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Investigating the Impact of Liquid Water in a PEFC by Electrochemical Impedance Spectroscopy

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1 Introduction

One challenge of a PEFC system is to avoid dehydration of the polymer membrane to ensure a proper protonic conductivity which forces the operating temperature to be below 100°C. This temperature limit dictates the operation of the fuel cell in the range where water also exists in liquid phase. Liquid water in the gas diffusion media and electrode causes mass transport limitations of the reactants, especially at high current densities. Thus, water accumulation has to be avoided. It is reported from many research groups that a micro porous layer (MPL), that is a layer of carbon particles impregnated with PTFE attached to the GDL, improves fuel cell performance [1,2]. The role of the MPL with regard to water transport is discussed contrary in the literature.

Several explanations are given for the measured performance enhancement. For example, Pasaogullari et al. [3] indicated that the MPL enhances the rate of water removal from the catalyst layer (CL) to the cathode gas diffusion layer (GDL), whereas other explanations base on measurements that reveal an increased back diffusion rate of water towards the anode side caused by a water barrier effect of the cathode MPL. Lower electrical contact and thermal resistance is also reported when using a MPL which strongly influences the temperature distribution within the cell and thus also the water management. To get a clearer picture of the MPL influence on water balance, further systematically experimental as well modelling work is required to reveal the mechanism by which the presence of the MPL affects PEM fuel cell performance. Since steady-state polarization measurements are strongly limited in their informative value concerning loss mechanisms, electrochemical impedance spectroscopy (EIS) is a powerful tool that may have the ability to give a closer look into the limiting transport processes.

The aim of this work is to provide a better understanding of the improvement of the mass transport related to the MPL presence. Therefore, a theoretical impedance spectroscopy analysis is conducted. ESEM imaging is used to investigate the wetting properties and liquid water transport of and through the porous media respectively.

2 Modelling Work

The impact and transport of liquid water in the porous media such as GDL, MPL and CL, its coupling with the protonic conductivity of the membrane via the ionomer water content and the kinetics, combined with phase transition is simulated with a 1D dynamic multi-phase agglomerate model. The model assumptions base mainly on a cathode model published in [4], whereas the presented new model is extended by the anode side. A schematic diagram is given in Figure 1.

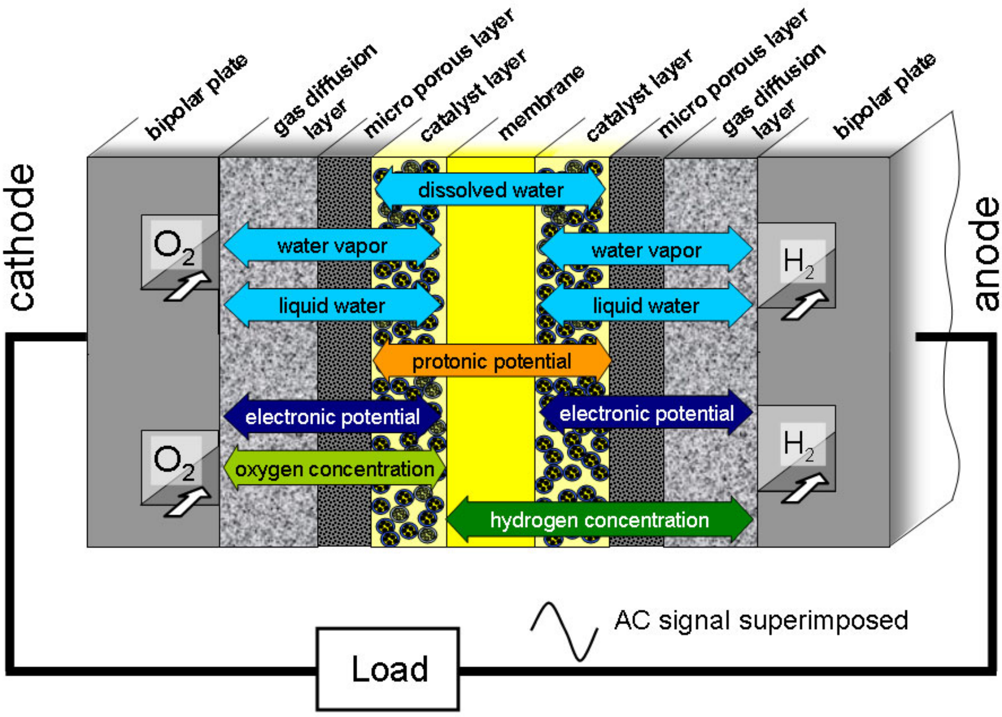

Figure 1: **Schematic diagram of the model domains. The arrows depict the domains where the solving variables are defined.**

A coupled PDE system describes the interaction of seven solving variables, namely dissolved water, vapour, liquid water, protonic and electronic potential, oxygen and hydrogen concentration. Besides the model parameterization, the interface conditions between the model domains (GDL, MPL, CL, Mem) are the critical input values and thus need specific attention. Regarding the MPL impact it is assumed, that liquid water can penetrate the MPL pores only in case of a certain defined CL saturation. Additionally, the shadowing effect of relatively large droplets at the interface of the coarse GDL structure to the fine micro porous structure of the CL is reduced with a MPL, implemented as a sophisticated functional dependency between oxygen flux und pore saturation.

Figure 2 shows a comparison of two polarization curves simulated with and without MPL at the same operating conditions. The results show an improved cell performance in the high current density range where liquid water is present in case of using a MPL. The liquid water flux towards the cathode GDL is blocked by the MPL as long as the saturation in the CL remains low. This leads to an increased back diffusion to the anode side (see Fig.2 top right). When a defined saturation is reached, water penetrates into the MPL, flows towards the cathode GDL and finally out of the cell.

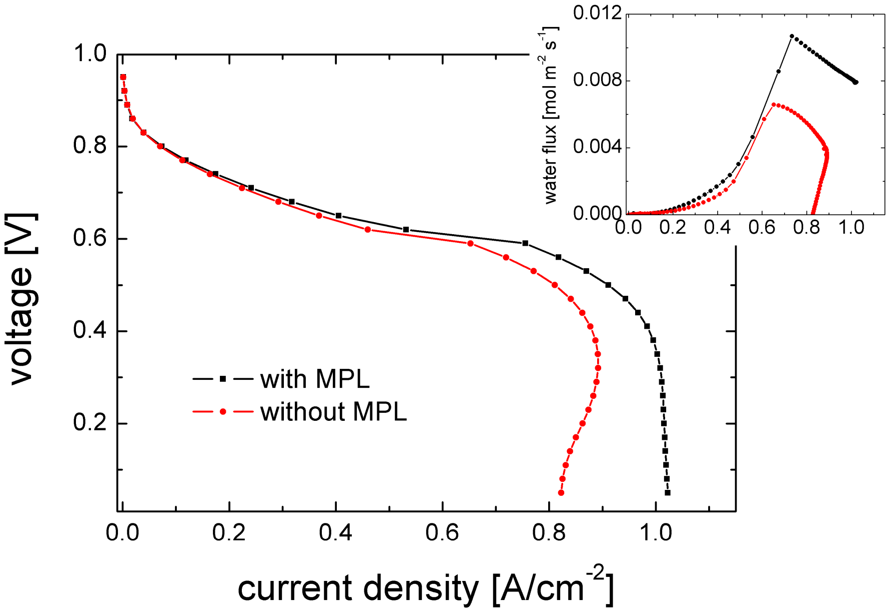

Figure 2: The simulated polarization curve using a MPL shows a higher limiting current density value which can be attributed to a higher water flux toward the anode.

Modifying the boundary condition of the electronic potential by superimposing a small sinusoidal signal $(V_{AC} \cdot \sin(\omega \cdot t))$ with frequency ω and amplitude V_{AC} to the steady-state voltage V_{SS}, the impedance $Z(\omega)$ can be calculated by the Fourier transform of the excitation signal *V(t)* and response signal *i(t)* followed by complex division

$$Z(\omega) = \frac{V(\omega)}{i(\omega)}.$$

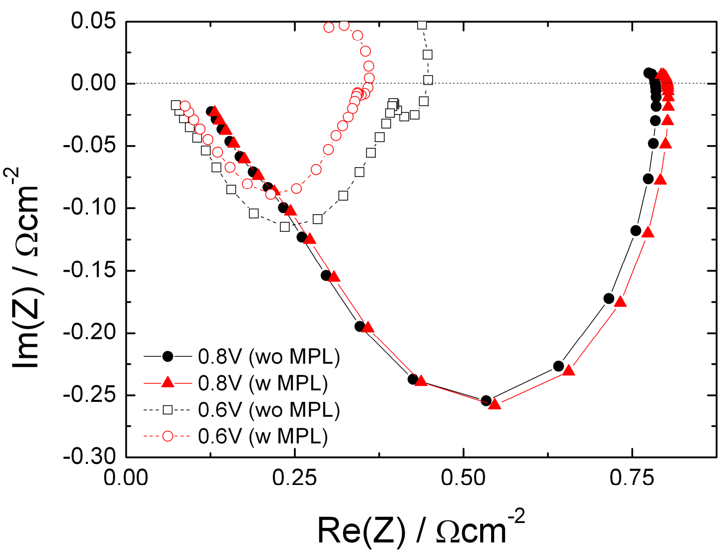

Figure 3: Simulated impedance spectra at 0.8 V and 0.6 V.

Figure 3 shows simulated impedance spectra. At high cell voltage (0.8 V) the spectra are nearly the same. Since no water is present in that operating state, the MPL acts as an additionally oxygen diffusion barrier which can be seen in a small enlarged impedance spectra. At 0.6 V liquid water is present in the porous media. The improved water management by the MPL leads to a smaller impedance arc in the Nyquist plot.

3 ESEM imaging

ESEM imaging is used to analyze the water transport properties of the porous media. By means of condensation experiments the wetting properties such as contact angle and immobile saturation are investigated. Figure 4 shows two identical GDLs from SGL (Sigracet BC 24) lying side by side, one with the MPL-side (left) and one with the GDL-side (right) facing the top. The strong hydrophobic nature of the MPL is clearly visible whereas the GDL side shows areas of contact angle in the range of 90° and below (film formation).

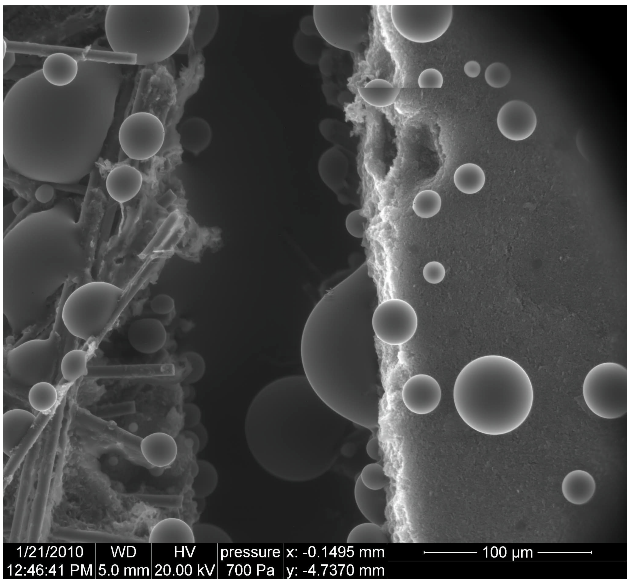

Figure 4: Water droplets on GDL fibers (left) and on MPL surface (right) are shown.

Gerteisen et al. [5] reported a performance enhancement by perforating the GDL. The observations are explained by the positive effect of artificial water transport channels, ‘sucking’ liquid water from their surrounding and finally reducing the overall saturation. This model assumption is now proven by ESEM imaging (see Figure 5), where droplets appear on the side walls of the hole and the water reaches the surface within the hole first.

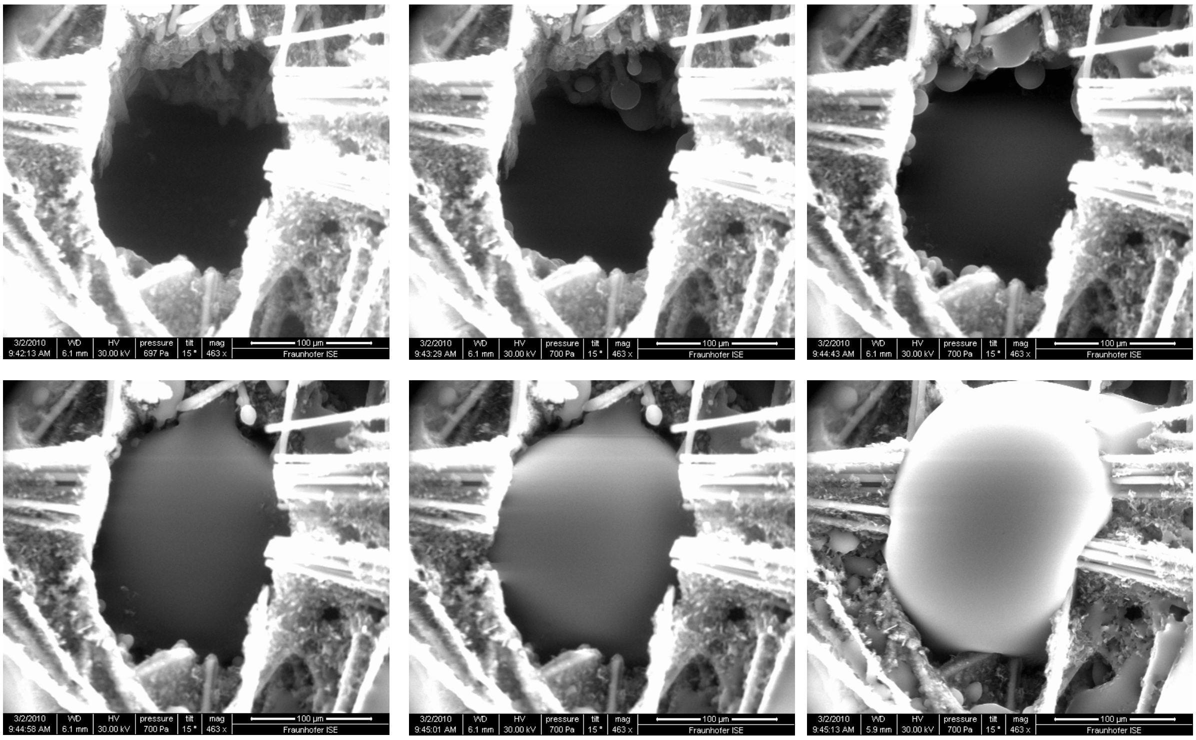

Figure 5: ESEM imaging of water build up in the artificial water transport channel.

4 Conclusion

A new developed multi-phase PEFC model is used to investigate the impact of a micro porous layer on the water management. By means of this model we are able to simulate impedance spectra which help to understand more clearly the water transport mechanism. ESEM imaging is used to analyze the wetting properties of the porous structures and to validate the model assumptions of an improved liquid water transport by providing artificial water transport channels in the GDL [5].

Acknowledgements

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References

[1] Dai et al., A review on water balance in the membrane electrode assembly of proton exchange membrane fuel cells, International Journal of Hydrogen Energy, 34, (2009), 9461-9478

[2] Li et al., A review of water flooding issues in the proton exchange membrane fuel cell, Journal of Power Sources 178, (2008), 103–117

[3] Pasaogullari et al., Two-phase transport and the role of micro-porous layer in polymer electrolyte fuel cells, Electrochmica Acta, 49(25), (2004), 4359-69

[4] Gerteisen et al., Modeling the phenomena of dehydration and flooding of a polymer electrolyte membrane fuel cell, Journal of Power Sources, 187, (2009), 165-181

[5] Gerteisen et al., Enhancing liquid water transport by laser perforation of a GDL in a PEM fuel cell, Journal of Power Sources, 177, (2008), 348–354