Short Communication

Directly coated membrane electrode assemblies for proton exchange membrane water electrolysis

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A B S T R A C T

We present a novel membrane electrode assembly (MEA) fabrication method for proton exchange membrane water electrolysis (PEMWE). Inspired by previous work on PEM fuel cells (PEMFCs), we fabricated PEMWE-MEAs via direct membrane deposition (DMD). DMD-MEAs were fabricated by spray coating the membrane directly onto the cathode electrode – in this case, a carbon cloth substrate with microporous layer coated with Pt/C. The complete DMD-MEAs consisted of the membrane-cathode compound assembled with an anode electrode, which is a porous titanium fiber substrate coated with IrO₂. Polarization experiments of DMD-MEAs show promising results: In comparison to a reference catalyst coated membrane (CCM) and a porous transport electrode (PTE) type MEA using a freestanding Nafion 117 membrane, we found very good electrochemical performances for DMD-MEAs. DMD-MEAs show slightly higher activation losses than the reference CCM. However, DMD-MEAs seem to exhibit reduced ohmic and mass transport losses compared to those manufactured using the CCM approach. Compared to the PTE-type reference DMD shows improvements for all three loss mechanisms. Similar as for PEMFCs, DMD may allow for a simplified fabrication route and higher degree of design freedom in PEMWE-MEA manufacturing due to the simple layer by layer fabrication approach.

1. Introduction

The membrane electrode assembly (MEA) is the central component of a proton exchange membrane water electrolysis (PEMWE) system with respect to performance, durability and cost [1,2]. The MEA typically consists of an Ir-based oxygen evolution reaction (OER) catalyst layer, a Pt-based hydrogen evolution reaction (HER) catalyst layer and a perfluorinated sulfonic-acid (PFSA) type proton exchange membrane. The membrane significantly contributes to ohmic losses within the PEMWE system and thereby strongly influences the window of reasonable operational current- and power-densities [2]. Typically, relatively thick membranes (120–200 µm), such as Nafion 115 and 117, are used in PEMWE, in order to ensure low gas crossovers (H₂, O₂) and mechanical robustness [1–3]. However, thick membranes come with relatively high ionic resistances [4]. Consequently, enhancing membrane stability and mitigating crossovers of thin membranes with low ionic resistances is an important task. Typical approaches for increasing membrane robustness and reducing gas crossover are the incorporation of nanofibers or nanoparticles to the membrane [4–6]. Another, yet sparsely explored approach, is the variation of the MEA design.

There are two main fabrication techniques for manufacturing PEMWE-MEAs: the first and almost exclusively used approach is the catalyst coated membrane (CCM) [7–9]. In the CCM approach typically two catalyst layers are either directly deposited onto the membrane or transferred onto the membrane via a decal process [7]. Both established CCM fabrication techniques require a freestanding, pre-manufactured membrane. In a PEMWE cell the CCM is clamped between an anode and cathode porous transport layer (PTL). Due to the corrosive environment at the anode side, the anode PTL typically consists of titanium [2]. For the cathode PTL, carbon substrates can be used. An alternative to CCMs is the fabrication of porous transport electrodes (PTEs). In this approach PTLs are coated with catalyst layers, thereby making them PTEs [10–13]. The anode and cathode PTEs are then assembled with a freestanding membrane in between. Recently, it was shown that PTE-type MEAs can be competitive with CCM-type MEAs in terms of electrochemical performance [14]. For proton exchange membrane fuel
cells (PEMFCs) a third MEA fabrication route was introduced by Klingle et al., where the membrane is directly deposited onto gas diffusion electrodes [15,16]. Fabricating PEMFC-MEAs via direct membrane deposition (DMD) led to enhanced electrochemical performances and increased catalyst utilization, especially under \( \text{H}_2 / \text{O}_2 \) conditions [15,17]. Furthermore, the DMD approach facilitates the variation of ionomers and the incorporation of nanofibers and nanoparticles into the MEA [18,19].

DMD for PEMWE-MEA fabrication was first proposed in a study of Bühler et al. [20], pointing out the difficulty of a symmetric DMD design, as it is typically used for PEMFCs, due to the large pores in commercial titanium PTLs. A first transfer of the DMD approach to PEMWE-MEA fabrication has been undertaken by Stähler et al. [21]. In their work they fabricated a MEA via a single slot die coating device by subsequently depositing the cathode catalyst layer, an approximately 20 \( \mu \text{m} \) thin membrane and the anode catalyst layer. The resulting CCM was then hot-pressed. To assemble a PEMWE cell the slot die coated CCM was sandwiched between two carbon paper PTLs. However, carbon at the anode side quickly corrodes under a PEMWE system operation and the very thin membrane is not suitable for realistic PEMWE operation conditions due to high gas crossover. Hence, the results of this study are a first proof-of-principle, but are not transferable to real operation conditions.

In this work, we present complete DMD-MEAs for PEMWE with a durable titanium substrate at the anode side and realistic membrane thicknesses. To circumvent the difficulty of fabricating a symmetric DMD design, we use an asymmetric approach, in which the membrane is deposited solely on the cathode PTE. Carbon substrates with micro porous layer (MPL) are commercially available and have a significantly smaller pore size compared to commercially available titanium PTLs. The MPL allows for the direct deposition of a homogeneous catalyst layer and a continuous membrane. We manufactured DMD-MEAs with three different membrane thicknesses (60 \( \mu \text{m} \), 200 \( \mu \text{m} \) and 230 \( \mu \text{m} \)) using a single spray coating device. Besides enabling high electrochemical performances, fabricating PEMWE-MEAs via DMD opens up a new fabrication route towards thin and additively manufactured MEAs.

2. Materials and methods

2.1. Membrane electrode fabrication

Since no anode PEMWE-PTEs are commercially available, anode PTEs were fabricated in house. By use of a commercial spray coater (Sono-Tek, Exacta Coat) with an ultrasonic nozzle type AccuMist (48 kHz), sintered titanium fiber substrates (1 mm thick, 57% porosity, 20 \( \mu \text{m} \) fiber diameter, Bekaert) were coated with 1.4 mg cm\(^{-2}\) \( \text{IrO}_2 \) (Iridium(IV) oxide, Alfa Aesar). The ink composition and spray parameters for anode catalyst manufacturing were previously reported [14].

In short: The \( \text{IrO}_2 \) ink consisted of 2 wt% solids and 98 wt% solvents (DI-water and 2-Propanol in equal parts). Of the ink solids 98 wt% were \( \text{IrO}_2 \) and 2 wt% were the solid parts of Nafion D520 (Nafion D520, FuelCellStore). After mixing all ink components, the catalyst ink was sonicated for 30 min (Hielscher, model UIS250L, 0.55W, 90% amplification). Via DMD a continuous membrane was successfully manufactured on top of the cathode PTE. During electrolys operation the membrane appears to be pressed into the channels of the cathode flow field. In future work the influence of mechanical stability of cathode PTLs and MEA compression on membrane deformation and possible effects on polarization behavior should hence be closely investigated and mitigated by the use of more rigid cathode PTL material.

2.2. Physical characterization

We acquired cross section images using a SEM (Zeiss, Gemini II) to analyse the membrane thickness of the DMD-MEAs. The samples were prepared for electron microscopy as follows: first the titanium PTL was carefully removed. Next, the MEAs were cut and embedded in epoxy resin. The sample block was ground on a rotary sander (Struers, LaboForce-100) using SiC sandpaper (up to 4000 grain, Struers) to expose the cross section of the MEA. Electron micrographs of membrane cross sections were segmented with ImageJ. Mean thicknesses were calculated using Matlab and rounded to the closest 10 \( \mu \text{m} \).

2.3. Electrochemical characterization

The test setup is described in our previous report [14]. The electric resistance of the custom made test cell was 56 \( \text{m} \text{\Omega} \text{cm}^{-2} \). After a stable cell temperature of 80 °C was reached, the test cell was conditioned via potentiostatic cycling from 1.4 V to 2.2 V (200 mV steps with a holding time of 30 s, 15 repetitions). Afterwards polarization data was recorded as follows: 0 A – 0.04 A in 10 mA steps, 0.05 A – 1 A in 50 mA steps, 1.25 A – 3 A in 250 mA steps, 3.5 A – 5 A in 500 mA steps and above 5 A in 1 A steps. The holding time for every step was 120 s. A cell voltage > 2.2 V or a current > 20 A were set as termination criteria. The high-frequency-resistance (HFR) was measured simultaneously at 1 kHz.

3. Results and discussion

3.1. Design of the DMD-MEA

The DMD-MEAs consisted of an anode PTE, a cathode PTE and a directly deposited membrane. PTFE frames were used to center the MEA. Membrane deposition on the anode PTE turned out to be impractical, due to the large pores of around 100 \( \mu \text{m} \) range [14]. Therefore, the membrane was deposited solely onto the cathode PTE, which had a MPL. In order to prevent water and gases from crossing over at the edges of the MEA, the membrane was deposited over both the cathode PTE and the PTFE frame. Therefore, cathode PTE and PTFE frame were assembled prior to membrane deposition. Membrane, cathode PTE and PTFE frame were then assembled as one cell component. Fig. 1A shows the three different analyzed MEA-types (CCM, PTE-type and DMD) and Fig. 1B illustrates the design of the DMD-MEA. The average membrane thicknesses of the DMD-MEAs were 60 \( \mu \text{m} \), 200 \( \mu \text{m} \) and 230 \( \mu \text{m} \). Fig. 1C shows representative cross-section images of the thinnest and thickest DMD-MEA, after electrochemical characterization. Via DMD a continuous membrane was successfully manufactured on top of the cathode PTE. During electrolysis operation the membrane appears to be pressed into the channels of the cathode flow field. In future work the influence of mechanical stability of cathode PTLs and MEA compression on membrane deformation and possible effects on polarization behavior should hence be closely investigated and mitigated by the use of more rigid cathode PTL material.

3.2. Electrochemical characterization

Polarization data of DMD-MEAs and the references are presented in Fig. 2. The polarization curves displayed in Fig. 2A indicate that DMD-MEAs exhibit an at least comparable electrochemical performance as the reference CCM and PTE-type MEA. At higher current densities the performance for the DMD-MEA with comparable membrane thickness...
was even slightly better than for the references. For DMD 200 µm the corresponding cell voltage at a current density of 2 A cm\(^{-2}\) was 1.95 V, while for the reference CCM the cell voltage was 50 mV higher. As shown in Fig. 2B, the improved cell performance can be mainly accounted to differences in HFR. This phenomenon was also observed by Stähler et al.\[21\]. Their slot die coated CCM exhibited a 10 mΩ cm\(^{-2}\) lower HFR than the reference CCM using a Nafion HP membrane. In our study, we find a 36 mΩ cm\(^{-2}\) lower average HFR for DMD 200 µm compared to the reference CCM. The differences in HFR are likely to originate from a changed interface when directly depositing the membrane onto the cathode electrode and from the fact, that the DMD membranes have not undergone any post treatments, such as thermal annealing, which might influence water uptake and thus proton conductivity\[22,23\].

As expected, the DMD-MEA with a membrane thickness of 230 µm showed a slightly worse overall performance and the DMD-MEA with a membrane thickness of 60 µm exhibited best overall electrochemical performance, which is mainly due to the difference in protonic resistance.

Plotting the HFR free cell voltage over current density with logarithmic scale in the low current density region (Fig. 2C) allows insights into the activation losses of the different MEAs. The reference CCM exhibits the best cell activation of all characterized MEAs. The PTE-type MEA exhibits highest activation losses. A possible explanation is the difference in electrochemically active surface area (ECSA), which needs to be analyzed in detail in future work. In the CCM-MEA design, all the catalyst is located directly at the membrane, whereas for the DMD-MEAs and PTE-type MEA the catalyst layers are deposited onto the PTLs. As suggested by Bühler et al. especially the large pores of the anode titanium PTL might lead to inactive catalyst islands\[14\]. With recent advances in the development of titanium PTLs with MPL, this problem could be counteracted\[24,25\]. The reasons for the lower activation losses for the DMD-MEAs compared to the PTE-type MEA are not yet elucidated. A possible explanation might be that the untreated, spray coated membrane attaches better to the PTE fibers than the Nafion 117 membrane\[22\]. The DMD-MEA with a 60 µm membrane exhibited the highest activation losses, which presumably stem from increased gas crossover due to the thin membrane\[26\]. Since low gas crossover is essential for PEMWE application, detailed permeability measurements need to be part of future research on DMD. Looking at the HFR-free polarization data at current densities above 1 A cm\(^{-2}\) in Fig. 2D, it is noticeable, that the HFR-free voltage rises at a greater slope for the CCM and PTE-type MEA than for the DMD-MEAs. For the CCM reference the HFR-free cell voltage increases from 1000 mA cm\(^{-2}\) to 2800 mA cm\(^{-2}\) by 59 mV, whereas for the PTE-type MEA the voltage increase over the same current range is only 48 mV. For DMD 60 µm and DMD 200 µm, the HFR-free voltage increase is 41 mV. This indicates slightly lower mass transport losses for the DMD-MEAs than for the CCM and PTE-type references\[7,27\]. It can therefore be noted, that DMD seems to slightly reduce both activation and mass transport losses compared to a PTE-type MEA and improves mass transport compared to a CCM-type MEA. Further experiments are necessary to fully understand and verify these findings.

4. Conclusion

In this work, we present a novel fabrication technique for complete PEMWE-MEAs using DMD. In contrast to the conventional PEMWE-MEA manufacturing route, where a CCM is fabricated and sandwiched between two PTLs, we use a PTE based MEA system and deposit the membrane directly onto the cathode PTE. DMD-MEAs show slightly
higher activation losses than the reference CCM. This is most probably due to inactive catalyst islands within the large pores of the anode PTE and could be solved by combining MEA fabrication via DMD with recent advances in the field of titanium MPLs. Another promising alternative for the fabrication of DMD-MEAs could be the deposition of the anode catalyst onto the spray-coated membrane. Zhang et al. already showed that catalyst deposition onto a rough, spray coated membrane enhances electrochemical performance [28]. DMD reveals slightly reduced ohmic and mass transport losses compared to the reference CCM. Compared to a PTE-type MEA with a freestanding membrane, DMD appears to have a positive effect on all three major loss mechanisms (kinetic, ohmic, mass transport) and thereby showed superior performance. In future research, gas crossover and the performance analysis of DMD-MEAs with low catalyst loadings need to be analyzed. Similar as in PEMFC-MEA fabrication, the DMD process allows for a higher degree of design freedom of PEMWE-MEAs.

CRediT authorship contribution statement

Peter Holzapfel: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. Melanie Bühler: Conceptualization, Methodology, Formal analysis, Writing - review & editing, Visualization. Chuyen Van Pham: Conceptualization, Formal analysis, Writing - review & editing, Visualization. Friedemann Hegge: Conceptualization, Software, Formal analysis, Writing - review & editing. Thomas Böhm: Software, Formal analysis, Writing - review & editing. David McLaughlin: Writing - review & editing, Visualization. Matthias Breitwieser: Conceptualization, Formal analysis, Resources, Writing - review & editing. Simon Thiele: Conceptualization, Formal analysis, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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