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Micro-perforation of the diffusion media for polymer electrolyte membrane fuel cells using short and ultrashort laser pulses

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Abstract

The water management within polymer electrolyte membrane fuel cells is one of the main challenges limiting their extensive commercial application. By introducing directed pores in the carbon-based diffusion media, the water transport properties can be improved. Thus, the performance at demanding operating conditions and the lifetime of the fuel cell can be enhanced. In this work, the microporous layer of a diffusion media was perforated by locally ablating material using short and ultrashort-pulsed laser radiation with infrared wavelength. The influence of the pulse duration as well as the peak pulse fluence and the number of pulses on the ablation rate and the surface quality was evaluated. Laser scanning microscopy was applied to assess the topography of the micro-drillings. The heat-affected zone around the micro-drillings was investigated by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The impact of short and ultrashort pulse laser radiation on the hydrophobic binder within the microporous layer was studied. Results showed a decreased binder evaporation in the vicinity of the micro-drillings by a reduction of the pulse length from the nanosecond to the picosecond range.

Keywords: fuel cell, pulsed laser ablation, water management, diffusion media, microporous layer;

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are a promising technology for powering a wide range of applications by converting chemically stored energy into electrical energy. In particular, PEMFCs are suitable for automotive applications due to their considerably high energy density at low operating temperatures, quick start-up capability, and high system robustness [1]. However, the relatively high material costs and the insufficient durability limit commercial usage [1]. Therefore, research focuses on the reduction of expensive materials, enhanced manufacturing methods, and the improvement of cell performance characteristics. The in-cell water management is decisive for the performance and the lifetime of PEMFCs. Structurally modifying the different layers inside the fuel cell has shown promising results in previous studies [2–7].

2. State of the art

A single PEMFC including two bipolar plates (BPP) and the membrane electrode assembly (MEA) is schematically shown in fig. 1. The MEA consists of a proton exchange membrane (PEM) in the center with catalyst layers (CL) on both sides. Between each CL and BPP, the diffusion media (DM) is located, consisting of a gas diffusion layer (GDL) and a microporous layer (MPL). The GDL is usually made of electrically conductive materials, e.g., carbon paper, which is often treated with hydrophobic fluoropolymers [8]. The GDL typically has a porosity of 65 % – 85 % and a thickness of 200 µm – 400 µm [9]. The MPL is a mixture of carbon

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particles with hydrophobic additives. It usually has a porosity of around 50 % and a thickness between 10 µm and 100 µm [10–11].

In a PEMFC, hydrogen and oxygen react to water ($2H_2 + O_2 \rightarrow 2H_2O$). During the reaction, the hydrogen provided at the anode side by the flow channels of the BPP has to diffuse through the DM to the CL. The hydrogen oxidation reaction ($2H_2 \rightarrow 4H^+ + 4e^-$) splits the hydrogen into protons and electrons. The protons move through the membrane to the cathode, while the electrons flow through an external current circuit. At the cathode side, the oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) takes place, where protons, electrons, and oxygen react to water. Excessive water must be dissipated from the fuel cell by passing through the DM to the BPP [12].

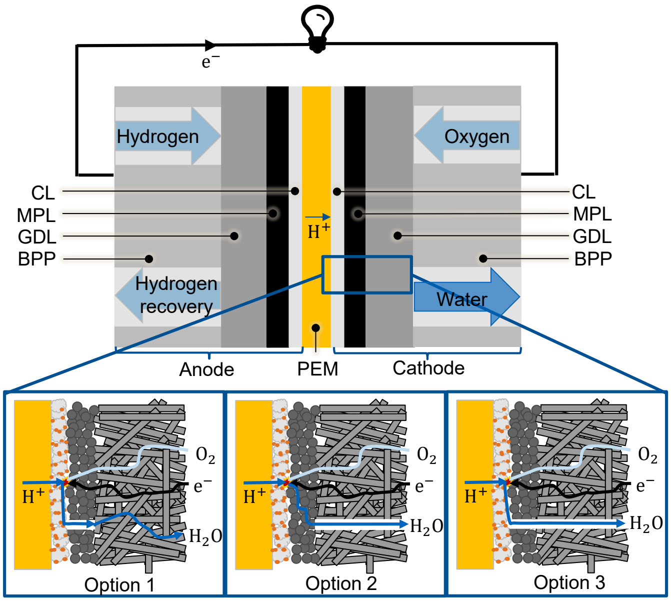

Fig. 1. Schematic illustration of a PEMFC and depiction of the three considered options including (Option 1) the selective perforation of the MPL, (Option 2) the selective perforation of the GDL, and (Option 3) the through-hole perforation of both layers.

The performance and durability of a PEMFC are highly dependent on the water management within the layers. Dry conditions lead to a reduced proton conductivity through the membrane, resulting in higher electrical losses and a reduced lifetime [13]. Another challenge arises from the liquid water generated at the cathode during the oxygen reduction reaction. Especially at high current densities, it is often difficult to remove the water fast enough, leading to liquid accumulations in the pores of the CL and the DM [1]. The impounded water blocks the transport ways and is the major cause of the limited transferal of oxygen to the CL of the cathode layer [1].

In previous years, considerable research in optimizing the water management in PEMFCs has been conducted [14–16]. The optimization of the layers is challenging due to the complex thermodynamics of the interacting factors like the capillary pressure-driven water transport, the gas diffusion, and the phase change within the DM [14]. Applying a hydrophobic coating on the GDL and introducing a hydrophobic binder in the MPL are the most common strategies to prevent cell flooding [8,15]. A promising approach to improve the water management is a structural modification of the DM. Previous studies investigated the effects of the pore size and the porosity of the MPL on the water management [15]. Additionally, it was shown that MPLs with a graded pore structure [16], directed pores introduced into the DM by mechanical structuring [2], or laser micro-drilling [2–7] allowed for an enhanced water management. Since the DM consists of two layers, the MPL and the GDL, there are three options for introducing perforations. Option 1 and 2 comprise a selective perforation of the MPL and the GDL, respectively, while the other component remains unaltered. For option 3, both layers are perforated. Which option is favorable depends on the operating conditions of the PEMFC [14]. Through-holes in the DM offering direct water pathways control the accumulation of liquid water near the catalyst layer. Thus, oxygen diffusion is ensured also at high current densities [7]. Perforating the MPL without perforating the GDL showed advantages at low current densities by preventing membrane drying because water accumulates in the pores [14]. So far, Manahan et al. and Alink et al. showed that laser structuring of the DM with nanosecond laser pulses results in removing the hydrophobic binder in the vicinity of the perforation [6,14]. The presence of hydrophilic regions resulted in an aggregation of water near the micro-drillings counteracting the favored water removal properties [6,14].

Currently, laser systems generating pulses with femto-, pico-, and nanosecond pulse durations are used for introducing micro-drillings [17]. Femto- and picosecond pulses allow precise material removal with a low thermal impact into the workpiece while nanosecond laser systems are more cost-effective and available at higher output powers [18]. For example, in lithium-ion battery production, micro-drillings introduced in the porous graphite anodes via ultrashort-pulsed laser radiation can improve the electrochemical performance [19–21]. Thus, this work concentrates on the influence of the pulse duration on the ablation behavior of the MPL of PEMFC, contributing to the design of a feasible structuring process. A laser pulse is defined as ultrashort when the thermal diffusion depth during the pulse is in the same order or less than the optical penetration depth [22]. The pulse duration of 8 ps will be considered as ultrashort for the materials to be perforated [22].

3. Experimental setup

Laser systems

For the experiments, two different laser beam sources were used. The first system was an ytterbium pulsed fiber laser (YLPP-1-150V-30, IPG Photonics Corporation, USA) with discrete pulse durations τ. The beam deflection was performed by a 2D scan head (Racoon 21, Novanta Europe GmbH, Germany) and focused by an f-theta lens (S4LFT0080/126, Sill Optics GmbH, Germany).

The second laser system used was a pulsed laser (Dart Picosecond Laser, Novanta Europe GmbH, Germany), which can provide laser pulses with $\tau = 8$ ps. For beam guidance, a 2D scan head (Racoon 21, Novanta Europe GmbH, Germany) was used and focused by an f-theta lens (JENar 160-1030...1080-110, JENOPTIK Optical Systems GmbH, Germany).

Materials

The experiments were carried out with a DM (H14CX653, Freudenberg Group, Germany) with an overall thickness of 185 µm. The MPL layer, composed of carbon black and a hydrophobic binder, had a thickness of ≈ 45 µm and a porosity of ≈ 66 % [23]. The MPL was attached to a carbon paper used as a GDL.

Table 1. Characteristics of the laser systems applied.

Laser system	IPG YLPP-1-150V-30	Novanta Dart Picosecond Laser
Operation mode	pulsed	pulsed
Central emission wavelength λ	1060 nm	1064 nm
Max. laser power P	30 W	56 W at 15 MHz
Pulse duration τ	150 ps, 1 ns, 2 ns, 5 ns	8 ps
Pulse repetition rate f_r	60 – 1200 kHz	100 – 15000 kHz
Spot diameter d_f	≈ 27 µm	≈ 26 µm
Beam quality factor M^2	< 2.0	< 1.2
Focal length	80 mm	160 mm

Analysis methods

High-resolution surface images and element maps were obtained using a scanning electron microscope (SEM) and the incorporated energy-dispersive X-ray spectroscopy (EDX) module (JSM-IT200, Jeol Ltd., Japan). The topography of the micro-drillings was analyzed with a 3D laser scanning confocal microscope (LSM) (VK-X 1000, Keyence Corporation, Japan). The lowest point of the micro-drillings compared to the average MPL surface was measured to determine the ablation depth. Each data point represents an average value from five micro-drillings The error bars in the figures indicate the standard deviation.

4. Results and discussion

The influence of the peak pulse fluence Φ_0 and τ on the ablation behavior was determined (see fig. 2). At $\Phi_0 \leq 0.68$ J·cm^{-2}, the ablation depth D was in the range of pores and inhomogeneities on the pristine surface of the MPL. For $\Phi_0 > 0.68$ J·cm^{-2}, D increased almost linearly with Φ_0. It becomes apparent that significantly more material is removed with a pulse duration of 8 ps compared to the longer pulse durations. Only a marginal difference in the ablation depth was detected for the pulse durations of 150 ps, 1 ns, and 5 ns. It is assumed that using picosecond pulses, a cold ablation process instead of the thermal ablation process occurs. Thus, energy loss and heat diffusion are minimized, resulting in higher material removal [22].

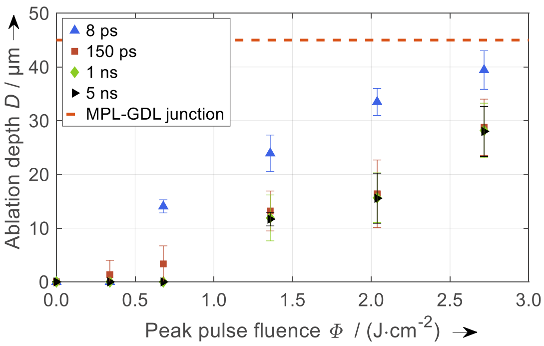

Fig. 2. Ablation depth in the MPL as a function of the peak pulse fluence for various pulse durations; a constant number of 100 pulses per drilling was applied at f_r = 1000 kHz.

The influence of the number of pulses n on the ablation depth at different pulse lengths is shown in fig. 3a). Overall, the ablation depth achieved using the ultrashort laser pulses exceeded the results of the short-pulse laser by up to ≈ 30 %. With the dashed line, the MPL thickness is schematically displayed. It can be seen that the standard deviation increased when the GDL was reached, which can be explained by the higher porosity and bigger pores within the GDL influencing the depth measurement.

As shown in fig. 3b), the ablation rate per pulse was reduced with an increasing ablation depth. The progressing conical tapering of the micro-drillings increases the area absorbing the laser radiation. As a result, the intensity is reduced, which could be the reason for a reduction of the ablation depth per pulse [24].

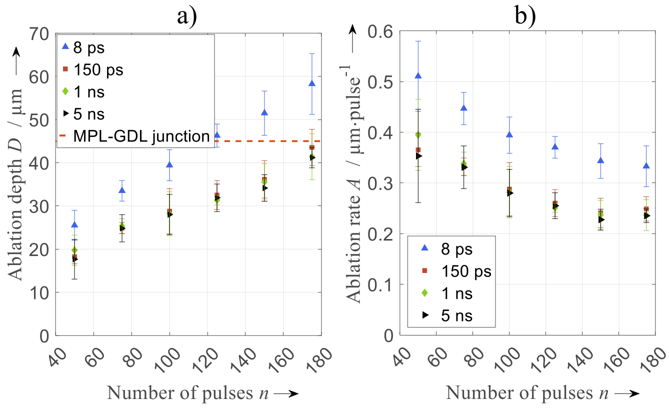

Fig. 3. a) Ablation depth in the DM and b) corresponding ablation rate for a varying number of applied pulses at f_r = 1000 kHz and Φ_0 = 2.72 J·cm^{-2}.

Surface analysis

The micro-drillings shown in fig. 4 were manufactured using Φ_0 = 2.72 J·cm^{-2} at a pulse repetition rate of 1000 kHz. To compare the different pulse durations for the described task, D was kept constant by adjusting the number of pulses applied. Consequently, for a pulse duration of 8 ps, the number of pulses per drilling was set to n = 50 and for the remaining pulse durations to n = 70 to achieve an ablation depth of D ≈ 28 µm. As it can be seen in fig. 3, the standard deviation of D was smaller for D < 45 µm, which was favorable ensuring an equal D for all τ. In fig. 4, the distribution of fluorine on the MPL surface after micro-perforation with different pulse durations is shown using EDX images. Around the holes, the absence of fluorine is visible for all pulse durations (highlighted by the red circles in fig. 4). For the hole perforated at τ = 8 ps, the region without fluorine surrounded the hole with a radius of r ≈ 15 µm. In contrast, fluorine-free areas were larger for the longer pulse duration with d ≈ 50 µm for τ = 150 ps, d ≈ 53 µm for τ = 1 ns, and d ≈ 56 µm for τ = 5 ns. The absence of fluorine is an indicator for the evaporation of the hydrophobic binder. It can be assumed that due to the higher energy input and the longer pulse duration, more heat accumulated near the micro-drillings, leading to the evaporation of the polymeric binder. As it has been shown by Alink et. al., the removal of the hydrophobic binder results in hydrophilic regions in the vicinity of the micro-drillings [14]. It can be assumed that water accumulations near the micro-drillings introduced by the ultrashort-pulsed laser can be significantly reduced since the hydrophobic properties remain preserved.

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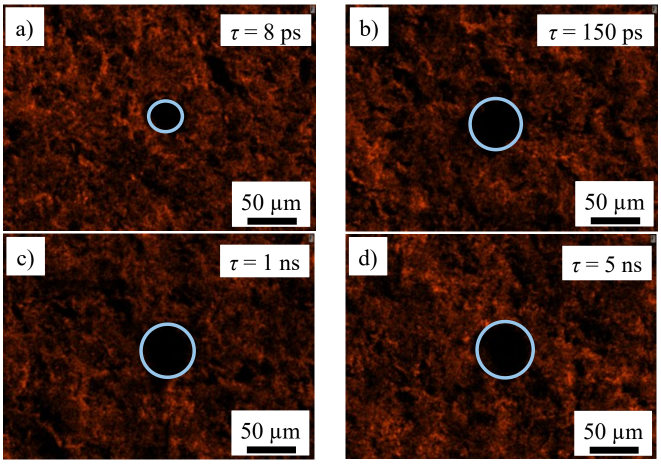

Fig. 4. Fluorine distribution on the surface of an MPL after perforation with pulse durations of a) 8 ps, b) 150 ps, c) 1 ns, and d) 5 ns at $\Phi_0 = 2.72\ J\cdot cm^{-2}$.

5. Conclusion and outlook

For this paper, the laser structuring of a PEMFC MPL using pulse durations in the nanosecond and picosecond time domain was investigated. Using pulses with $\tau = 8$ ps, the ablation rate is higher, resulting in micro-drillings with smaller heat-affected zones. The EDX analysis showed that micro-drillings can be introduced into the MPL with significantly less evaporated hydrophobic binder in the vicinity of the perforations. This can be advantageous for the water removal properties of the DM. In future studies, the perforation of the GDL will be investigated. It can be assumed that the process strategy has to be adjusted since the material, the porosity, and the thickness differ from those of the MPL. Additionally, the advantages of micro-drillings introduced with ultrashort-pulse laser radiation should be tested in fuel cells to validate the improved water management under different operating conditions.

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