crack-free at the micrometer scale. Such cracks are generally considered to be important for water management in the MPL [20,21]. However, in

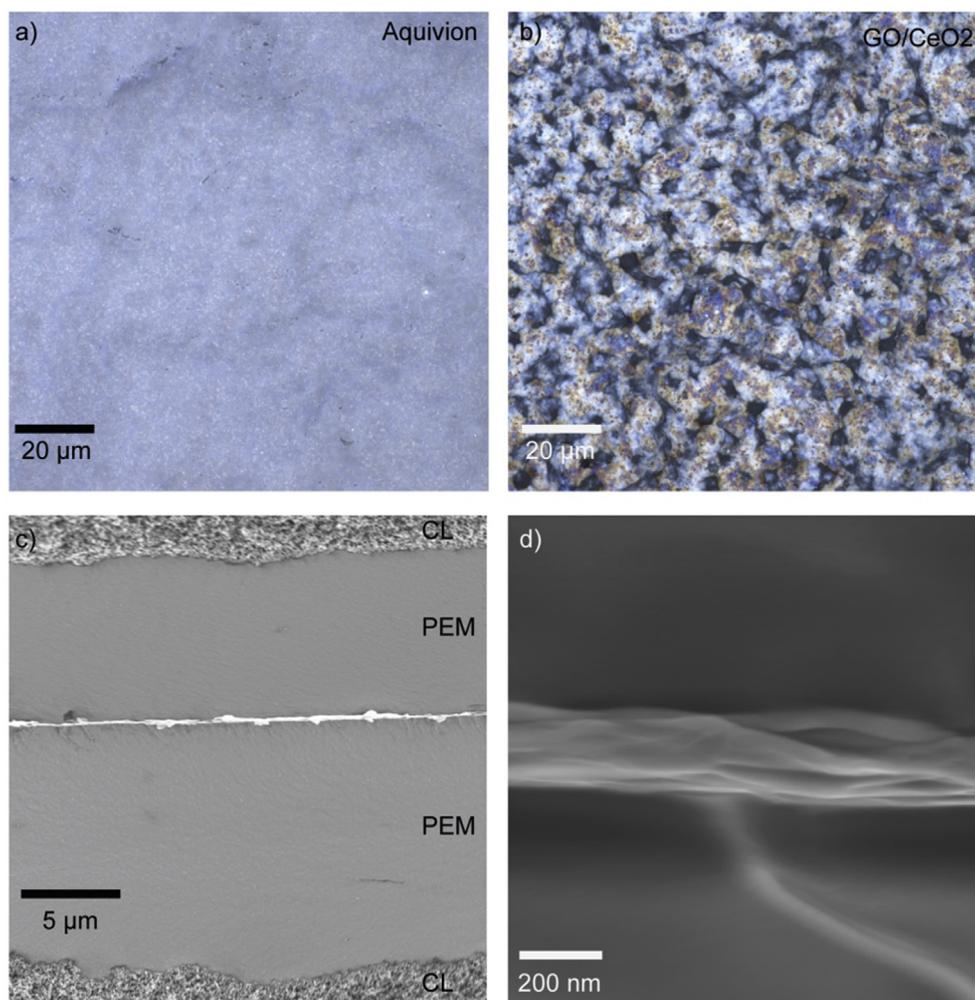


Fig. 2. Confocal light microscope images of (a) the ionomer surface and (b) the GO/CeO₂ interlayer surface. Cross-sectional SEM images of the multilayer MEA showing (c) the catalyst layer (CL), the sprayed ionomer layers, and the GO/CeO₂ interlayer sandwiched between two microporous layers (MPLs); and (d) a higher magnification image of the GO/CeO₂ interlayer.

this case where DMD was applied, they affect the morphology of the sprayed catalyst and ionomer layers, resulting in pinholes and unacceptably high hydrogen crossover. This was recently highlighted in work by Bayer et al., where a DMD-type fuel cell was fabricated based on a Sigracet 25 BC substrate with a high MPL crack density [22]. The height distribution within the examined area in Fig. 1 a) is in the range of about $\pm 20 \mu\text{m}$, and unsuitable features such as abrupt edges or cracks are not observed. Therefore, this GDL is expected to be sufficiently flat and crack-free for subsequent spray deposition of the CL and ionomer layers. In Fig. 1 b) a confocal laser scanning microscope image of the MPL-surface with higher magnification ($100\times$) is shown. The white structure in the center of the image corresponds to a single carbon fiber from the GDL penetrating through the MPL surface. This fiber sticks out of the MPL surface by about $10 \mu\text{m}$, highlighted in the inset, which shows a plot of the z-coordinate along the path of the white dashed arrow. The considerable height of this protrusion is a likely candidate for electrical shorting in DMD fuel cells, even after subsequent catalyst layer and membrane deposition. Locally thinned membranes due to membrane degradation or features such as the observed fibers have already been recognized as source of electrical shorting [23–25].

In Fig. 2 c), confocal light microscopy images show the surface of (a) a sprayed Aquivion membrane layer ($10 \mu\text{m}$ ionomer film thickness), and (b) the 200 nm GO/CeO₂ layer sprayed on top of the Aquivion surface. The Aquivion surface has a smooth and homogeneous appearance, confirming that the spray-deposition method was successful in forming a continuous membrane on top of the smooth MPL. The GO/CeO₂ interlayer surface has a more inhomogeneous appearance with features in the range of several μm , in the range of the flake size of the employed GO ($5 \mu\text{m}$).

A cross-sectional SEM image of the MEA with a GO/CeO₂ interlayer is shown in Fig. 2 c). As previously reported for Nafion, also the Aquivion ionomer deposited by the spray-coating process does not penetrate significantly into the pore-space of the catalyst layer, and forms a homogeneous membrane [26]. Further high resolution SEM images of the CL/PEM interface are provided in the Supplementary Material (Fig. S4). From these images a small infiltration depth of $100\text{--}300 \text{ nm}$ can be estimated, which forms a preferential 3D PEM|CL interface [26,27]. The bright line observed crossing the center of Fig. 2 c), between the two Aquivion PEM-layers, corresponds to the GO/CeO₂ interlayer. To further study the morphology of the GO/CeO₂ interlayer, a higher magnification image is shown in Fig. 2 d). The interlayer has a thickness of about 200 nm , and a horizontally layered structure is visible, corresponding to horizontally orientated GO sheets. This is in agreement with previous work, in which GO layers were applied onto cast membranes and displayed similar lamellar alignment on the membrane [14].

3.2. Fuel cell testing

Polarization data for the three different DMD fuel cells is shown in Fig. 3 a). At first, in order to maximize the achievable power density using this test setup, $10 \mu\text{m}$ -thick pure Aquivion MEA was operated with back pressure, at a total pressure of 300 kPa . This resulted in a peak power density of 1.6 W/cm^2 and a current density of 2.5 A/cm^2 at 0.6 V cell voltage. This is in line with the highest reported values recently reported in literature from the automotive industry, using comparably thin ($10 \mu\text{m}$), reinforced membranes [28]. At atmospheric pressure ($100 \text{ kPa}_{\text{abs}}$), the $10 \mu\text{m}$ Aquivion MEA provides the highest power density of the three cells (0.93 W/cm^2), as expected. The $20 \mu\text{m}$ Aquivion MEA shows a slightly lower peak power density (0.83 W/cm^2), followed by the $20 \mu\text{m}$ Aquivion MEA with GO/CeO₂ interlayer (0.76 W/cm^2). The slight difference in peak power density despite the similar membrane thickness of

$20 \mu\text{m}$ can be explained by Fig. 3 b). Here it is clear that the inclusion of the GO/CeO₂ interlayer results in an increase in the cell resistance. Whilst the $20 \mu\text{m}$ Aquivion MEA displays a cell resistance of $32 \text{ m}\Omega\cdot\text{cm}^2$, the interlayer-containing MEA shows a resistance of $48 \text{ m}\Omega\cdot\text{cm}^2$. This is likely due to the lower proton conductivity of the interlayer compared with Aquivion and additional contact resistances at the extra interfaces.

LSV measurements for all three samples are shown in Fig. 3 c). The pure $10 \mu\text{m}$ and $20 \mu\text{m}$ Aquivion samples have similar electrical resistance of about $150 \Omega\cdot\text{cm}^2$ (taken from a linear fit between 0.4 V

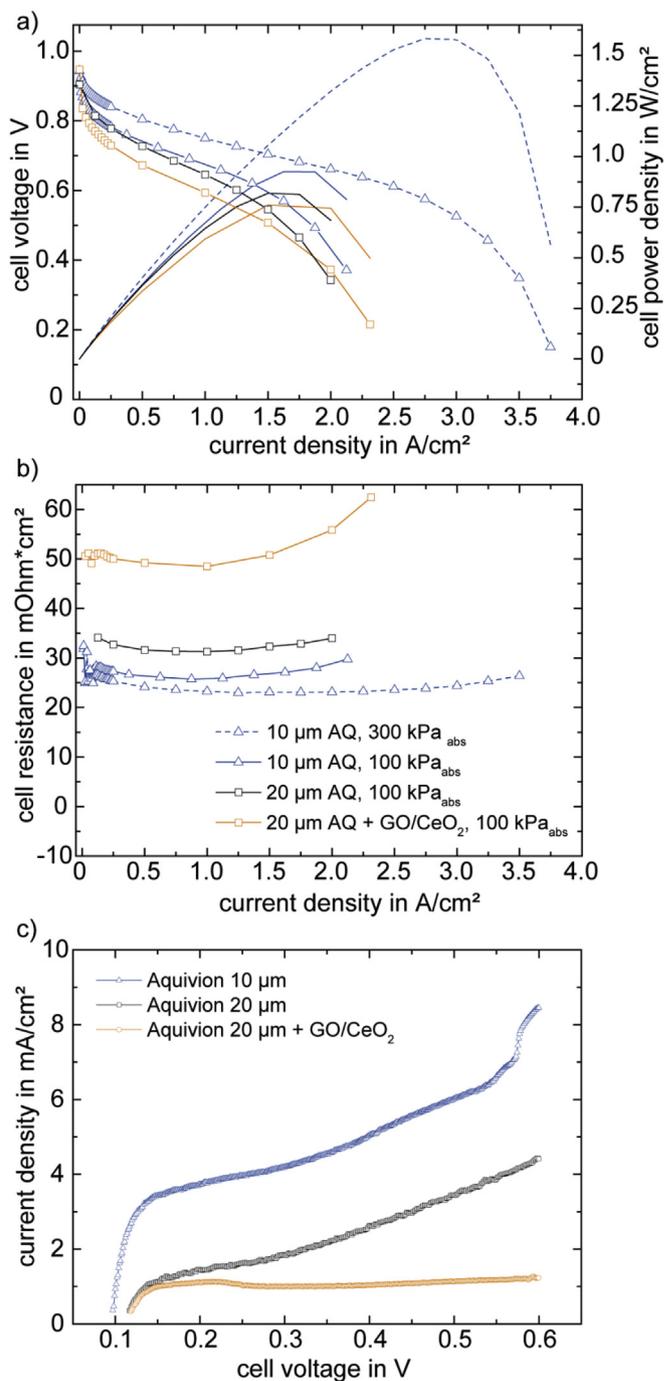


Fig. 3. (a) Polarization data, and (b) the respective cell resistances of 10 and $20 \mu\text{m}$ -thick Aquivion membranes and $20 \mu\text{m}$ multilayer Aquivion/GO/CeO₂ interlayer membrane. (c) Linear sweep voltammetry.

and 0.6 V), which is likely caused by GDL fibers penetrating through the MPL, as observed Fig. 1 b). The magnitude of this electrical short is in the same range as measured previously for DMD cells with a pure Nafion membrane of identical thickness and a similar Freudenberg H23 gas diffusion substrate [2]. Further evidence, that the GDL fiber spikes are the most probable reason for the observed, low electrical resistance was reported previously: Mench et al. stated that ‘soft electrical shorts’ with a comparable resistance above $100 \Omega \text{ cm}^2$ are typically linked to a protrusion of electrically conductive features through the membrane [23]. A similar conclusion was drawn by Baik et al., who measured lower OCV values, when a GDL with rough MPL surface was used [31]. The hydrogen crossover current density scales as expected with membrane thickness. This is about 2 mA/cm^2 for the $20 \mu\text{m}$ membrane, and 4 mA/cm^2 for the thinner $10 \mu\text{m}$ membrane, which is in good agreement with literature values measured for Nafion NR-211 ($25 \mu\text{m}$ membrane thickness) [29]. The MEA with the GO/CeO₂ interlayer shows both a low hydrogen crossover current density of 1 mA/cm^2 , and effectively infinite electrical short circuit resistance. The reduction of the hydrogen cross-over current density is in good agreement with literature, where the excellent gas barrier properties of GO sheets have been reported [30], with up to two orders of magnitude lower hydrogen diffusion through GO compared to Nafion. The elimination of the short circuit current, and the reduced hydrogen crossover current density by using the GO/CeO₂ interlayer is in line with previous work on DMD composite membranes. By using an electrospun reinforcement mesh of cerium-decorated nanofibers also an elimination of electrical shorts in the membrane and a comparably low hydrogen crossover density of about 1 mA/cm^2 , even after 100 h of accelerated degradation under OCV conditions was observed [19]. This is also in agreement with literature, where the use of membrane reinforcement is recommended to inhibit electrical shorts as well as excessive fuel crossover [23].

4. Conclusion & outlook

A MEA fabricated entirely by spray-coating with a low equivalent weight ionomer membrane is presented in this work. A sprayed MEA with ionomer membrane thickness of $10 \mu\text{m}$ displayed a very high power density of 1.6 W/cm^2 , measured with H₂/air as reactant gases at $300 \text{ kPa}_{\text{abs}}$. By means of confocal microscopy, vertical GDL-fibers were observed to penetrate through the microporous layer, which are believed to cause the low electrical resistance of about $150 \Omega \text{ cm}^2$. It was shown that a 200 nm GO/CeO₂ interlayer helped to prevent electrical shorts in the fuel cell. Furthermore, the interlayer reduces the hydrogen crossover density to about 1 mA/cm^2 . Despite inclusion of the relatively insulating interlayer, the power density dropped by less than 10% compared with a pure Aquivion membrane of similar thickness. This unique, fully sprayed, multilayer membrane architecture could also be highly promising for direct methanol fuel cell (DMFC) or intermediate-temperature fuel cell applications, where a high reactant cross-over still limits fuel cell performance [32]. Thin interlayers of several 100 nm thickness can be easily integrated with the ‘bottom-up’ DMD approach. Future work needs imperatively to focus on the choice (or fabrication) of more suitable gas diffusion substrates with minimal crack density in the MPL, as well as the elimination of carbon fibers protruding through the MPL.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2017.03.085>.

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