



A completely spray-coated membrane electrode assembly



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ABSTRACT

We present a proton exchange membrane fuel cell (PEMFC) manufacturing route, in which a thin layer of polymer electrolyte solution is spray-coated on top of gas diffusion electrodes (GDEs) to work as a proton exchange membrane. Without the need for a pre-made membrane foil, this allows inexpensive, fast, large-scale fabrication of membrane-electrode assemblies (MEAs), with a spray-coater comprising the sole manufacturing device. In this work, a catalyst layer and a membrane layer are consecutively sprayed onto a fibrous gas diffusion layer with applied microporous layer as substrate. A fuel cell is then assembled by stacking anode and cathode half-cells with the membrane layers facing each other. The resultant fuel cell with a low catalyst loading of 0.1 mg Pt/cm² on each anode and cathode side is tested with pure H₂ and O₂ supply at 80 °C cell temperature and 92% relative humidity at atmospheric pressure. The obtained peak power density is 1.29 W/cm² at a current density of 3.25 A/cm². By comparison, a lower peak power density of 0.93 W/cm² at 2.2 A/cm² is found for a Nafion NR211 catalyst coated membrane (CCM) reference, although equally thick membrane layers (approx. 25 μm), and identical catalyst layers and gas diffusion media were used. The superior performance of the fuel cell with spray-coated membrane can be explained by a decreased low frequency (mass transport) resistance, especially at high current densities, as determined by electrochemical impedance spectroscopy.

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1. Introduction

Membrane electrode assemblies (MEAs) in proton exchange membrane fuel cells (PEMFCs) are responsible for 35–45% of the costs of a fuel cell stack [1]. Most related research is focused on cost-reduction of the oxygen reduction catalyst [2–5], or cost-reduction of the proton exchange membrane [6–9], and little fundamental research has focused on alternative MEA manufacturing routes as a means of cost-reduction [10,11]. Two established manufacturing strategies exist for building MEAs: either a pre-cast polymer electrolyte membrane foil (PEM) is coated with catalyst layers by spray-coating or decal techniques to form a catalyst coated membrane (CCM), which is then stacked between gas diffusion media, or gas diffusion electrodes (GDEs) are stacked with a PEM foil in between [12]. Both approaches require a free-standing membrane foil, limiting membrane thickness and causing high production costs from the foil processing of the polymer electrolyte

[1]. In industrial applications, CCM fuel cells are predominantly employed, due to their relatively better adhesion of catalyst layer and membrane, resulting in higher achievable power densities and mechanical durability [1]. Recently, a new approach to MEA fabrication was presented in which a thin layer of polymer electrolyte dispersion was inkjet-printed directly onto GDEs, these layers functioning as a membrane [10,11]. This provided a complete substitute for the membrane foil, representing a high potential for cost savings by eliminating the foil processing step. Additionally, it was shown that without the need for free-standing membrane, much thinner membranes can be formed without the risk of gas crossover (as shown by accelerated mechanical and chemical stress cycling [11]). Superior maximum power densities were achieved by the membrane-foil-free MEAs compared to conventional CCM references. However, inkjet-printing as a membrane deposition technique is slow, thus unsuitable for industrial-scale MEA manufacturing. We therefore investigate membrane deposition by spray-coating as a fast technique for MEA manufacturing viable on the industrial scale. By spray-coating, manufacturing times for a 5 cm² MEA can be reduced from 10 to 20 min to below 60 s. Additionally, since catalyst layers are already spray-coated in many industry-scale

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MEA production lines, spray-coating of the membrane does not require any additional tooling for MEA production. Hence, membrane spray-coating allows for complete MEA production by a single device.

In this work, we present an MEA production route where catalyst layers and membrane layers are consecutively spray-coated onto a carbon-fiber gas diffusion layer with applied microporous layer as substrate. To form a fuel cell, anode and cathode half-cells are assembled with the membrane layers facing each other. A cross-section of the resultant DMD fuel cell is shown in Fig. 1b.

We show that a PEMFC constructed this way outperforms a state-of-the-art Nafion NR211-based CCM reference in terms of cell power and cell resistance, although in both samples the membrane layers are equivalent in terms of membrane thickness (ca. 25 μm); catalyst layer material, loading, and fabrication method; and gas diffusion media.

2. Methods

A 4 cm^2 PEMFC was manufactured by consecutively spray-coating catalyst layers and ionomer layers directly onto the microporous layer (MPL) of gas-diffusion layers (GDLs). To form a fuel cell, the resultant anode and cathode half-cells were assembled with the membrane layers facing each other, with a subgasket used to prevent gas crossover through the edges of the electrodes [11]. As a GDL-MPL substrate, SGL Sigracet 24 BCE was used. For the spray-coating of the catalyst layer and membrane layer, a commercially available table-top spray-coater (Sono-Tek Exacta-Coat SC) was used.

The catalyst-ink preparation comprised 1 wt.% solids in 3:1 MeOH:H₂O, the solids 30 wt.% Nafion ionomer (based on Nafion D520) and 70 wt.% Pt/C (46.4 wt.% Pt, TKK TEC10E50E). A catalyst layer with a Pt loading of 0.1 $\text{mg Pt}/\text{cm}^2$ (corresponding to 2–3 μm CL thickness) was spray-coated onto the GDL-MPL to form a GDE. This resulted in a symmetric loading of each 0.1 $\text{mg Pt}/\text{cm}^2$ on anode and cathode side. No penetration of catalyst particles into the MPL by spray-coating was found, as can be observed from the sharp separation of Pt-C particles from MPL particles in Fig. 1b.

For the membrane coating, commercially available Nafion D520 dispersion was used. The ink was stirred for several hours to prevent polymer agglomerates. To create a spray-coated membrane layer with a total thickness of ca. 25 μm , 12.5 μm Nafion was sprayed onto each anode and cathode half-cell, corresponding to 2.55 $\text{mg Nafion}/\text{cm}^2$ on each electrode.

The fuel cell characterization was performed on a fuel cell test station (Scribner Associates Inc.) with a 5 cm^2 fuel cell fixture with

serpentine flow channels. Galvanostatic polarization data was recorded with pure H₂ (0.25 slpm) and O₂ (0.5 slpm) feed, at 80 °C cell temperature and 92% relative humidity (RH) at atmospheric pressure (100% RH was avoided to prevent the cell from flooding). Data was recorded at increments of 10 mA/cm^2 from OCV to 200 mA/cm^2 with hold times of 1 min/point to resolve the kinetic polarization, followed by increments of 200 mA/cm^2 from 200 to 3000 mA/cm^2 with hold times of 5 min/point to ensure the measurement of static fuel cell characteristics. Electrochemical impedance spectroscopy was conducted throughout the whole range of current densities with 0.25 slpm H₂ and 0.5 slpm O₂ gas flow at 80 °C and 100% RH with a frequency range of 0.1 Hz to 10 kHz. To gain insight into catalyst layer proton conductivity, the cell was equilibrated to a steady low potential <0.15 V under 0.25/0.25 slpm H₂/N₂ and impedance spectroscopy was conducted at 80 °C cell temperature and 30% RH in a frequency range of 0.1 Hz to 10 kHz. Linear sweep voltammetry (LSV) was conducted under 0.2/0.05 slpm H₂/N₂, 100% RH at a rate of 1 mV/s from open circuit to 600 mV.

A reference Nafion NR211 CCM-type MEA with equal membrane thickness, catalyst layer composition, and gas diffusion media was used. The CCM was tested under the same conditions as the completely spray-coated MEA.

3. Results

Gas crossover, especially hydrogen crossover from anode to cathode side, limits cell lifetime and lessens cell performance [13,14]. Hence, it is particularly important for commercial fuel cells to exhibit as little gas cross-over as possible. Hydrogen crossover can be determined in situ by LSV. Typical values for a fully hydrated Nafion NR211 membrane are in the range of 1–2 mA/cm^2 [15]. Fig. 2a shows the LSVs of the spray-coated DMD and the CCM fuel cell.

Both samples show a crossover current density <1 mA/cm^2 . This shows that the spray-coated membrane is no less gas impermeable than the commercial Nafion NR211 membrane. In addition, no electrical shorting was identified (observed in LSVs as a linear increase of the current density with increasing cell voltage), proving excellent electrical insulation between electrodes by the spray-coated membrane.

Polarization and power density data comparing the completely spray-coated DMD fuel cell and CCM reference are shown in Fig. 2b. A 1.39 times higher cell power density of the DMD fuel cell when compared to the CCM reference is observed. This result is surprising, since equally thick membranes and equal catalyst layers with respect to catalyst (46.4 wt.% Pt/C) at low loading (0.1 $\text{mg Pt}/\text{cm}^2$) were used in both

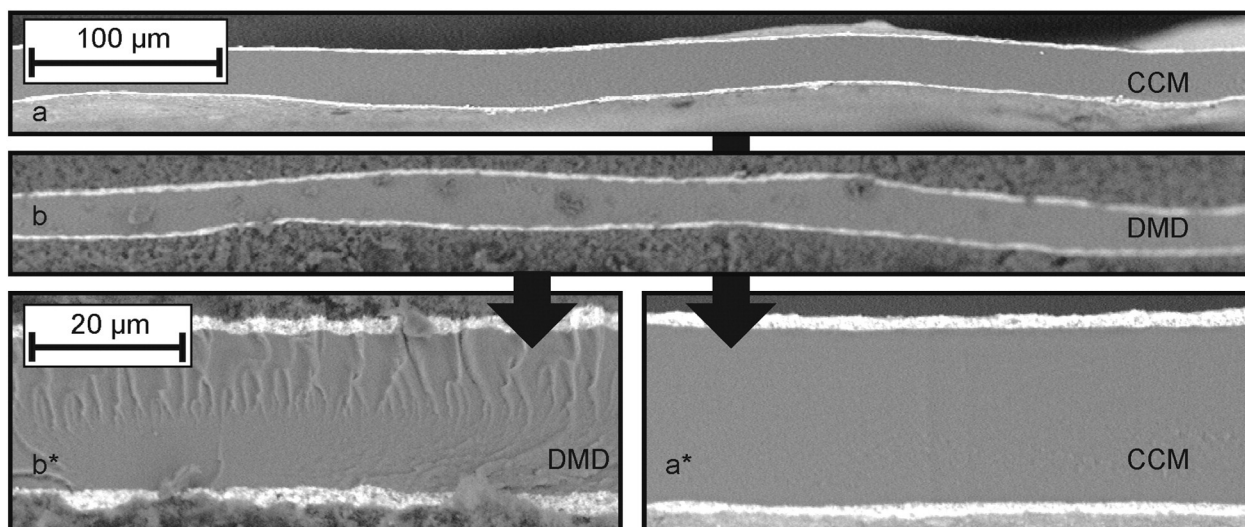


Fig. 1. Cryo-fractured cross-sections of the spray-coated DMD fuel cell (b) and the reference Nafion NR211 CCM (a). The rough surface of the DMD cross-sections is an artifact from the sectioning procedure, which occurs when GDL fibers are still attached while fracturing.

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