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MODEL BASED INVESTIGATION OF PE FUEL CELL PERFORMANCE WITH FOCUS ON POROUS LAYER PROPERTIES

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ZUSAMMENFASSUNG

Understanding of mass transport limitations in PEFC is of prime importance for optimizing performance and for better understanding of degradation. The anisotropic, porous gas diffusion structures (GDL) play an important role in the transport between channel and catalyst. Under condensing conditions (the general case), liquid water will occupy part of the void in the porous structure and thus change the properties of the pore network for gas transport.

In 2007 gas diffusion structures have been analyzed **by x-ray micro-tomography**. Images with a resolution of 0.7 µm were obtained. For the first time data was measured under compression (as is the real case in the fuel cell). The images were assembled to 3D-structures and surfaced. From these data critical properties, such as the anisotropic effective relative diffusivities and the anisotropic heat conduction can be obtained by calculation.

A **multiphysics model** of a membrane electrode assembly of a PEM fuel cell has been formulated in 2007. The model describes the interaction between charge transport, the electrochemical reactions, heat transport, and heat production. The model was implemented in the programming language C in a numerically robust way to allow for run-time efficient computer simulations for a wide range of boundary conditions.

Projektziele

In PEFC research the understanding of **mass transport limitations** on all scales is of prime importance for the development of the involved structures. This applies to membrane (charge and water transport), catalyst layer (CL, gas-, water- and charge transport), and gas diffusion layers (GDL, gas-, water- and charge transport). While membrane and CL have been largely in the focus of past and current work, GDL are relatively unexplored. GDL collect current over the channels in the flow field and provide access for the gases under the lands between the channels (see Figure 1). The anisotropic porosity and possibly high tortuosity of these materials strongly affect and limit the mass transport through the porous structure, which in turn has a strong influence on the current distribution [1], fuel cell performance and degradation. Under condensing conditions (the general case), **liquid water** will occupy part of the void in the porous structure and thus change the properties of the pore network for gas transport.

To understand these interactions of transport and saturation modelling and component characterization is needed. The **goals** are therefore twofold:

- **Characterization of GDL materials** in order to generate the basic knowledge of the structure-property relations with respect to gas transport and water saturation in the GDL.
- **Develop modelling tools** with different depth of comprehension to correlate the physical materials properties with fuel cell experiments.

In 2007 the following progress has been made:

- In characterization of the **structure** of **dry GDL**. It has been possible for the first time to determine the spatial structure **under compressed conditions**. The obtained data from the measurements at x-ray micro-tomography (Tomcat) beamline of the Swiss Light Source (SLS) have been evaluated to reconstruct the structures they have been surface for further treatment.
- A multiphysics **model of a membrane electrode assembly** has been formulated and implemented using a finite element discretization.

Durchgeführte Arbeiten und erreichte Ergebnisse

GDL-Characterization

The x-ray micro-tomography (Tomcat) beamline of the Swiss Light Source (SLS) was used to determine the anisotropic micro pore structure of gas diffusion layer (GDL) materials. The important influence of compression and hydrophobic agent distribution on the pore structure was investigated. Therefore special sample holders for diameters of only 1.3 mm were designed and constructed. Therewith different GDL materials were successfully scanned at a resolution of 0.7 x 0.7 x 0.7 µm. This resolution is high enough to resolve the smallest relevant structures in a GDL in 3D. As a novelty images at different compressions were taken in order to investigate the behavior of fibers, binder and pores under mechanical stress. This first campaign opened up 3D structural insights into dry GDLs that could not have been captured by other means. REM images only dissolve the outermost structure while microscopic cross sections are purely 2D. The 3D geometry provides valuable insights into a multitude of transport phenomena. Furthermore several new ideas arose for future campaigns.

A) Sample Holders

The sample holders had to be mechanically strong enough to compress the GDL with compressive stresses up to 13 MPa and still have an acceptably low x-ray absorbance at the around 10 keV. This required the integration of a screw and a controlled torque by a torque meter (0.5-1.0 Ncm). The shear applied to the sample was minimized with a tapered screw and a bolt. The wall of the holder had to be as thin as possible (200 µm) and of a material with a high transmission and high mechanical strength. These requirements were met with TORLON4203, a polyamide-imide with an X-ray transmission of 0.85 at a cumulative thickness of 400 um and 10 keV. In Fig.1a transmission factors of different relevant materials with a thickness of 1mm are compared. An x-ray energy of 10 keV was chosen in order to have an optimal overall transmission of about 0.3. The thicknesses of the different solid phases in a GDL are not equal. Fig.1b shows the transmission factors corrected by the estimated phase thicknesses. With more realistic phase thicknesses the contrast between carbon and PTFE vanishes. The

required resolution for the fibrous structure was 0.7 x 0.7 x 0.7 µm resulting in a maximum field of view of 1.43 x 1.43 mm at 10x magnification. During rotation the sample should not leave the field of view. Therefore samples were punched with a diameter of 1.3 mm. Fig.2 shows the drawing of the sample holder.

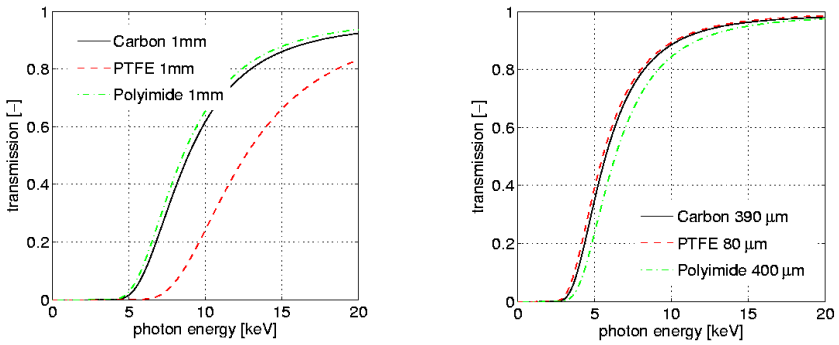

Figure 1: Transmission as function of photon energy for the relevant materials with (left) 1mm thickness and (right) real estimated thicknesses. For the realistic thicknesses the contrast between carbon and PTFE vanishes.

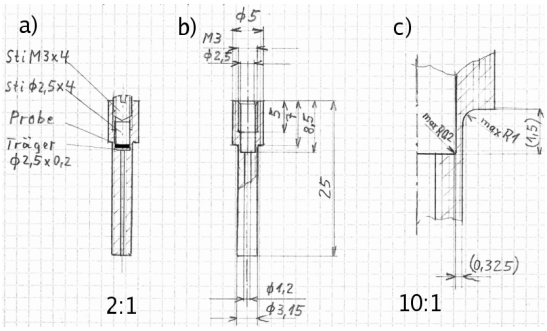

Figure 2: Drawing of sample holder for x-ray micro-tomography of dry GDL materials.

B) Quality of Data

Within the three allocated shifts 10 GDL materials from different manufacturers, with different compositions at different compressions could be measured. Overall 21 scans were performed each taking about 45 minutes. This included about 15 minutes to record the views, 15 minutes to analyze the validity of data and 15 minutes to change the sample holder and adjust the front end of the beamline. A view is made up of 2048 x 797 pixels. Each pixel corresponds to 0.7 x 0.7 µm of the GDL. Consequently a scan with 2000 views at 16bit produced about 10 GB of data.

The large amount of data is currently analyzed. First reconstructions show a good contrast between solid and void. This confirms that the sample holder did not influence the quality of data. Only weak ring artifacts were detected at the interface between sample holder and sample. They were removed by the post processing software. As expected the contrast between different solid phases (fiber, binder, PTFE, MPL) was not high enough for a phase separation. Nevertheless the structural change introduced by an additional phase is visible by comparing with a plain GDL.

A resolution of 0.7 x 0.7 µm was sufficient for the smallest, transport-relevant structures in a GDL. The corresponding field of view of 1.43 mm was also large enough for a representative section. The fringe effects due to punching of the samples were marginal. Although the quality of data was satisfactory, a reduction of file size is desirable for efficient post processing. In the next campaign the views should be captured as 8bit tif images resulting in a significant data reduction without loss of quality. The use of binned images may further decrease the file sizes and maintain the quality of data at the same time. However, this should be tested previously.

The sample thicknesses are extracted from the views. The main compression is already applied at 0.5 Ncm. At 1.0 Ncm the material thickness does only change by 10-20%. Furthermore the measured thickness at 0.0 Ncm do not agree with the ex-situ measured, uncompressed thickness. Therefore the compression adjustment for the next campaign has to be improved.

C) Status & Progress of Evaluation

At the moment the following tasks have been successfully conducted:

- The quality of raw data was checked during the shifts. This revealed a good contrast and a sufficient resolution.
- The real compression was measured by image processing of a view.
- It turned out that 256 grayscales are sufficient. Therefore the 16bit raw data was cropped and reduced to 8bit for efficient post processing.
- All materials were intensely analyzed with reconstructed 2D slices and 3D surfaces using image processing software (Amira™). The procedure includes reconstruction of through-plane slices, cropping of redundant data, phase segmentation with subsequent 3D reconstruction and porosity calculation.

The following tasks are work in progress and will be finished in 2008:

- Detailed investigation of solid and pore structures including different treatments (PTFE, MPL) and different compressions.
- Extracting effective transport properties by mathematical treatment (i.e. Lattice Boltzmann method) in collaboration with "Fraunhofer Institut Techno- und Wirtschaftsinformatik" in Kaiserslautern, Germany.

D) Results

Fig. 3 shows two through-plane slices of the same material at the same position with different compressions. The sample holder is visible as a light gray region above and below. While Fig.3a) illustrates the GDL structure under a flow field channel, Fig.3b) shows the structure under a rib. A first comparison reveals that the blocks of binder are mechanically stable and do not deform. Instead they shift into neighboring pores if present. This results in highly dense regions with porosity near zero as visible in the middle of Fig.3b). These regions prevent in-plane mass transport which is essential under the rib. A first conclusion is that the amount of binder and agglomerated zones should be minimized. On the other hand the fibers show an elastic behavior as no broken fibers were found.

The reconstructed slices were processed to a 3D body in the visualization software Amira™. For this, every pixel in a slice was classified as interior (solid material) or exterior (pore). In Fig.4 a small 3D-reconstructed section of Toray T060 without PTFE is shown. In this section the number of pixels labeled as solid is 1886290. With a total amount of 7642624 pixels this corresponds to a porosity of 75% (79% by manufacturer). This accuracy is surprising as the small section was not assumed to be representative. However, the classification between carbon and PTFE is expected to be prone to errors as their X-ray transmission factors are similar (Fig.2).

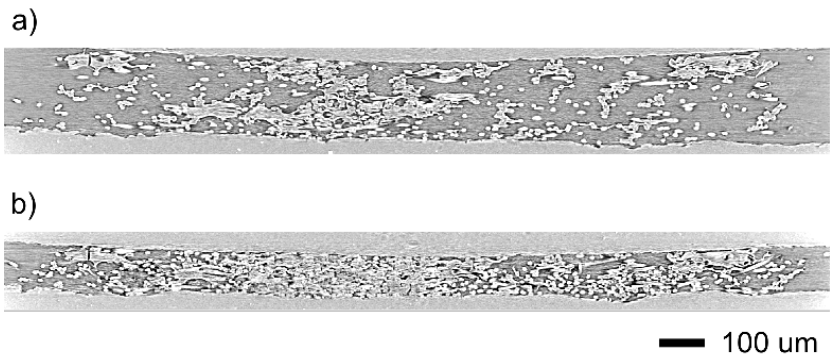

Figure 3: Through-plane slices of Toray T060 without PTFE. On top and bottom of the GDL material the sample holder is visible: a) with low compression and b) with strong compression.

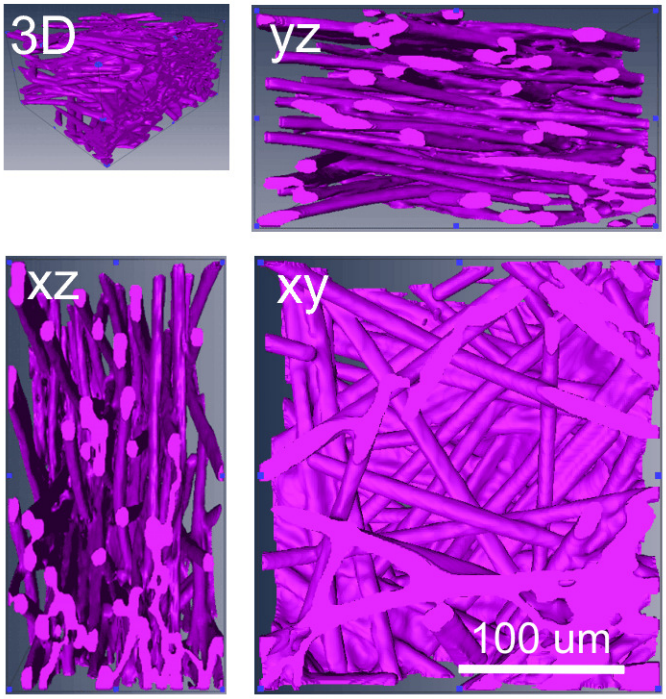

Figure 4: Reconstructed and surfaced images of a small volume of Toray T060 without PTFE, given for isometric view (top left) and for the view planes indicated. Single fibers are well resolved showing that resolution and contrast are good.

E) Conclusions

Micro-tomography images of GDLs under different compressions have been successfully captured for the first time. Although the reconstruction of all the data is work in progress, several setup improvements and new ideas already arose. As mentioned the compression adjustment of the current sample holders is insufficient. If possible the amount of data should be reduced for the ease of handling. A new proposal has been submitted for 2008 with the focus on liquid water distribution. For this 5 shifts were allocated by SLS. The advantage of using x-ray micro-tomography instead of neutron imaging to investigate liquid water in the GDL is the high resolution and the possibility to capture the 3D distribution. The main barrier is expected to be the mobility of liquid water during the scans.

Model of a membrane electrode assembly

A) Formulation of the coupled PDE model

The model consists of a system of coupled differential equations describing the physical and electrochemical processes in the membrane electrode assembly (MEA) of a PEM fuel cell. The model is one dimensional, and the spatial coordinate is oriented in the through-plane direction, i.e. along a cut-line through the MEA sandwich. The following regions are included in the model: the gas diffusion layers, the catalyst layers, and the proton conducting membrane. This model takes into account the

- (spatially distributed) electrochemical reactions in the catalyst layers,
- charge transport for the electrons and the protons,
- heat transport and heat production.

On the nano-scale, there are two charge conducting phases in the the MEA. Electrons are conducted in the solid phase (carbon fibres) of GDL and in the catalyst layers (CL), while the membrane is assumed to be an electronicaly insulating. The protons are conducted in the ionomer of the CL and within the proton exchange membrane (MEM). Therefore we solved for an electronic and a protonic potential to model the charge transport coupled with the electro-chemical processes in the catalyst layers. The electro-chemical reactions in the catalyst layers are described by the Butler-Volmer equation. The electronic potential shows a linear behavior in the GDLs, since there are no charge sources

or sinks in this domain. The same holds for the protonic potential in the membrane. Both potentials show a nonlinear behavior in the catalyst layers. This is due to the nonlinear charge sources in the anodic CL. While the electronic potential is fixed at the outer boundaries by Dirichlet boundary conditions (0.0 V at anode and 0.7 V at cathode), the protonic potential is bounded only by zero Neumann flux boundary conditions between the catalyst layers and the gas diffusion layers. Heat conduction is solved for in all sub-domains. We account for the ohmic heat production and the heat production due to the reaction entropy of the electro-chemical reactions.

B) Discretization of the differential equations

The discretized 1D model of the MEA and the GDLs is created from the symbolic weak form expressions of the coupled transport phenomena. The integrands of the tangential element stiffness matrix and the element residual vector of the coupled finite element problem are computed analytically by the computer algebra software Mathematica. Since the tangential element stiffness matrix and the element residual vector depend on the degrees-of-freedom variables we obtain a nonlinear system of equations.

The expressions for the tangential element stiffness matrix and the element residual vector are converted to the programming language C by Mathematica and used to assemble the system matrix.

C) Numerical solution and results

The convergence of an isothermal version of the 1D-FEM GDL/MEA model with only electronic and protonic potential is very robust. Convergence is reached for a wide range of boundary conditions. Making the fully coupled 1D model non-isothermal by introducing temperature as a field variable and adding the heat sources, convergence problems occurred at low cell voltage (V_{cell} lower than 0.8V). Therefore, we introduced a damping scheme for the heat sources, however the charge sources and sinks remain undamped. The damping coefficient is slowly increased during the iterative solution process of the nonlinear FEM problem. By doing so, we get a very stable convergence behavior of the non-isothermal 1D-FEM GDL/MEA model. A typical result is shown in Fig. 5.

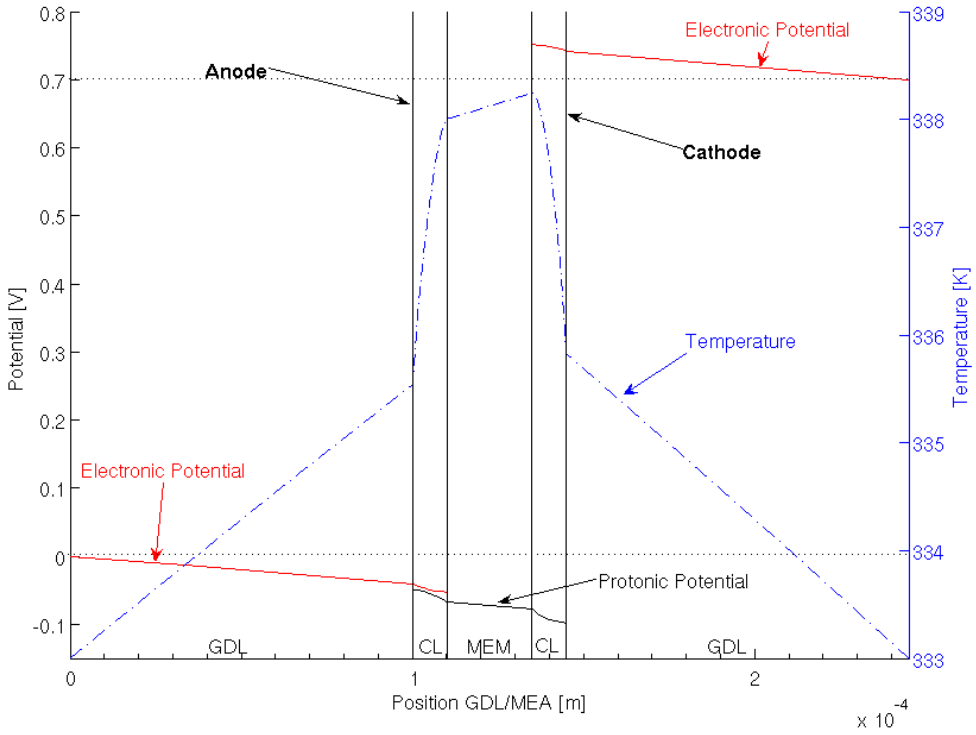

Figure 5: Simulated electronic potential, protonic potential, and temperature distribution for the through-plane direction of the MEA. The cell voltage was set to 0.7 V (0 V at anode). The electronic and the protonic potentials show a nonlinear shape in the catalyst layers (CL), where the electrons and protons are produced (anode) or consumed (cathode). Heat production due to the reaction entropy of the electrochemical reactions is higher on the cathodic side. Therefore, the temperature is higher within the cathodic CL in comparison to the anodic CL.

D) Conclusions and Outlook for 2008

The MEA model is an important tool to understand and analyze the loss mechanism in technical fuel cells. Material properties of the fuel cell components can be included in the model to describe the transport mechanisms in the MEA. These material properties are electrical conductivity-values for the electrons, and protons, the heat conductivity, etc. An extension of the model is planned for 2008 that includes gas transport in the GDLs and the CLs, and liquid water transport. Here, the GDL material properties are important input parameters to the model.

The purpose of the MEA model is two-fold. In its current form the 1D model is suitable to describe the physical and electrochemical processes of small test fuel cells that are operated at low current density. On the other hand, it serves to couple the anodic and the cathodic 2D domains of a 2+1D model allowing for numerical simulations of technical fuel cells under realistic operating conditions.

A proof of principle was given for the utilization of the isothermal 1D-FEM GDL/MEA model within the 2+1D modeling approach. Two flow-field shapes were investigated, an along-the-channel shape, and a meander-shaped flow field was simulated in 2D. In-plane electron conduction and species transport were accounted for, both, on the anode side and on the cathode side. The local depletion of oxygen and hydrogen, and the accumulation of water vapor along the flow-field was calculated.

Nationale Zusammenarbeit

The present project is a collaboration between Paul Scherrer Institut and Zürich University of Applied Sciences in Winterthur (ZHAW). In 2008 the ties to other BFE projects will be intensified.

Internationale Zusammenarbeit

Collaboration with "**Fraunhofer Institut** Techno- und Wirtschaftsinformatik" in Kaiserslautern, Germany in ordero extract parameters from the obtained GDL structures obtained with x-ray micro-tomography is in progress.

The Institute for Computational Physics of ZHAW is organising the 5th Symposium on Fuel Cell Modelling and Experimental Validation that will take place in Winterthur in march 2008. The aim of the symposium is to give an overview on research activities that are related to the mathematical modelling of PEM and SOFC fuel cells, and on experimental techniques for model validation. The major part of the participants will be from Switzerland, Germany, and Austria. One aim of the workhop is to stimulate new collaborations between these three countries in the field of fuel cell modelling.

Bewertung 2007 und Ausblick 2008

The experimental work in 2007 contained a **successful campaign** at the x-ray micro-tomography beamline (Tomcat) of the Swiss Light Source (SLS) to reveal **DRY GDL** structures. A proposal has been submitted for beamtime in **2008 in order to investigate WET GDL structures**. The data obtained is very valuable and world wide unique.

The modelling framework that was built in 2007 serves as a basis to **understand and analyze** the interaction of the **transport processes,** and the **electrochemical reactions** in PEM fuel cells. The **material properties** that are extracted from measurements can be included in **numerical simulations**.

Referenzen

[1] S.A. Freunberger, M. Reum, J. Evertz, A. Wokaun, F.N. Büchi, *Measuring the Current Distribution in PEFCs with Sub-Millimeter Resolution,* J. Electrochem.Soc., 153, A2158 (2006)