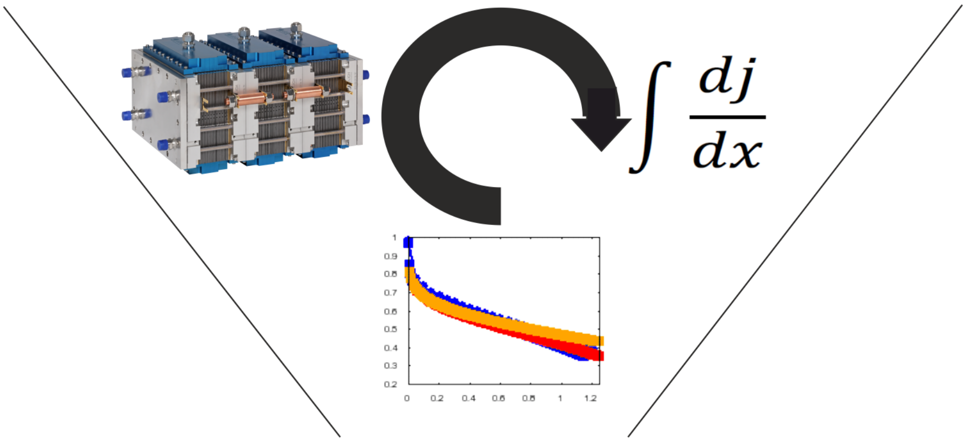
Book of abstracts - ModVal 8

8th Symposium on Fuel Cell Modeling and Experimental Validation
March 8-9, 2011, Bonn, Germany

Revised version, March 4, 2011



ModVal 8

The symposium is focused on advances in modeling of all fuel cell types with the emphasize on PEFC, HT-PEFC, DMFC and SOFC. This year battery modeling is included into the program to represent the growing trend of linking fuel cell and battery research.

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Preface

Time is running and in two years we will celebrate 175th anniversary of fuel cell discovery made in 1838 by Christian Friedrich Schönbein and Sir William Grove. It took 173 years of research to get to the point we are in now, with numerous examples of fuel-cell-based applications, ranging from mW class experimental implantable devices to operating 100 kW class SOFC stacks. No other technology of power generation can beat fuel cells in terms of this tremendous scalability and environmental friendliness.

However, in spite of 173 years of research we still do not see fuel cells in a supermarket, as fuel cells are still either expensive, or not reliable for mass production. The reason for this is poor knowledge of many aspects of fuel cell operation.

Understanding fuel cells is the main goal of continuing symposium *Fuel Cell Modeling and Experimental Validation*. Here at Forschungszentrum Jülich, we consider it a great pleasure and honour to host the 8th symposium of the series this year. We look forward to having interesting talks and fruitful informal discussions, which is a nice tradition of this symposium.

On behalf of the local organizing committee of MODVAL 8,

Andrei Kulikovsky

Organizing committee:

Werner Lehnert
Uwe Reimer
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Program / overview

Tuesday, March 8

Part A

8:00 Welcome / organizers

8:10 Plenary talk: **Electrochemical and Thermal Analysis of Small-Scale SOFC's** Nigel Sammes

8:50 **Spatially resolved modeling of nickel oxidation in SOFC anodes** – J. Neidhardt, W. G. Bessler

9:10 **Elementary kinetic modeling and experimental validation of CO electrooxidation on Ni/YSZ pattern anode** – V. Yurkiv, A. Utz, A. Weber, E. Ivers-Tiffée, H.-R. Volpp and W. G. Bessler

9:40 **On the Integration of Degradation Effects in SOFC Modeling** – A. Gubner

10:10 Coffee break (20 min)

Part B

10:30 **Diagnostics and analysis of electrochemical energy storage and conversion devices, components, and materials with synchrotron x-ray and neutron scattering and spectroscopy** – Artur Braun

11:00 **A new model for detailed simulation of multiple transport and conversion processes in SOFC stack repeat units** – Yasser Safa and Thomas Hocker

11:30 **Cell and System Modeling for Pressurized SOFC Applications** – F. Leucht, M. Henke, J. Kallo, W. G. Bessler, K. A. Friedrich

12:00 **Model studies of a direct ethanol fuel cell anode** – J. Melke, F. Ettingshausen, A. Schoekel, D. Dixon, C. Cremers, D. E. Ramaker, C. Roth

12:30 Lunch break (1.0 h)

13:30 Poster Session (1.5 h)

Tuesday, March 8

Part C

15:00 **From fuel cells to batteries: Synergies, scales and simulation methods** – W. G. Bessler

15:30 **Sub-zero isothermal start-up of PEFC visualized with neutron imaging** – P. Oberholzer, P. Boillat, R. Siegrist, A. Kästner, E. H. Lehmann, G. G. Scherer, A. Wokaun

16:00 **Assessing the effect of liquid water on PEFC performance by the combined use of transient Helox operation and neutron imaging** – P. Boillat, P. Oberholzer, R. Siegrist, A. Kästner, E. H. Lehmann, G. G. Scherer, A. Wokaun

16:30 Coffee break (20 min)

Part D

16:50 **Stochastic 3D Modeling of Tomographic Image Data** – Volker Schmidt

17:20 **3D analysis, modeling and simulation of transport processes in fibrous microstructures, using the Lattice Boltzmann method** – D. Froning, W. Lehnert, R. Thiedmann, G. Gaiselmann, and V. Schmidt

17:50 **Neutron and synchrotron X-ray imaging – powerful analysing tools for fuel cell research** – C. Tötzke, I. Manke, T. Arlt, H. Markötter, A. Hilger, N. Kardjilov, P. Krüger, J. Scholta, K. Wippermann, A. Schröder, J. Bahnhart

18:20 **Progress in quantitative analysis of in-situ X-ray Tomographic Microscopy of PEFC** – J. Eller, J. Roth, A. Wokaun, F. Marone, M. Stampanoni, F. N. Büchi

19:30 Conference dinner

Wednesday, March 9

Part A

8:00 Organizers

8:10 Plenary talk: **Nanoscale Phenomena in Catalyst Layers of PEM Fuel Cells: From Modeling to Advanced Design** Michael Eikerling

8:50 **Spatially resolved voltage, current and electrochemical impedance spectroscopy measurements** – D. Gerteisen, W. Mérida, T. Kurz, R. Alink, A. Spadinger, M. Schwager, C. Hebling

9:10 **Possibilities and Limits of Magnetotomography for Fuel Cells** – H. Lustfeld, J. A. Hirschfeld, M. Reißel, U. Schmidt, H. Soltner, B. Steffen, J. Wackerl

9:40 Coffee break (20 min)

Part B

10:00 **Local degradation of the gas separation in PEM membranes** – S. Kreitmeier, G. A. Schuler, A. Wokaun, F. N. Büchi

10:30 **A 1D Model for the Chemical Degradation of Nafion: Impact of Microstructure Modification on Cell Potential** – Romain Coulon, Elke Bäder, Sylvain Passot, Wolfgang G. Bessler and Alejandro A. Franco

11:00 **1D Model-based approximation of PEM fuel cell degradation** – S. Goessling, D. Herfert, P. Beckhaus, A. Heinzel, H. Voigt

11:30 **Cell degradation caused by undesired side reactions under hydrogen starvation conditions** – J. H. Ohs, U. Sauter, S. Maass, D. Stolten

12:00 Lunch break (1.0 h)

Part C

13:00 **Aging mechanisms in fuel cell and battery and their correlation in a car model** – Frieder Herb

13:30 **Autonomous potential oscillations in a PEM Fuel Cell with a Pt anode under CO poisoning** – T. Kadyk, S. Kirsch, R. Hanke-Rauschenbach and K. Sundmacher

14:00 **Influence of Convective Transport on CO Oxidation on Pt** – J. Fuhrmann, H. Zhao, H. Langmach

14:30 Organizers, discussion, outlook: next ModVal

15:00 Closing

List of posters

1. **Modelling extreme case scenarios for cathodic water supply in Alkaline Direct Methanol Fuel Cells (ADMFCs)** – C. Weinzierl, U. Krewer

2. **Physically based modeling and simulation of a $LiFePO_4$-based lithium-ion battery** – C. Hellwig, D. N. Fronczek, S. Sörgel, W. G. Bessler

3. **Multiphysics simulation of a short PEM-FC stack with a faulty cell - impact on neighbouring cells and surrounding magnetic field** – C. Fink, N. Fouquet

4. **Analysis of Dynamic Operating Conditions in PEMFC using ANSYS FLUENT CFD** – S. Enz, T. Nguyen-Xuan, M. Messerschmidt, J. Scholta

5. **Time Resolved Measurements of Proton Conductivity of Nafion: an Incentive for Theoretical Modelling** – S. Hink, W. G. Bessler and E. Roduner

6. **Two frequency impedance measurement for improved in-system diagnostic** – S. Keller, A. Zaghloul, Q. Meder

7. **New type monoclinic-$Li(Li_{0.08}Ni_{0.34}Mn_{0.50}Co_{0.08})O_2$ phase for Li-battery material** – T. W. Huang, A. Braun, H. S. Chang, H. Y. Tang and Maw-Kuen Wu

8. **Discrete, fiber-based modeling of liquid water transport in gas-diffusion layers for PEM Fuel Cells** – R. Alink, W. Mérida, D. Gerteisen

9. **A Multi-Scale Thermal Model of a High-Power $LiFePO_4$ Lithium-Ion Cell** – M. W. Tahir, C. Hellwig, C. Merten, W. G. Bessler

10. **Influence of Liquid Saturation in Transient Bi-Domain 1D PEFC Model** – M. Zaglio, J. Roth, J. Mantzaras, F. N. Büchi

11. **Challenges in measuring low magnetic field changes for magnetotomography** – J. Wackerl, H. Lustfeld, M. Reißel, H. Soltner, K.-P. Hollfeld

12. **Transmission Line Model of Water Fluxes in the Cathode Catalyst Layer of a Polymer Electrolyte Fuel Cell** – J. Liu, J. Gazzarri, M. Eikerling

13. **Pore-scale Modeling of Ultrathin Catalyst Layers in Polymer Electrolyte Fuel Cells** – Karen Chan and Michael Eikerling

14. **Model-Based Evaluation of Pt Loss Mechanisms and Evolution of the Particle Size Distribution in Polymer Electrolyte Fuel Cells** – S. G. Rinaldo, W. Lee, J. Stumper and M. Eikerling

15. **Molecular Modeling of Interfacial Proton Transport in Polymer Electrolyte Membranes** – S. Vartak, A. Roudgar, M. Eikerling
16. **Validation of Current Distribution Diagnostics for Fuel Cell Stacks** – J. Hirschfeld, R. Lambertz, H. Lustfeld, M. Müller, M. Reißel, B. Steffen A. Schulze Lohoff
17. **1-D Phenomenological Model for the Water Flooding in the Cathode Gas Channel of PEFCs** – Chaozhong Qin, Dirk Rensink, Stephan Fell, S. Majid Hassanizadeh
18. **Impact of Synchrotron Radiation on Fuel Cell Imaging Experiments** – Armin Schneider, Christian Wieser, Ingo Manke, Lukas Helfen

Presentations on Tuesday, Part A

Tuesday, Part A / Talk No. 1

Electrochemical and Thermal Analysis of Small Scale SOFC's

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There are a number of factors affecting the performance of a SOFC. These can be related to the cell geometry, material properties or fuel cell operation. Changes in the dimensions of the cell are assumed to come along with the uncertainties in the kinetic parameters, as the latter is not independent from of the electrode microstructure. Since a change in the geometry shows a change in the kinetic parameters, the estimated values for the fitting parameters will not be coherent with the new geometry. The choice of different materials also affects the performance of the cell. However, same reasoning applies here as the use of new materials comes with new uncertainties because material properties, such as ionic conductivities and kinetic parameters, are strictly related to the fabrication and processing techniques such as sintering, ball milling or the extrusion method. Also the interfacial properties would not be the same when different materials are used, as the structure of the interface depends on the nature of the material used in the fabrication of the cell. Thus in this study we solely focus on the effects of the operating parameters of the cell such as the effects of temperature, fuel flow rate, fuel composition, inlet humidity and back pressure of the anode chamber. Although there are numerous efforts in modeling of SOFC's, the number of models focused on the parametric analysis is not abundant. Many of these models emphasize the geometrical aspects of the system [1-6]. These studies neglect the above-mentioned uncertainties arising with the change in the electrode geometry and are incapable of providing a precise tool to assess the effects of the geometrical parameters. Some studies also focus on the operational parameters such as utilization, flow rate, temperature and pressure [1,3,4,7-11]. However, these models are not rigorous enough to cover the sophisticated transport phenomena in the fuel cell. Our goal in this study is to develop a rigorous model for a micro-SOFC to address the effects of operating parameter on the performance of both a single cell fuel cell, and a small stack. The 2D model exploits the axial symmetry of the tubular geometry assuming the cathode is coated evenly for current collection and the wires attached to the anode have a homogeneous contact along the inner perimeter of the tube. Our model incorporates mass, species, momentum and heat balance along with charge conservation equations. The model is also capable of capturing the internal current leaks through the electrolyte due to the mixed ionic-electronic conductor (MIEC) behavior of the electrolyte material, gadolinia doped ceria (GDC). The modeled cells were fabricated and characterized [12]. The cells were composed of NiO-GDC anode, GDC electrolyte and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)-GDC cathode. The common problem with ceria based electrolytes is that they can be reduced under fuel cell operating conditions became electronically conductive [13] to allow electron transfer from anode to cathode. As a result the cell is short circuited and decrease of the cell efficiency is observed in terms of drops in open circuit voltage (OCV).

The fuel cell model domain is shown in Fig.1. The actual geometry can be visualized by revolving the figure around the symmetry axis. The equations solved in the model are specified in each section on the figure. The momentum equation is solved with continuity equations in both air and fuel channels. In the electrodes, momentum equations are modified to cover transport in a porous media. Species balance is taken care of via Maxwell-Stefan equations in the air and fuel channels and the electrodes. To account for porosity, diffusion coefficients are modified in the electrodes. Heat equations are solved all over the modeled domain. Conservation of charge is taken into consideration separately for both ionic and electronic charges in a form similar to Ohm's Law. Ionic charge equations are solved in the electrolyte and MIEC electrodes, whereas electronic charge equations are solved within the MIEC electrodes. 3D models have also been developed to study the heat, mass and stress distribution in micro-stacks.

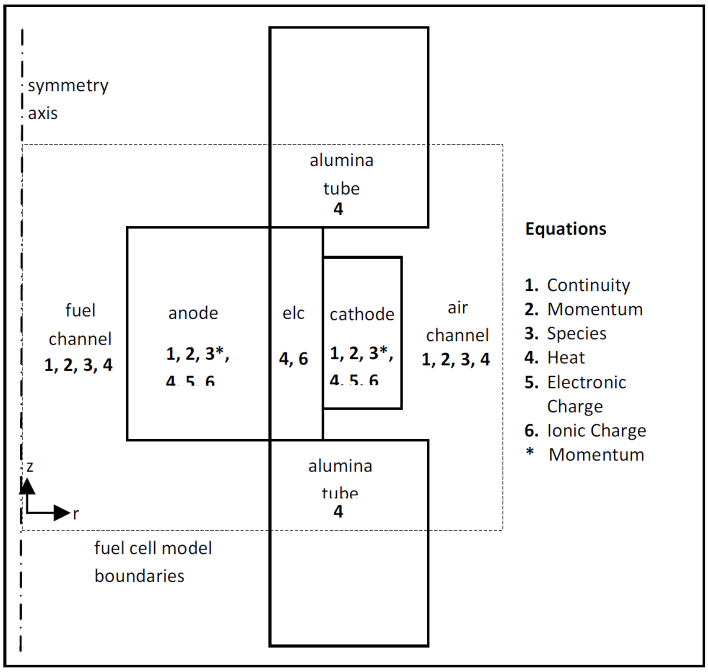

Figure 1: Model geometry and the equations solved in each section (not to scale)

Model results are compared with the experimental results of Suzuki et al. [12] for three different temperatures at 450 °C, 500 °C and 550 °C. As it is seen in Fig.2 a good match is obtained between the simulation results and the experimental data. The model is capable of covering the OCV drops due to internal current leaks due to electronic conduction through the electrolyte. Related current leaks are more dominant at higher temperatures.

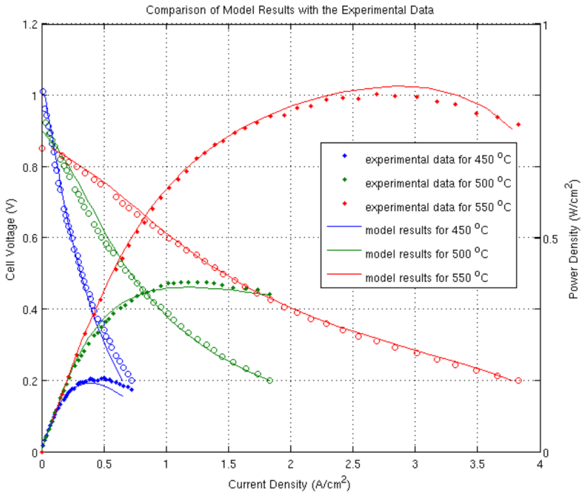

Figure 2: Comparison of Experimental Results with Model results

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Tuesday, Part A / Talk No. 2

Spatially resolved modeling of nickel oxidation in SOFC anodes

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Understanding the mechanisms of performance degradation is of key importance for increasing the lifetime of solid oxide fuel cells (SOFC). The aim of this work is to achieve a deeper understanding of the processes leading to nickel oxidation at Ni/YSZ composite anodes. We present a kinetic model of chemical nickel oxidation taking into account two oxidation pathways. The first one is a pure chemical reaction,

$$\mathrm{Ni} + 0.5\,\mathrm{O_2} \rightleftharpoons \mathrm{NiO} \quad \text{and/or} \quad \mathrm{Ni} + \mathrm{H_2O} \rightleftharpoons \mathrm{NiO} + \mathrm{H_2}$$

occurring if the fuel utilization is too high causing a very low H_2 to H_2O ratio at some parts of the cell. The second reaction pathway is the electrochemical oxidation of nickel,

$$\mathrm{Ni} + \mathrm{O^{2-}} \rightleftharpoons \mathrm{NiO} + 2\,\mathrm{e^-}$$

taking place in the case of low cell voltages. This may be the case, for example, upon an interruption of the fuel supply during galvanostatic operation. Both mechanisms were integrated into a two-dimensional SOFC cell model. The feedback between nickel oxidation and cell performance was modeled by taking into account both, a loss in kinetic performance (via reducing three-phase boundary length) and a reduction in gas-phase diffusivity (via porosity decrease upon solid volume expansion). The simulation allows the spatially resolved prediction of nickel oxide formation over time and its influence to the cell performance under arbitrary operation conditions (Fig. 1).

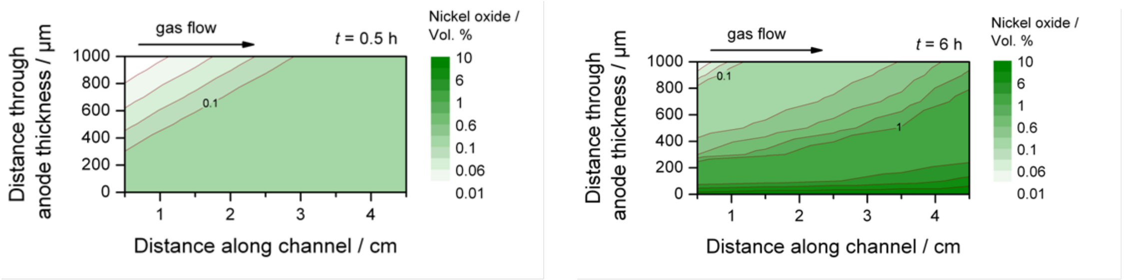

Figure 1: Spatial evolution of nickel oxide formation inside a SOFC anode at operation with 97 % H_2, 3 % H_2O. The figures show NiO volume fraction 0.5 h (left) and 6 h (right) after lowering the cell voltage from OCV to 0.2 V

Tuesday, Part A / Talk No. 3

Elementary kinetic modeling and experimental validation of CO electrooxidation on Ni/YSZ pattern anode

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In practical solid oxide fuel cell systems nickel and yttria-stabilized zirconia (Ni/YSZ) composites are frequently used as anodes. The elucidation of the microscopic details of the electrochemical reaction mechanism requires elementary kinetic numerical simulations along with electrochemical characterization experiments performed with geometrically well-defined model anode structures [1].

In the present work, the results of a comprehensive modeling and experimental study of electrochemical CO oxidation on well-defined Ni/YSZ patterned model anodes are presented. A computational model representing the coupled behavior of heterogeneous chemistry and electrochemistry in terms of elementary reactions was developed (Fig. 1 left), which allows for a quantitative description of the complete experimental data set, which covers a wide range of CO/CO_2 gas compositions ($4.0 \cdot 10^2\,\text{Pa} \le p_{CO} \le 5.1 \cdot 10^4\,\text{Pa}$ and $9.5 \cdot 10^2\,\text{Pa} \le p_{CO2} \le 9.2 \cdot 10^4\,\text{Pa}$ and operating temperatures ($973\,\text{K} \le T \le 1073\,\text{K}$) (Fig. 1 right).

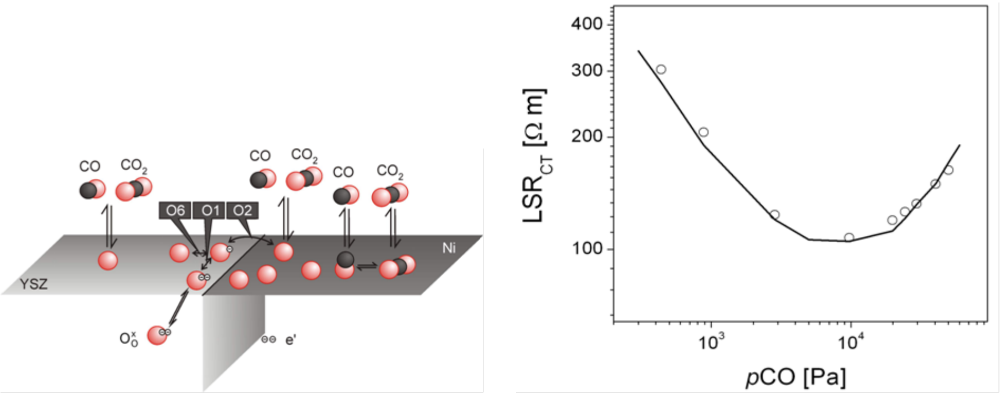

Figure 1: left – Schematic illustration of the reaction mechanism and the different charge-transfer pathways taking place at the three-phase boundary of Ni, YSZ and gas phase; right – Comparison between experimental (open symbols) and simulated (lines) line-specific resistance (LSRCT) of a Ni/YSZ pattern anode as a function of CO partial pressure for a constant CO_2 partial pressures of $2.0 \cdot 10^4$ Pa at $T = 1073\,\text{K}$.

References

[1] Bessler, Wolfgang G.; Vogler, Marcel; Störmer, Heike; Gerthsen, Dagmar; Utz, Annika; Weber, André; Ivers-Tiffée, Ellen, PCCP, 12 (2010), pp 13888-13903.

Tuesday, Part A / Talk No. 4

On the Integration of Degradation Effects in SOFC Modeling

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The intention of the presentation is to contribute to the discussion about modeling SOFC degradation and lifetime. Limited lifetime due to electrochemical degradation issues is still one the greatest technological obstacles in the way of a successful commercialization of the fuel cell technology.

The emphasis of the talk will be put on some simple ideas for modeling degradation phenomena and how to set up a simple SOFC lifetime model. Hence no finalized solutions will be presented and no in-depth scientific discussion on individual effects will be given. That discussion must be left to future work. It is certainly a great challenge to isolate individual degradation phenomena and to develop well founded models for them.

In order to relate the discussed simple ideas for degradation models to already existing knowledge, three papers from the 8th European SOFC Forum in Lucerne 2008 [1,2,3] will be referenced. That is certainly not to be understood as a comprehensive survey.

Figure 1 below shows the decline of the cell voltage V_{cell} over time as calculated using the simple model. The calculation was carried out for internal CH_4 reformation using a steam to carbon ratio $S/C = 2$ and a fuel utilization of $U_f = 75\,\%$. The initial value of the area specific resistance was set to $\mathrm{ASR}(t = 0) = 0.3\,\Omega\,\mathrm{cm}^2$.

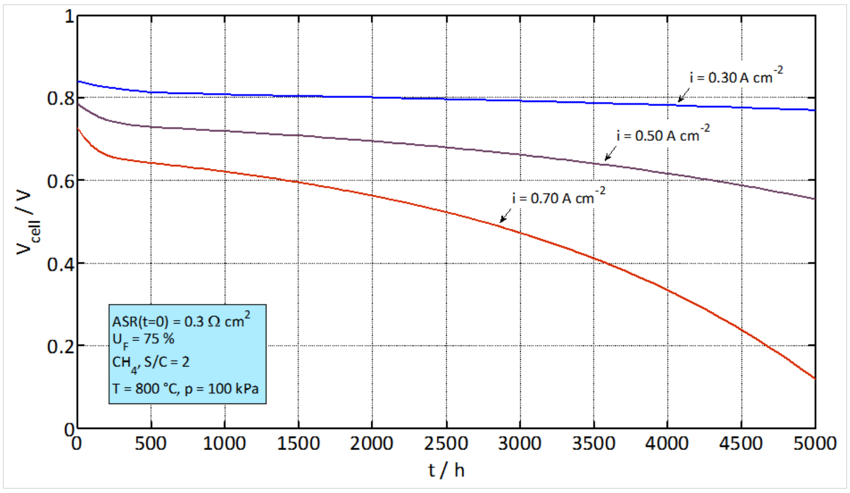

Figure 1: Cell Voltage Degradation for Different Current Densities

It was assumed that the degradation of the SOFC is caused by an increase of the ASR over time due to different degradation phenomena that might follow a first order rate equation. For instance, one may assume that the loss rate of electrochemical contact area due to sintering depends on the number of remaining contacts that are still intact and available for current conduction. Second, there were hints that increasing the current density increases the degradation rate considerably. This phenomenon was included into the rate equation by assuming that the degradation rate depends linearly on the current density as a first step.

The result shown in figure 1 tends to be in agreement with experimental observations [3]. It also confirms the small dependence of the degradation rate on the fuel utilization (not shown in this abstract) and it comprises different degradation time domains. Whereas the degradation behavior in case of 0.3 A/cm^2 seems linear and a life time of e. g. 5000 h is not in jeopardy, it is revealed that the degradation rate increases massively at 0.5 A/cm^2 and 0.7 A/cm^2. It seems that the degradation rate turns from linear into exponential behavior. It is shown by the simple model that the same degradation model can explain both the linear and the exponential behavior. The current density seems to act as an amplifier which suggests carrying out life time tests at a greater current density than that intended for service.

The model certainly is just a starting-point. It will have to be verified experimentally by additional independent tests. However, if it can be verified, then increasing the current density may be a way to accelerate tests considerably and to reduce testing time.

Other future work may include modeling non-isothermal degradation behavior, establishing individual polarization contributions of anode, cathode, electrolyte, contacts etc., and revisiting SOFC modeling fundamentals for accommodating time- and spatial variations of the ASR or the polarization curve, respectively. The content of this presentation can found in detail in the literature as well [4].

References

[1] Nature of Electrode Degradation in SOFCs, Dimitri Bronin et. al., 8th SOFC Forum Lucerne, 2008

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[3] Stack Degradation in Dependence of Operation Parameters; the Real-SOFC Sensitivity Analysis, L. G. J. de Haart et. al., 8th SOFC Forum Lucerne 2008

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Presentations on Tuesday, Part B

Tuesday, Part B / Talk No. 1

Diagnostics and analysis of electrochemical energy storage and conversion devices, components, and materials with synchrotron x-ray and neutron scattering and spectroscopy

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X-rays and neutrons successfully probe condensed matter at the molecular scale. In *materials for the energy sector*, scattering and spectroscopy contribute to the progress of batteries and fuel cells, development. I show a number of x-ray and neutron analytical techniques which help better understand the functionality of devices, and their correlation with their morphology, crystallographic and electronic structure. An overview is presented how the diverse toolbox gives deeper insight in chemistry and electrochemistry of energy materials and how degradation issues, via the transition from chemical changes towards structure and morphology changes, can be monitored. Examples include battery cathodes with operando XANES, resonant XRD and anomalous SAXS and photoemission [1-4], SAXS and SANS to measure the pore topology in carbon supercapacitors [5-7], in-situ resonant photoemission, QENS and resonant XRD for structure and dynamic studies on ceramic proton conducting fuel cell electrolytes [8,9], and anomalous ultra small angle x-ray scattering [10], NEXAFS and photoemission spectroscopy for the studies on solid oxide fuel cell cathode materials at high temperature and associated metal-insulator transitions, and XANES [15] and AUSAXS [10] for learning about the sulfur chemistry on SOFC anodes and their degradation.

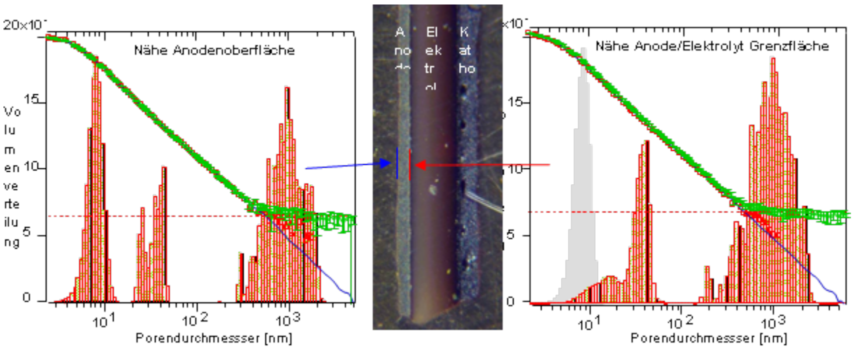

Figure 1: Gradient of pore size distributions in top of anode and at anode/electrolyte interface of a thin SOFC assembly as obtained with ultra small angle x-ray scattering [10]. Note the absence of the fine mode at 8 nm at the anode/electrolyte interface (right panel graph with gray shaded area).

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Tuesday, Part B / Talk No. 2

A new model for detailed simulation of multiple transport and conversion processes in SOFC stack repeat units

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Progress in the study of local reactive transport phenomena in SOFC stacks has been achieved based on both advanced physical and numerical approaches. Specifically, the numerically unfavorable high aspect ratio of about 1'000 between a typical stack diameter and a typical cell thickness has been successful treated using the ADI (Alternating Direction Implicit) numerical scheme [1]. Unlike conventional methods, ADI allows one to predict local gradients of chemical species and electrical charges with low computing costs and unconditional numerical stability. This is especially important in the vicinity of a current collector rib and under extreme operation conditions, e.g. when the fuel gets depleted. Furthermore, the convection-dominant transport within the gas distribution channels has been accurately calculated without using an additional (artificial) numerical diffusion.

Concerning the gas flow in the channels along a porous electrode, another important feature of our model is the non-zero slip velocity at the electrode surface. In conventional approaches, this slip velocity is often estimated empirically [2]. Alternatively, the hydrodynamic flow field is calculated from the Navier Stokes equations which are simultaneously solved in the open flow channel and the porous electrode. Within the electrode, the velocity field is then penalized artificially by adding the Karman Kozeny term. However, such a penalization suffers from inaccurate velocities in the vicinity of the electrode surface. In our approach, the compressible flow in both regions is treated in a unified manner in which the slip velocity is not known a priory, but follows from requiring continuous shear stresses at the electrode surface [3].
As an example, simulation results for the influence of the current-collection pattern (displayed in Figure 1) on the hydrogen and ionic potential distributions within an SOFC repeat unit are shown in Figure 2.

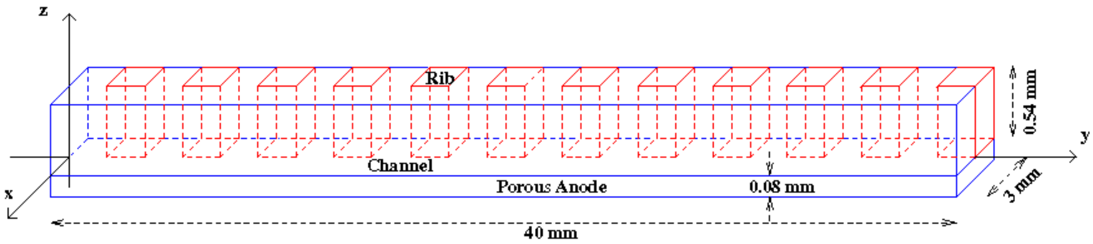

Figure 1: Modeled repeat unit geometry including the anode, the open flow channel and the current collection ribs.

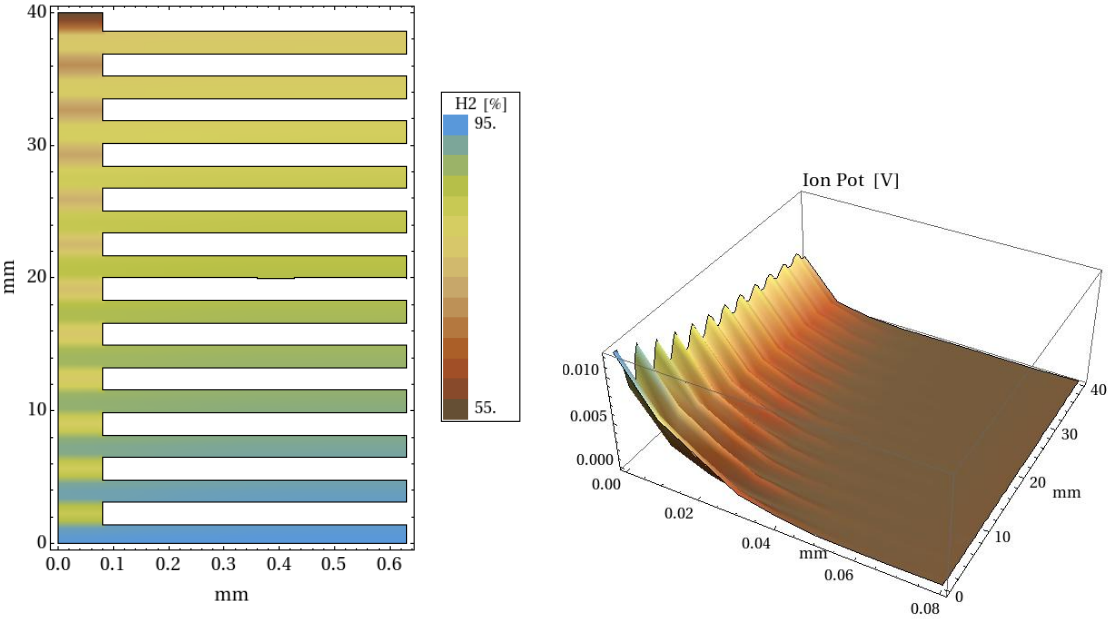

Figure 2: Simulation results in a vertical cross-section of a SOFC repeat unit. left: hydrogen distribution in channel and electrode, right: ionic potential in electrode.

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Tuesday, Part B / Talk No. 3

Cell and System Modeling for Pressurized SOFC Applications

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Pressurized solid oxide fuel cells (SOFC) are in consideration for application in hybrid power plants. These plants combine a gas turbine with an SOFC subsystem. Highest efficiencies can be reached when the SOFC is operated under pressurized conditions. First, this is due to the fact that the SOFC delivers higher power densities with higher pressure and second, the waste heat of the SOFC can be directly utilized in the gas turbine without further need of combustion.

This presentation will focus on the cell and system level modeling performed at DLR. Cell modeling gives an insight into the pressure dependence of the governing reactions in SOFC as well as possible degradation effects at pressurized operation. The modeling results presented are based on our in house simulation tool using an elementary kinetic approach. Current work focuses on the validation of the model under pressurized conditions. We use the simulations as a tool for understanding experimental results and gaining a deeper understanding of the ongoing processes. Furthermore the detailed cell model can be implemented into the system model.

On the system level the presentation will show the influence of various operating strategies on the system efficiency during load following operation. It will be shown that it is possible to maintain the heat in the fuel cell system during low-load operation while keeping the system efficiency high. Furthermore, it will be shown that the system is able to perform minor load changes with only little penalty to the exhaust gas temperature, which is essential for the operation with a gas turbine.

Tuesday, Part B / Talk No. 4

Model studies of a direct ethanol fuel cell anode

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Fuel cell models need to be validated, which is mostly done by studying *U*/*i*-characteristics. But especially in the case of more complicated, multistep reactions like the methanol oxidation reaction or ethanol oxidation reaction (EOR) further experimental data are necessary to provide additional information beyond the electrode polarization. A measurement of different adsorbate coverages on the catalyst or electrodes of the operating fuel cell significantly enhances the reliability of the models. However, these data are difficult to obtain.

X-ray absorption spectroscopy is one of only a few methods which are suitable for in-situ investigations of catalysts. It is usually applied to investigate the nanoparticle structure of the catalyst. However, it can also be used to obtain information about adsorbate coverage and binding sites using the $\Delta\mu$ XANES analysis [1,2] method. With this method we were able to follow OH, n-fold O and C_n-species coverages of a fuel cell anode with time during the EOR, similar to previous studies in continuous operation [3].

In this study, coverage and current data were obtained during several potential steps. The interpretation of the data was done by modelling the essential reaction steps using a modified Butler-Volmer approach. The simulation is in excellent agreement with the experimental data, as shown in Fig. 1. We were able to distinguish 3 different potential regions and our simulation shows that every region is characterized by another limiting mechanism of the EOR.

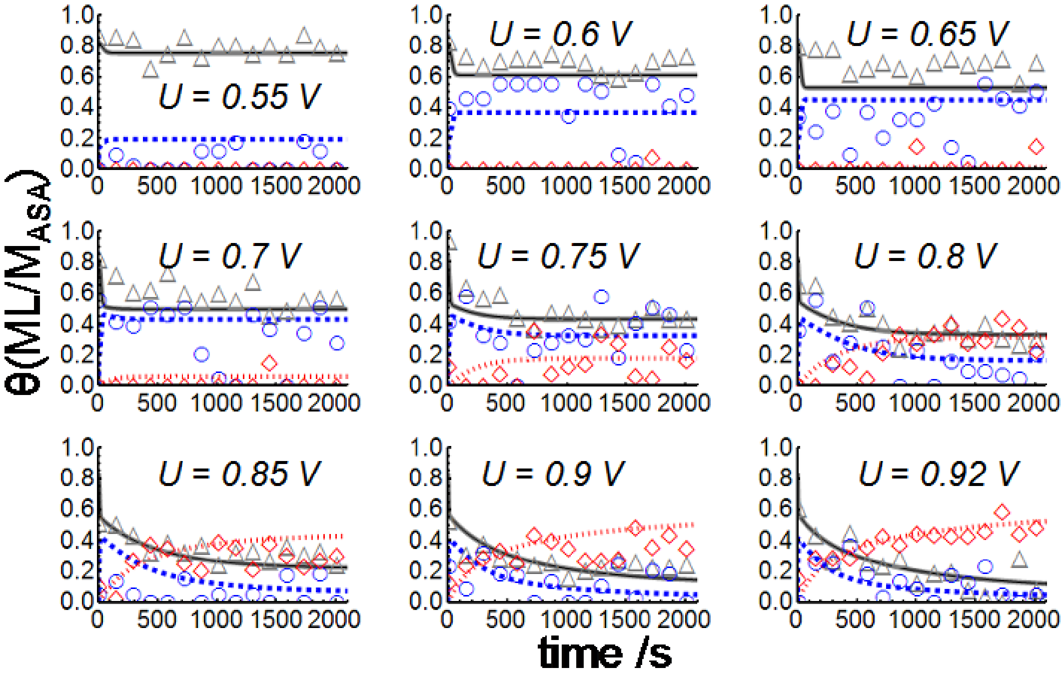

Figure 1: Time-resolved OH (atop) (○), O (n-fold) (♢) and C-species (Δ) coverage during EOR at several potential steps from 0.45 V measured vs. DHE.

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Presentations on Tuesday, Part C

Tuesday, Part C / Talk No. 1

From fuel cells to batteries: Synergies, scales and simulation methods

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The recent years have shown a dynamic growth of battery research and development activities both in academia and industry, supported by large governmental funding initiatives throughout the world. A particular focus is being put on lithium-based battery technologies. This situation provides a stimulating environment for the fuel cell modeling community, as there are considerable synergies in the modeling and simulation methods for fuel cells and batteries. At the same time, battery modeling activities have been, and are still today, considerably weaker than fuel cell modeling activities, in particular within Europe. A strong modeling and simulation support is therefore urgently needed to push forward battery technology.

This presentation discusses relevant scales and open questions in battery modeling and simulation. The state of the art is reviewed. Synergies and dissimilarities between fuel cell and battery modeling approaches are discussed. For example, while we often model fuel cell performance in terms of stationary operating points, the battery is an inherently instationary system and always requires transient simulations.

Examples will be given from both, state-of-the art lithium-ion batteries, and next-generation lithium-metal systems. We furthermore present results of our own activities that are in the fields of multi-scale electrochemical and thermal models of $LiFePO_4$-based lithium-ion batteries as well as detailed kinetic models of lithium-sulfur cells.

Tuesday, Part C / Talk No. 2

Sub-zero isothermal start-up of PEFC visualized with neutron imaging

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Amongst others, sub-zero degree Celsius is one specific condition in which a polymer electrolyte fuel cell (PEFC) must be able to be operated, if it is implemented as major power source for automotive applications. The use of a polymer electrolyte offers sufficient proton conductivity at these temperatures so that electrical current can be drawn. The major issue occurring is the poor evacuation rate of the water electrochemically produced and converted into ice. In the catalyst layer, water accumulated after a given operation time can hinder the access of oxygen to active sites so that the cell voltage drops and current supply is diminished.

In the present work, neutron imaging is employed as visualization tool in in-plane configuration [1] for tracking the water accumulation during sub-zero isothermal cold-start (Figure 1). The sudden increase of water content observed only in the membrane/catalyst layer area during the drop (at $t = 15\,\text{min}$) confirms the hypothesis of a blockage of the catalyst pores. Contrary to many assumptions made in the literature, condensed phase of water is also observed in the gas diffusion layer (GDL) in this experiment. As it positively impacts the water removal rate (reduction of the accumulation rate in the membrane at $t = 5\,\text{min}$), we suppose as an explanation the presence of a super-cooled state of the water, as it was seen in other studies [2].

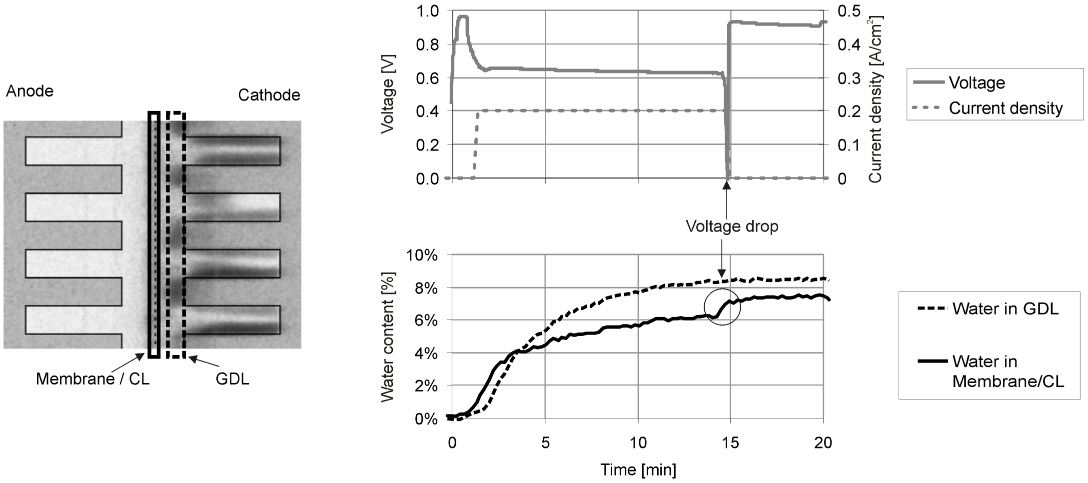

Figure 1: Isothermal start-up at $T = -10\,^{\circ}\text{C}$, $0.2\,\text{A/cm}^2$

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Tuesday, Part C / Talk No. 3

Assessing the effect of liquid water on PEFC performance by the combined use of transient Helox operation and neutron imaging

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The loss of performance related to diffusive mass transport is one of the factors limiting the maximum power density of PEFCs. These losses particularly affect high current density operation and can be significantly increased by the presence of liquid water in the porous gas diffusion layers (GDL).

In order to quantify the losses related to molecular diffusion, the voltage in normal operation (H_2/air) was compared to the voltage using a Helox mixture (21 % O_2 in 79 % He) on the cathode. Instead of repeating each experiment twice (once with air and once with Helox, as for example reported in [1]), the cell was operated normally with air, occasionally switching to Helox (2 s each 30 s). This transient method bears significant advantages over the traditional approach:

- The measurement does not rely on the repeatability between two experiments.
- Due to the short time of operation under Helox, effects related to Helox operation, such as modification of the water distribution (c.f. [2]), are minimized or completely suppressed.

The repetition of 'Helox pulses' each 30 s provides a sufficient time resolution to catch the evolution of diffusion losses in transient experiments, following for example a change in the relative humidity of the gas flows (c.f. Figure 1). Simultaneously, time resolved neutron imaging with high spatial resolution [3] was performed in order to measure the quantity of water in the GDLs. Observation of the response to a change in the relative humidity of the gas flows indicates a good correlation between the temporal evolution of diffusion losses and the evolution of water quantity in the GDL region under the channels.

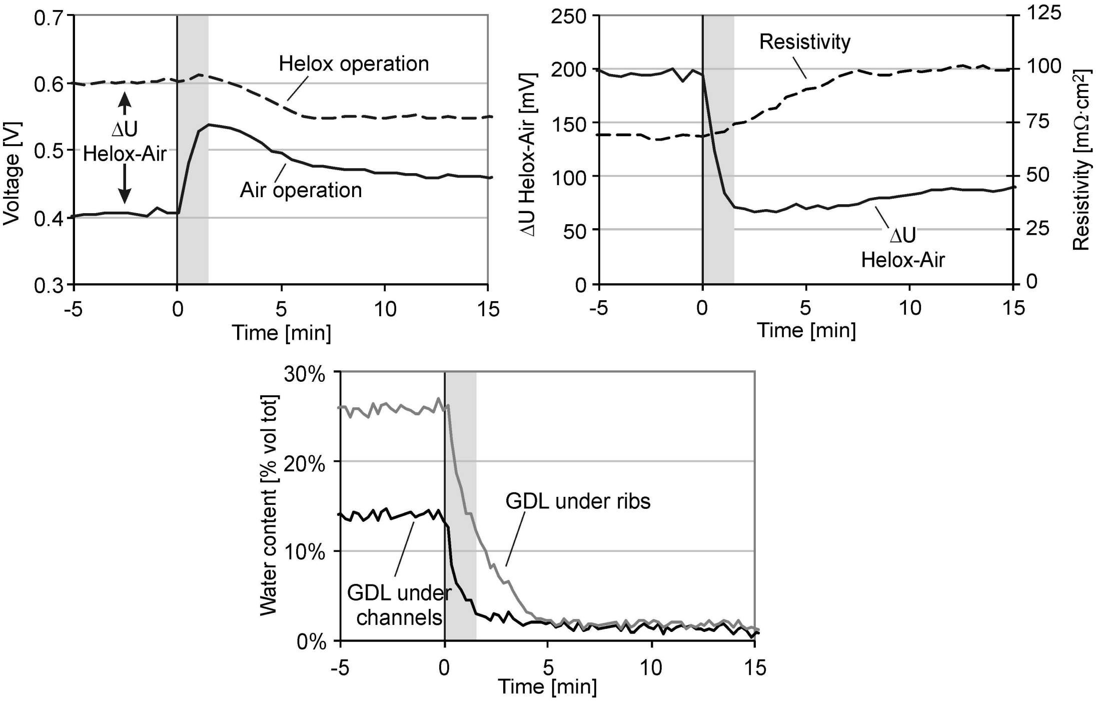

Figure 1: Temporal evolution of diffusion losses and GDL water content following a change of relative humidity at $t = 0$ (change from 100 % RH on both sides to 40 % RH on anode and 0 % RH on cathode). Current density: 1.5 A cm^{-2}, Temperature: 70 °C, Pressure: 2 bar abs.

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Presentations on Tuesday, Part D

Tuesday, Part D / Talk No. 1

Stochastic 3D Modeling of Tomographic Image Data

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The morphological microstructure of complex porous or composite materials is closely related to their physical properties, in particular with transport processes of gases, fluids, or charges, and with degradation mechanisms occurring in these materials. Thus, the systematic development of ‘designed’ morphologies with improved physical properties is an important problem which has various applications, e.g., in batteries, fuel cells, and solar cells. Mathematical models from stochastic geometry can help to solve this problem, since they can be used to provide a detailed, quantitative description of complex microstructures in existing materials. Moreover, systematic modifications of model parameters and the combination of stochastic microstructure models with numerical transport models offer the opportunity to construct new 'virtual' morphologies with improved physical properties, using model-based computer simulations.

In this talk we present a new approach to stochastic segmentation and modeling of 3D images, which show complex microstructures reconstructed by electron or synchrotron tomography. Using a multiscale approach, it is possible to decompose complex microstructures into several (less complex) components. In particular, a macroscale component is determined by morphological smoothing, which can be represented by unions of overlapping spheres. This leads to an enormous reduction of complexity and allows us to model the macroscale component by random marked point processes, which is one of the most fundamental classes of models in stochastic geometry. On the other hand, by the morphological smoothing, a small fraction of voxels is misspecified. The set of these misspecified voxels is interpreted as the microscale component of the microstructure. It is modeled separately, using random particle systems of Cox type. Finally, integrating the microscale model into the macroscale model, a complete stochastic model is obtained for geometrically complex 3D morphologies.

Tuesday, Part D / Talk No. 2

3D analysis, modeling and simulation of transport processes in fibrous microstructures, using the Lattice Boltzmann method

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The gas diffusion layer (GDL) is a key component of fuel cells based on polymer electrolyte membranes (PEFC, DMFC and HT-PEFC). The efficient operation of fuel cells requires good transportation properties of GDL which allow educts to reach the electrodes out of the gas channels as well as to transport products from the electrodes back to gas channels.

The microstructure of GDL can easily be viewed via 2D SEM images. We have developed a 3D stochastic simulation model including a technique to fit its parameters to 2D SEM images. The details of the stochastic methods and their application are presented in a separate contribution [1]. For the model validation, full 3D information of the microstructure from images gained by synchrotron X-ray tomography has been used [2].

In addition to stochastic modeling of the microstructure, one- and two-phase transport processes within the GDL are numerically modeled wherefore the Lattice Boltzmann method is used. This approach has the advantage that numerical transport simulations can massively be parallelized in order to run them on supercomputers. The geometry created by the stochastic simulation model can be treated as a random variable. As a conclusion, all results from numerical simulations on such geometries are of stochastic nature even if they are calculated numerically. We show that an ensemble of geometries – all of them realizations of the stochastic simulation model – leads to results that can be interpreted under a stochastic view. We take special account on the tortuosity and permeability of a GDL to show the potential of a combined stochastic and numerical modeling for fuel cell research.

The general objective of our research is the construction of microstructures of GDL which are favorable for mass transport in fuel cells. Preliminary investigations of GDL microstructures with respect to transport relevant structural properties have been reported in [3]. In the present work, we go one step further and investigate transport properties of GDL not only by considering structural characteristics, but incorporating numerical models for one- and two-phase transport processes. Therefore simulations of transport processes by means of the Lattice Boltzmann method are applied, where the stochastic model for the microstructure mentioned above is used in order to generate the underlying geometric structures. In this way, a large spectrum of problems is covered: beginning from high resolution imaging of GDL microstructures, via stochastic modeling of microstructures, to numerical simulation of transport processes. This provides the opportunity to simulate transport processes in virtual structures, to detect quantitative relationships between functionality, and microstructure of GDL in fuel cells, and to design virtual GDL materials with improved transport properties.

This research is funded by BMBF, within the priority program *Mathematik für Innovationen in Industrie und Dienstleistungen*. Simulations are running on hardware of the Jülich Supercomputing Centre.

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Tuesday, Part D / Talk No. 3

Neutron and synchrotron X-ray imaging – powerful analysing tools for fuel cell research

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Effective water management is of vital importance for successful and reliable fuel cell operation. We use a complementary approach of neutron and synchrotron X-ray imaging to study water and media distributions in fuel cells [1-4]. While neutron imaging is the preferred method to visualize the water distribution for large cell areas or entire cells [5], synchrotron X-rays provide deeper insights for particular cell details at higher resolution (up to $< 1\,\mu\text{m}$). Radiographic as well as tomographic methods are applied to address various questions. The influence of different flowfield geometries and surface treatments on the water distribution is studied, as well as deterioration effects of GDL and catalysts. Combined in situ measurements of current flow density and water distribution facilitate the interpretation of various operation states with respect to reasonable water management [6]. Furthermore, tomographic studies reveal preferred transport paths for water and gas in the GDL, illustrating the correlation between the GDL structure and mass transport. The selected results demonstrate the capability of the imaging tools to analyze media transport in fuel cells and to validate corresponding transport models.

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Tuesday, Part D / Talk No. 4

Progress in quantitative analysis of in-situ X-ray Tomographic Microscopy of PEFC

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Understanding the mass transport properties of the GDL is essential to comprehend and improve the water management and power density of PEFC in the high current domain.

X-ray imaging, allows the simultaneous *in-situ* imaging of water and carbonaceous structures in the GDL. With the high flux available at synchrotron-based installations, an exposure time for a radiogram of considerably below 1 s is achieved and therefore X-ray tomographic microscopy (XTM) is feasible within relative short measurement times (few minutes). In-situ XTM experiments are developed and carried out at the TOMCAT beamline of the Swiss Light Source (SLS). With the standard camera and the 4× microscope objective a pixel size of 1.85 µm and a field of view of 3.8 mm is obtained.

Based on previous work [1,2], we report on further development of the *in-situ* XTM experimental set-up and data treatment for visualizing water and carbon on the pore scale level of the GDL. One of the difficulties for extraction of quantitative data from tomographic structures is the segmentation of the liquid, solid, and void phases. Here progress has been made with the development of a script referencing 'wet' to 'dry' structures, similar to the procedure used in the evaluation of neutron radiography data of PEFC.

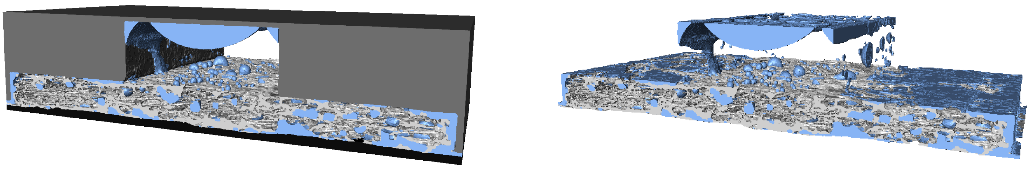

Figure 1: Surface rendering of segmented section of cathode channel. Data obtained from *in-situ* XTM at 0.5 A/cm^2. Cell temperature 40 °C.

Figure 1 shows the surface rendering of segmented XTM data of a cathode channel section. The segmentation allows for extracting quantitative *in-situ* properties of the GDL such as local saturation or analysis of the liquid water droplet size.

A critical point of the XTM method is the use of ionizing radiation. Significant radiation damage may be induced during the measurement [3]. Careful consideration is therefore needed to avoid radiation damage and measurement biasing. The issue will be discussed briefly.

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Presentations on Wednesday, Part A

Wednesday, Part A / Talk No. 1

Nanoscale Phenomena in Catalyst Layers of PEM Fuel Cells: From Modeling to Advanced Design

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Progress in power density, cost reduction and durability of polymer electrolyte fuel cells (PEFCs) demands drastic improvements in the design of cathode catalyst layers (CCLs). The major objective of CCL research is to significantly reduce the Pt loading while maintaining the present level of electrochemical performance and enhancing the stability of the precious metal catalyst to electro-dissolution. These competing challenges entail a hierarchy of structural effects on transport and interfacial kinetics. The intrinsic activity of the catalyst and local reaction conditions at the catalyst surface depend on structure and properties of the catalyst-support system, including size, shape and composition of catalyst nanoparticles, porous structure and mixed wettability of carbon support materials, oxygen incorporation in metal-oxide based support materials, structure and distribution of ionomer, and the distribution of liquid water in pores and at interfaces. As a metric for evaluating CCL design, we employ the effectiveness factor of Pt utilization, which accounts for the impact of random heterogeneous structure, non-uniform reaction conditions, and transport phenomena on the CCL performance under PEFC operation. It was predicted theoretically [1,2] and recently confirmed in experiment [3] that the Pt effectiveness factor of conventional CCLs is low, viz. in the range of $\sim 5\,\%$.
The first part of the presentation will give a brief overview of recent research on Pt nanoparticle electrocatalysis and dissolution, [4,5,6] electrostatic phenomena and Pt effectiveness in nanostructured catalyst layers, [7] and macroscale modeling of catalyst layer structure, properties and operation. The major theme, addressed thereafter, will be the coupling of the Pt-phase electronic structure, the surface oxidation state of Pt, the surface charge density at the Pt-ox surface, and the local reaction conditions, involving proton concentration and solution phase potential at the reaction plane. The key variable that controls this coupling is the metal phase potential. We have recently explored this coupling in a modeling study of oxygen reduction in a water-filled nanopore with smooth walls made of Pt. The effective rate of current conversion in the pore is determined by an interesting interplay of electrostatic and electrokinetic phenomena. Model predictions were found to agree well with electrochemical data for ionomer-free, ultrathin catalyst layers. Results will be discussed in view of materials selection, nanostructured design of porous media, ionomer impregnation of catalyst layers, and water distribution for an advanced catalyst layer design.

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Wednesday, Part A / Talk No. 2

Spatially resolved voltage, current and electrochemical impedance spectroscopy measurements

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The physical processes relevant for describing the PEM fuel cell characteristics seem to be well understood, at least in the bulk material of the different layers. But the complex couplings of these interacting processes and the insufficient knowledge of interfacial phenomena limit the predictive capability of the available fuel cell models to a small operating range. Additionally, the two-phase transport in PEM fuel cells intensifies the limitations of CFD models as design tools. Since traditional polarization curves of single cell measurements are not suitable for 3D model validation, a larger data base of spatially resolved measurements in necessary. Additional information such as membrane conductivity, mass transport limitations or local reactand starvation has to be provided for model developers and CFD end-users to adjust their model parameters.

In this work a fifty-channel characterisation system for PEM fuel cells is presented. The system is capable of traditional electrochemical measurements (e.g., staircase voltammetry, chronoamperometry and cyclic voltammetry), and concurrent EIS measurements to locally analyse and discriminate the performance losses on different time scales. Unlike previous implementations, this system relies on dedicated potentiostats for current and voltage control, and independent frequency response analysers (FRAs) at each channel. Segmented fuel cell hardware was used to illustrate the system's flexibility and capabilities. The results reported here include steady-state data for cell characterisation under galvanostatic and potentiostatic control as well as spatially resolved impedance spectra.

Figure 1: Novel 50-channel characterization system capable for steady-state and transient measurements such as pulse and impedance techniques.

Wednesday, Part A / Talk No. 3

Possibilities and Limits of Magnetotomography for Fuel Cells

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Using magnetotomography, it is in principle possible to reconstruct the current density $j(r)$ through the MEA from measurements of the external magnetic field [1]. However, limited access to relevant measuring positions, limited precision of measuring devices and noise can strongly influence the quality of this reconstruction. Therefore reasonable estimates are required, but can only be obtained if

a) realistic computations of magnetic fields are done under typical operational conditions of a fuel cell
b) a well adapted scheme of magnetotomography is applied
c) an experimental design is set up guaranteeing well defined i.e. reproducible states of a fuel cell.

In this talk realistic solutions of the magnetic field computations are presented, in which the corresponding 3D partial differential equations have been solved under various typical conditions that occur during the operation of a fuel cell. Furthermore, a tomographic procedure is presented leading to appropriate tomographic reconstructions by use of modified singular value decompositions.

Ideas and details leading to an experimental model of a fuel cell having reproducible states are presented in a different contribution (Wackerl et. al. – Challenges of measuring low magnetic fluctuations in magnetotomography).

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Presentations on Wednesday, Part B

Wednesday, Part B / Talk No. 1

Local degradation of the gas separation in PEM membranes

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Degradation in Polymer Electrolyte Fuel Cells (PEFC) is an important issue for commercialization. One of the components under concern is the polymer electrolyte and in particular the temporal development of its gas separation properties. In order to identify and understand these degradation mechanisms, *in-situ* diagnostic tools are required. As the processes are local or originate from local effects the investigation of the gas separation degradation requires an in-situ experimental technique with spatial resolution.

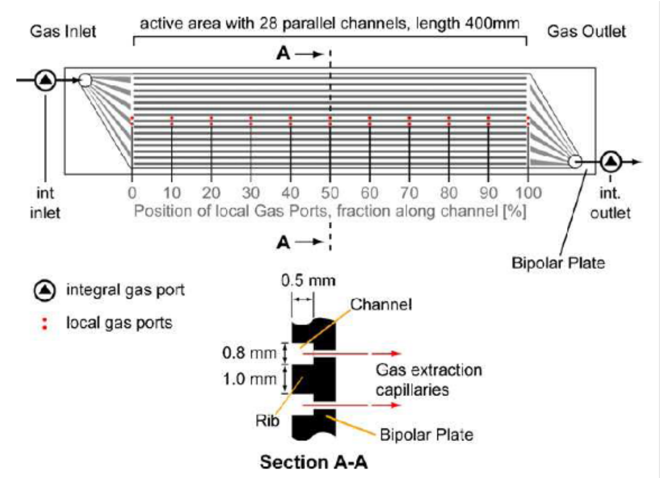

Figure 1: Schematic of cell instrumented for local gas analysis.

We have developed in previous work [1] the methodology for *in-situ* local gas analysis in technical sized fuel cells. 11 gas extraction ports, both at anode and cathode, are distributed equally along the length of the channel as shown schematically in Figure 1. Gas analysis is performed using a quadrupol mass spectrometer (QMS 200M1 Pfeiffer). Local gas permeation can thus be measured through the polymer electrolyte membrane during fuel cell operation using a tracer gas concept. To the hydrogen gas flow at the anode a percentage of helium is added. Both gases permeate through the membrane to the cathode. While hydrogen is consumed at the cathode by oxygen, helium is inert and its permeation through the membrane can be locally quantified. By applying pressure gradients between anode and cathode, diffusive and convective gas transports can be distinguished, which allows for *in-situ* investigation of gas diffusion and gas transport through pinholes independently.

The local degradation of the gas separation in Nafion 211 was investigated in different accelerated stress tests (AST). While gas diffusion is the main gas transport mechanism for a new membrane, convective gas transport appears due to the formation of pinholes and becomes the dominating gas transport mode after a few hundred hours of AST. Pinholes with diameters of 1-10 µm were found in post-mortem investigation using X-ray tomographic microscopy. Pinholes are mainly formed by mechanical stress of the membrane. Carbon fiber endings, which originate from the gas diffusion electrode, deform the membrane during swelling and shrinking at locations where humidity fluctuations prevail. As humidity fluctuations are distinct along the channel, pinhole formation was found to be inhomogeneous as well. As a conclusion, inhomogeneity in material and process management results in pinhole formation, which is the dominant mechanism for the degradation of the gas separation.

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Wednesday, Part B / Talk No. 2

A 1D Model for the Chemical Degradation of Nafion: Impact of Microstructure Modification on Cell Potential

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Today the use of polymer electrolyte membrane (PEM) fuel cells in mobile and stationary applications represents a promising alternative to fossil energies. However, there are a number of challenges for technology introduction, including optimization of water and air management, cost reduction, and most importantly, increase of durability and reliability. Experimental activities provide evidence concerning the behavior of fuel cells under specific operating conditions. However, it is always difficult to derive conclusions about the origin of the phenomena one can observe due to the complexity of this system. Therefore, over the last years, Franco et al. and Bessler et al. developed novel modeling approaches of physical electrochemistry based on non-equilibrium thermodynamics and elementary kinetics [1-3]. By modeling the vicinity of the catalyst surface where electrochemical reactions occur, and by calculating the potential in each electrode, the models permit to calculate at a given working current the corresponding cell potential.

Our work presented here comes in the continuity of our previous work [4]. We are modeling the feedback between chemical degradation of the membrane and transport properties. For that, we simulate the permeation of oxygen through the membrane leading to the formation of water peroxide at the interface anode/membrane. This peroxide can initiate the formation of aggressive radicals in the membrane which attack the membrane and lead to a modification of transport parameters.
Because of the lack of kinetic and thermodynamic data for the elementary reactions, these values were fitted to experimental measurements. This was performed for the chemical production rate of H2O2 at the anode as well as for the degradation of the membrane side-chain. The simulations allow drawing conclusions regarding the localization of degradation in the membrane thickness by analyzing the sulfonate group concentration profile. Furthermore, the impact of the concentration of Fenton ions on the global degradation of the membrane was investigated.

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Wednesday, Part B / Talk No. 3

1D Model-based approximation of PEM fuel cell degradation

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Within the IGF project *Model based state detection of PEM fuel cells* (16160 BG) a real time model is being developed with the objective of reducing the required sensor technology for fuel cell system controlling. Due to the fact that the fuel cell performance decreases in its life cycle by about 10 % [1] it is necessary to approximate the degradation in the real time model. This enables the differentiation between unfavourable operating conditions and a power loss that is caused by degradation. The approximation of the degradation is based on the analysis of a long-term test. The test is performed under constant operating conditions and degradation is measured in one week intervals employing online electrochemical impedance spectroscopy. These weekly spectra are analysed with a separate model, which is described in this presentation. It is built to identify and quantify the different degradation mechanisms. This in turn enables a more detailed approximation of the degradation in the real time model for the state detection.

The fuel cell model described in this presentation is one dimensional, it is based on an electro-chemical equivalent circuit that represents the whole fuel cell and it is developed in Matlab/Simulink®. The parameters of the fuel cell model are fitted to each weekly spectrum by automated parameterisation algorithm. Depending on the results of the parameterisation, the model is varied in its structure which contains elements like the cathode and anode, consisting of a capacitor and resistor, inductive-element, Nernst-impedance and Warburg's-diffusion-element. These elements are varied for the equivalent circuit. To perform the parameterisation an Active-Set Method was chosen. The only difference in applying the algorithm to the various models is caused by the different dimensions of the search space (Number of parameters). The method also takes into account the value ranges of parameters (Inequalities) and additional relations between the parameters (Equalities). During the investigation it was observed that the complex models provide only slightly better results. The most significant difference in the high frequency range (over 1000 Hz) between the models is caused by the inclusion of inductance. In the lower frequency ranges only very small differences between the models are found. Overall, we can conclude that the algorithm presented in this presentation ensures a very stable convergence in all models and only very small deviations of the different parameters from their average values were found in all models.

This talk will give an outline on the parameterisations applied to different models, on the significance of simplified models and the reproducibility of complex models with eight and more variables. Finally the results and conclusions of the long-term tests are presented.

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Wednesday, Part B / Talk No. 4

Cell degradation caused by undesired side reactions under hydrogen starvation conditions

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Cell degradation is one of the main challenges for developing a commercial fuel cell system for automotive application. In our work, we focus on degradation of the electrodes in PEM fuel cells caused by undesired side reactions under hydrogen starvation conditions.
A drop of the membrane potential is observed in the hydrogen starved region of the cell. Consequently, the cathode potential exceeds 1 V with respect to the membrane resulting in carbon corrosion and water electrolysis. This phenomenon is known as reverse current decay mechanism in literature.
We have built up a stationary 2D model of a single cell in through-plane direction and along the channel in order to analyse the reverse current decay mechanism. Hydrogen oxidation, oxygen reduction, carbon corrosion and water electrolysis are modelled by Butler-Volmer equations. Furthermore, we account for the local water content within the membrane and permeation of hydrogen, oxygen and nitrogen trough the membrane.
We consider a decreasing hydrogen stoichiometry due to anode gas dilution by nitrogen permeating through the membrane as it occurs in an anode gas recycle loop. As soon as the hydrogen concentration locally drops to zero close to the cell outlet, carbon corrosion is observed at significant reaction rates. Additionally, we consider local hydrogen starvation due to a partial blockage of the gas pathways within the anode.

The results show that there is severe degradation at the cathode side in the hydrogen starved region of the cell leading to irreversible cell degradation. It is not possible to detect this mechanism by measuring the cell voltage or cell current. In order to avoid undesired side reactions and optimise long-term stability, a sufficient supply of hydrogen to the entire anode has to be assured during fuel cell operation.

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Presentations on Wednesday, Part C

Wednesday, Part C / Talk No. 1

Aging mechanisms in fuel cell and battery and there correlation in a car model

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The topic of this thesis is a systematic analysis of battery and fuel cell aging. Therefore aging mechanisms and aging failure modes were investigated and stress factors are identified focusing on specific aging tests. These tests are used to simulate the aging of battery and fuel cell individually as well as in a car model. The individual aging models of battery and fuel cell are validated. The car model allows to show the influence of different battery and fuel cell sizes to the aging of both components. Further, the balance of fuel cell and battery dynamics and their impact on the aging are investigated.

Wednesday, Part C / Talk No. 2

Autonomous potential oscillations in a PEM Fuel Cell with a Pt anode under CO poisoning

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The behaviour of a PEMFC with Pt anode under CO poisoning was experimentally investigated. Especially, the possibility and conditions for the occurrence of autonomous potential oscillation in galvanostatic operation were analysed [1]. A specific experimental setup, consisting of a differential fuel cell in H_2/H_2 operation, was used in order to eliminate the masking effect of the cathode and to avoid spatial distributions along the channel. In galvanostatic operation, potential oscillations were observed (Fig. 1). In a first measurement series, the influence of CO concentration on the behaviour of the oscillations was analysed. Higher CO concentrations were found to increase the oscillation frequency because of enhanced CO adsorption [2].
In a second measurement series, the influence of the cell temperature was investigated. By means of activation energy analysis, an unequal influence of the temperature on the oscillation frequency has been found for Pt catalyst ($E_A = 40.5 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$) compared to the previously reported case at PtRu ($E_A = 60.9\,\mathrm{kJ\,mol^{-1}}$) [3].
Additionally, oscillations were found in H_2/O_2 operation, too. They occur if the anode overpotential is forced to increase until the onset potential for CO oxidation is reached. Nevertheless, in technical fuel cells operated with passive loads, the anode overpotential does usually not reach such high values, because a large fraction of the voltage loss is caused by cathodic and ohmic losses.

As an additional side effect, an increase of the Tafel slope at $\eta_A \approx 350\,\mathrm{mV}$ was observed in some of the galvanostatic polarisation curves. Two hypotheses for the occurrence of a second Tafel slope were drawn: on the one hand, the Heyrovski mechanism could enhance hydrogen adsorption at higher overpotentials; on the other hand, spatial distributions of the overpotential could lead to local CO oxidation and with this to enhanced hydrogen oxidation in parts of the reactor (e.g. under the ribs, where CO transport could be diffusion limited).
Finally, a model of Zhang and Datta [3], developed for PtRu and recently applied to PtPd [4], was adapted to fit the measurements. The adapted parameter set was compared to the original values and reasonable physical explanations for the adaptations were given. The main differences between Pt and PtRu were found to be a lower water dissociation constant and a lower CO oxidation constant.

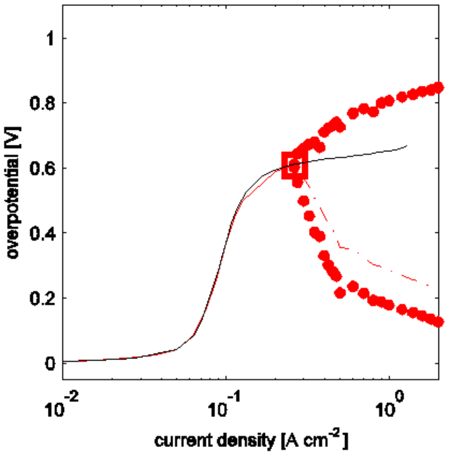

Figure 1: Bifurcation diagram of the anode overpotential in H_2/H_2 operation with 100 ppm CO at 80°C. Black line marks potentiostatic operation (non-oscillatory) and red lines mark galvanostatic operation (oscillatory); solid line = stable part; ☐ = bifurcation point; • = min and max values of oscillations and dash-dotted line = mean value of oscillations.

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Wednesday, Part C / Talk No. 3

Influence of Convective Transport on CO Oxidation on Pt

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Understanding the behavior of CO during catalytic processes on Pt surfaces contributes to the understanding of the more complex kinetics of methanol oxidation in direct methanol fuel cells.

A large body of work has been devoted to experimental and model based investigations of CO electrooxidation on Pt, see [1] and the references cited therein. The modeling approach in [1] is based on the model introduced in [2], and reduces the influence of mass transport to species diffusion in a boundary layer of constant thickness, regardless of the state of the catalyst surface. At the same time, it includes surface diffusion and proton potential. In particular, the model gives a possible explanation to experimentally observed bistability phenomena [1]. As one may expect that the rate of CO consumption at the electrode depend on the coverage of the catalyst, the assumption of constant thickness of the boundary layer may deserve additional verification.

Coupled transport and catalytic CO oxidation on Pt has been modeled on a more or less conceptual level, ignoring the effect of double layer potential, in a rectangular flow cell with constant potential [3] and in a cylindrical flow cell [4]. As a consequence, these models are not able to explain the observed bistability phenomena.

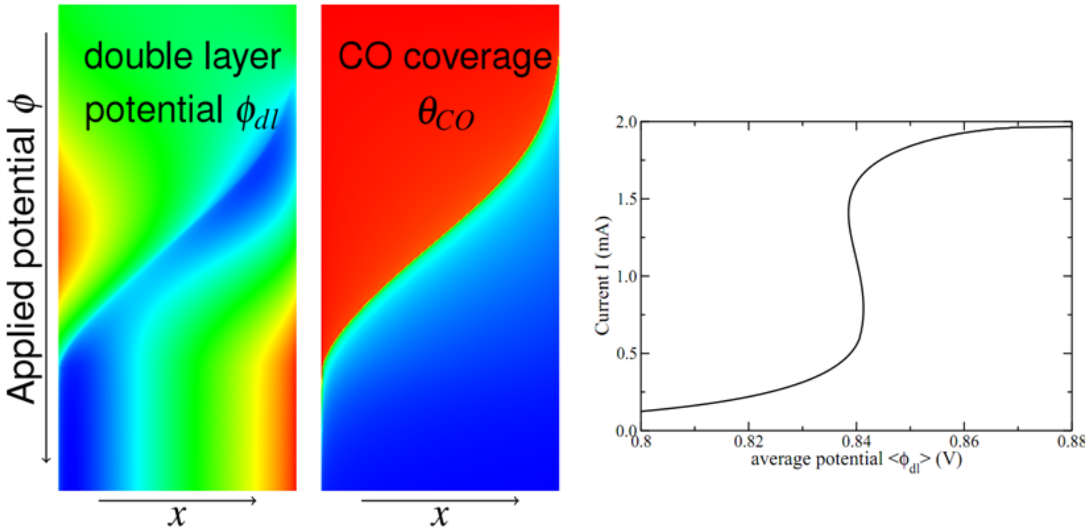

Figure 1: Left: Double layer potential vs space coordinate (in flow direction) and applied potential. Center: CO coverage vs. space coordinate and applied potential. Right: Current vs. double layer potential.

Based on well known analytical and semi-analytical solutions to the Navier Stokes equations in a rectangular channel and at the rotating disk, resp. mass conservative finite element solutions [5], we present a two- and three dimensional numerical model for CO electro-oxidation on Pt which includes convective transport of dissolved species, detailed surface kinetics due to [2], Ohm's law for proton conduction in the electrolyte and CO diffusion on the catalyst surface. We attempt to establish bistability patterns close to those found on a rotating ring electrode [1]. For similar parameters, we indicate that bistability as well may be found in a rectangular flow cell exhibiting Hagen Poiseuille flow, see Fig. 1. Here, for a given value of the double layer potential, we observe two stable configurations of the stationary solution, one with low, and one with high CO coverage. Symmetry is broken due to convection, therefore the applied potential influences the subdivision of the catalyst surface between the two states in a well defined manner.

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Poster presentations

Poster No. 1

Modelling extreme case scenarios for cathodic water supply in Alkaline Direct Methanol Fuel Cells (ADMFCs)

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Direct methanol fuel cells (DMFCs) are a promising alternative to batteries as a power supply for portable electric devices because of the high energy density of methanol. For low temperature fuel cells like the DMFC, it is common to use platinum (Pt) as catalyst which increases the cost of the fuel cell enormously. Hence, a way of operating DMFCs without platinum as catalyst could help for wide-spread commercialisation of DMFCs. One opportunity to achieve this aim is the usage of alkaline fuel cells (AFCs) since Pt-free catalysts show better stability and activity in alkaline media than in the acidic media present in DMFCs.

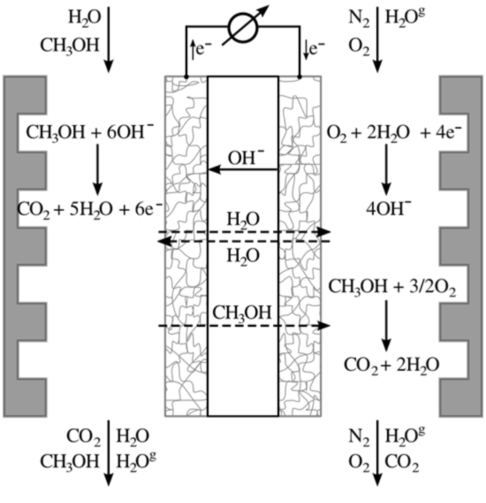

Figure 1: Principle of an ADMFC with electrolyte membrane including reactions and mass transport

The water balance in ADMFCs is very important and mass transfer through the membrane is one of the essential key points. In contrast to DMFCs, water transport from anode to cathode through the membrane is desirable in ADMFCs. To analyse the water balance and to detect the required conditions for operating an ADMFC, the modelling of the ADMFC was started by describing different extreme case scenarios.

A first scenario, which assumes zero mass transport through the membrane except for the conduction of the hydroxide ions, indicates that water supply to the cathode side of the fuel cell may become a major problem. As a consequence, the air excess ratio has to be adjusted to very high values to ensure sufficient water supply for the electrochemical reduction of oxygen at the cathode for inlet temperatures below 300 K, even though the relative humidity of the inlet gas is 100 % and all water in the cathode chamber is consumed (Figure 2).

Further scenarios concerning the water balance were modelled to identify limiting values for important parameters like diffusion coefficients and to analyse the effect of processes like methanol cross-over and water drag on the system and its state variables.

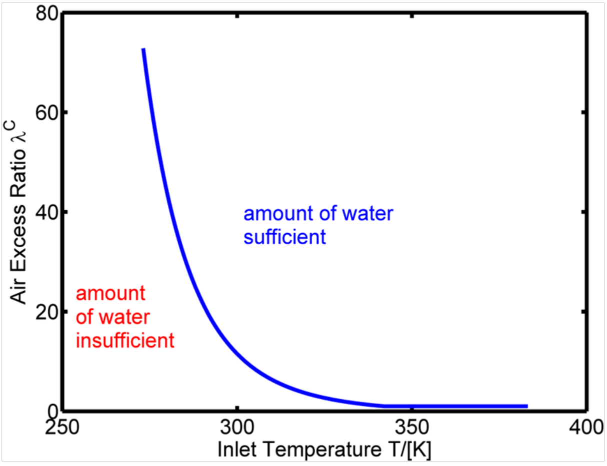

Figure 2: Extreme case scenario for zero mass transport through the membrane

Poster No. 2

Physically based modeling and simulation of a $LiFePO_4$-based lithium-ion battery

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We present a detailed electrochemical model of a $LiFePO_4$ battery based on a multi-scale continuum description of chemistry and transport [2]. Thermodynamic properties of active materials in form of enthalpy and entropy contribution are also included as electron transfer processes using Butler-Volmer type equations. Chemistry is coupled to mass, charge and heat transport taking place on multiple scales (atoms and electrons inside the solid active materials, ions in the liquid electrolyte, electrons in the current collectors, heat within the full cell). The model is parameterized and validated using experimental impedance data and discharge curves obtained by using commercial high-power cells (A123).

The simulation agrees very well with the experiments obtained and allows a detailed insight into the electrochemical behavior of the cell as a function of operating conditions and state-of-charge. Discharge curves at different C-rates as well as simulated impedance measurements for different state-of-charges show the same behavior like experimental data.

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Poster No. 3

Multiphysics simulation of a short PEM-FC stack with a faulty cell - impact on neighbouring cells and surrounding magnetic field

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From an automotive manufacturer point of view, fuel cells have evolved, over the past couple of decades, from a laboratory experiment to one of the most probable successors to the internal combustion engine. In order to be further developed and achieve widespread use, the technology will have to meet stringent cost, security, availability and durability targets. 3D multiphysics simulation is the tool of choice to achieve quick design optimization as well as gain deep understanding of the underlying physics.

This poster shows how such a model is used to get insights in the reconfiguration of current production within a 3-cell stack with a faulty cell as well as in the influence on the cell surrounding magnetic field.

The multiphysics simulation was conducted with the software FIRE by AVL List GmbH. In order to perform the simulation, a 40 cm^2 geometry featuring three serpentine channels in parallel was used. Three cells with corresponding bipolar plates and surrounding air were meshed. From the electrical point of view, the three cells are fully coupled together through the bipolar plates. In nominal conditions and with healthy cells, the current production is thus evenly distributed among the three cells, as shown in Figure 1.

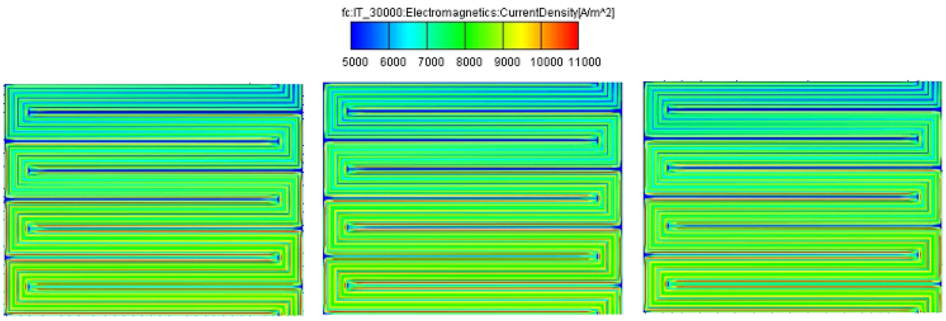

Figure 1: Current production on the stack's three healthy cells.

A fault is then triggered on the middle cell, on which approximately one eighth of the active area on the cathode side becomes inactive. As shown in Figure 2, high current densities appear around the failure in order to ensure that total current remains the same over the whole area of the middle cell. This reconfiguration of the current production impacts neighboring healthy cells as well.

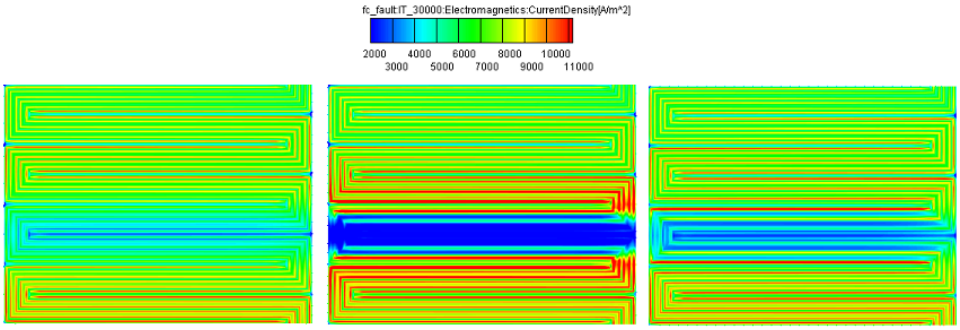

Figure 2: Current production with a failure on the middle cell

The reconfiguration of the current production also has an impact on the magnetic field generated by the fuel cell. As shown in Figure 3, the magnetic field increases in the vicinity of the failure, due to the current increase right next to the failure. Such modifications of the magnetic field could be measured and serve as indicators of the fuel cell's state-of-health.

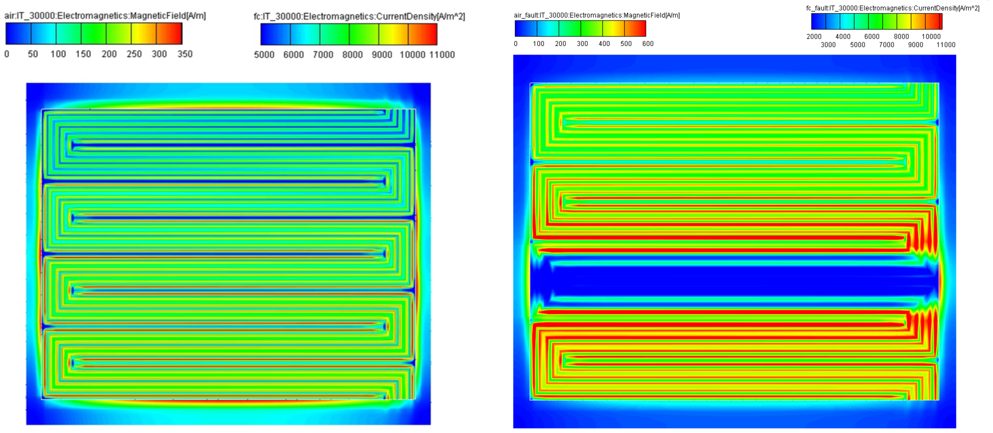

Figure 3: Surrounding magnetic field for a healthy fuel cell (left) and a damaged one (right).

Poster No. 4

Analysis of Dynamic Operating Conditions in PEMFC using ANSYS FLUENT CFD

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For Polymer Electrolyte Membrane Fuel Cells (PEMFCs) durability is one of the key factors regarding their commercialization. In recent years, many studies on degradation mechanisms have been accomplished. Irreversible processes, like catalyst metal degradation or carbon-support oxidation are known as the main factors influencing lifetime of fuel cells [1]. Transient operating conditions are suspected to induce faster degradation than one can observe under steady state conditions. As an example for accelerated degradation mechanisms, carbon corrosion on the cathode side may occur due to fuel and oxidant starvation or start up/ shut down cycles [2]. The main focus of our work is to identify dynamic operating conditions which may result in an accelerated PEMFC degradation.

Spontaneous higher power requirements occur during transient conditions. The operation respective to these dynamic conditions inside the PEMFC is analyzed using ANSYS FLUENT as CFD simulation software in order to illustrate the dynamic behaviour of a PEMFC single cell regarding pressure and velocity distribution, gas composition and relative humidity, respectively. For the simulation a PEMFC single cell cathode or anode consisting of a flowfield, a gas diffusion layer (GDL) including a multi porous layer (MPL) and catalyst is used. Dynamic operating conditions of a PEMFC are simulated using load steps from a value of 20 % to a target value of 100 % and pressure steps with a heightening of 1 bar. Initially a stationary isothermal case is calculated as starting point for further dynamic investigations. Then, transient calculations are performed with time steps of 1-5 ms in which load or pressure change steps, comparable with dynamic operating conditions are accomplished. Therefore, the reactant source terms at corresponding current density or pressure are increased up to the target value while the mass flow rate is kept constant for a time interval of maximal 100 ms in order to simulate the dynamic behaviour and to visualize the operation of PEMFC during dynamic operating conditions.

Several flowfield designs are studied under stationary and transient conditions. For the flowfield geometry a straight-shaped and a meander-shaped design is investigated. The CAD geometry of the bipolar plate (BPP) is created with ANSYS Design Modeler and discretized with ANSYS Meshing software. The mesh is generated with hexahedrons as Finite Volume elements resulting in a total number between 3 and 5 million elements.

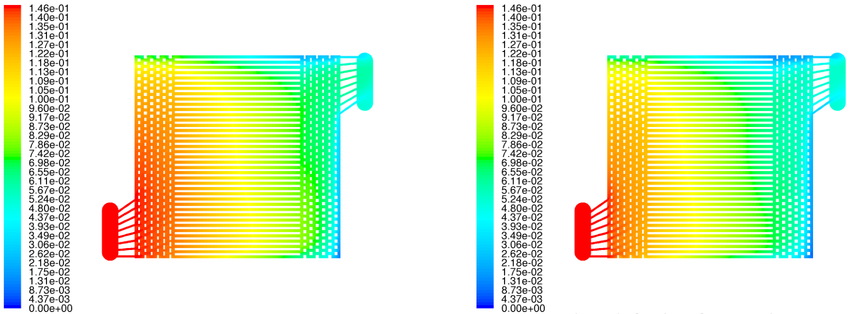
Fuel and oxidant starvation as well as water distribution within the different components (flowfield, GDL, MPL, catalyst) can be studied. Additionally, critical states according to transient conditions can be identified and investigated. An example for the development of the mole fraction of oxygen at the cathode side at a load step from 0.2 A/cm^2 current density to 1 A/cm^2 within 100 ms is shown in Figure 1. The lower the mole fraction of oxygen is (blue colored regions) the higher the mole fraction of water.

Besides the CFD simulation, an experimental study on dynamic operating conditions will be performed.

Measurements of current density, temperature, impedance and analysis of the fuel cell exhaust via NDIR-spectroscopy will be performed to identify critical operating conditions corresponding to accelerated degradation. Furthermore, the water management inside a PEMFC will be estimated using neutron radiography experiments. CFD simulations as well as experimental results will be applied to develop an optimized strategy for dynamic operating conditions and to improve the lifetime of PEMFCs under transient conditions.

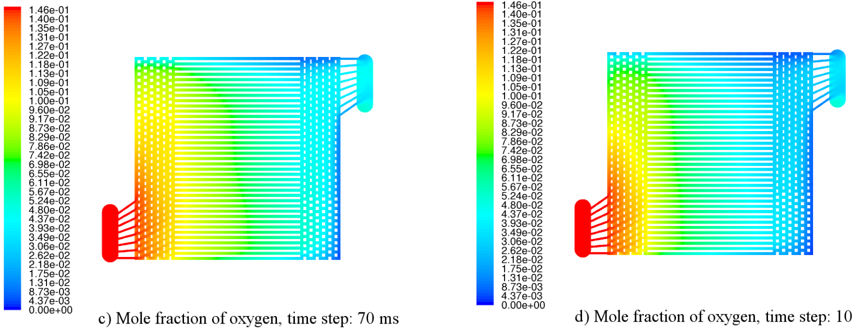
Furthermore, multiphase flow simulations will be performed in order to estimate the transport of condensate (liquid water) inside a flowfield channel. The dynamic behaviour of current density distribution within PEMFCs will be investigated using ANSYS FLUENT PEMFC module.

Funding by the Federal Ministry of Transport, Building and Housing (BmVBS, Germany) of the project FC-Dynamics (Experimental study of the dynamic operation of PEMFC - stacks, grant agreement number: 03BV111) within German Chinese Sustainable Fuel Partnership (GCSFP) is gratefully acknowledged.



a) Mole fraction of oxygen, time step: 5 ms

b) Mole fraction of oxygen, time step: 35 ms



c) Mole fraction of oxygen, time step: 70 ms

d) Mole fraction of oxygen, time step: 100 ms

Figure 1: Dynamic simulation of mole fraction of O_2 at different time steps

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Poster No. 5

Time Resolved Measurements of Proton Conductivity of Nafion: an Incentive for Theoretical Modelling

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Electrochemical atomic force microscopy allows spatially resolved measurements of proton conductivity of proton exchange membranes on a nanoscale [1].
A potential step perturbation is applied to the electrochemical cell which consists of a platinum layer (typically acting as anode) on a commercially available Nafion 212 membrane and the platinum coated tip of the atomic force microscope in an environmental chamber. Depending on the gas composition, different electrochemical reactions can be investigated. In the case of using hydrogen the potential step leads to proton formation at the anode and backformation of hydrogen at the cathode. The dynamic information of the system is included in the response current and the related voltage-time signal. A Fourier Transformation converts the data to the frequency domain and the impedance can be calculated [2]. In principle, this technique provides the same information as electrochemical impedance spectroscopy, but due to the spatial resolution of a few nanometers a detailed view of proton conductivity within a proton exchange membrane is accessible. The results and their comparison with simulations may be used to develop a much more sophisticated model of a proton exchange membrane fuel cell.

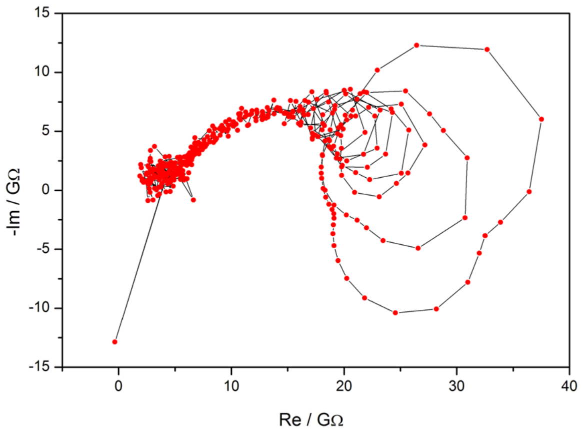

Figure 1: Nyquist plot of the experimental impedance in a frequency range of 1 kHz to 0.1 Hz, following a voltage jump from 0.5 V to 1.0 V in a hydrogen atmosphere.

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Poster No. 6

Two frequency impedance measurement for improved in-system diagnostic

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One key issue for fuel cell performance is the water balance in the interior of a fuel cell. Accumulation of liquid water inside the gas diffusion layer has to be avoided while at the same time the membrane needs adequate humidification to ensure good proton conductivity. Electrochemical impedance spectroscopy is a suitable and powerful diagnostic method for single fuel cells as well as stacks. However, impedance spectra usually include several frequencies to distinguish between different loss mechanisms which requires a complex and bulky measurement and analysis setup. This again makes integration into a portable fuel cell system difficult.

In this study impedance spectra of different stacks including a 28 cell Mark 1020ACS from Ballard were analysed at varying operation conditions. A 50 channel measurement system was used to simultaneously acquire spectra of each single cell inside a stack. Parameter variations at different operation conditions such as load condition, humidification, stoichiometry and temperature were performed. In order to reduce the complexity of the in-system diagnostic tool two discrete frequencies were chosen to provide information about the water balance inside the stack.

- The High Frequency Resistance (HFR) gives information about the water content of the membrane and is therefore used as a significant indicator regarding the dehydration of the membrane
- The Low Frequency Resistance (LFR) provides information about mass transport losses which are often caused by blocked gas transport paths due to excessive water or insufficient gas supply.

Experimental results show that this approach delivers more information about the state of health of the stack than can be obtained only by the voltage data. The additional measurement equipment required can be significantly reduced due to the acquisition of only these two discrete frequencies. This makes integration into portable systems feasible. The additional information provided can then be used as input for improved controlling algorithms that lead to a more stable and efficient operation as well as reduced degradation while keeping costs and effort at a minimum.

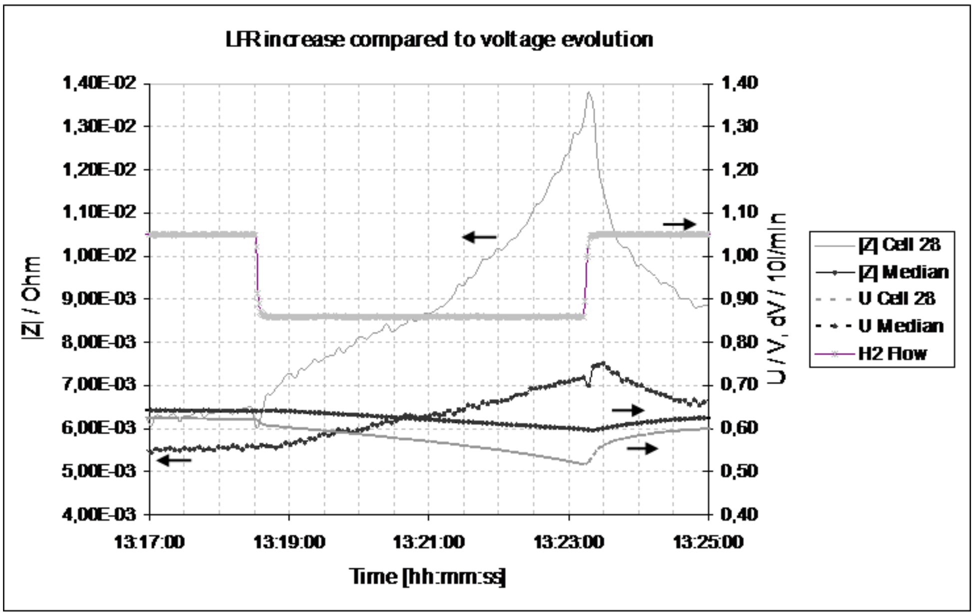

Figure 1: Increase of LFR after reduction of anode stoichiometry. Data show absolute value of LFR and cell voltage of a boundary cell of the stack (cell 28) compared to the median of all single cell values. The LFR of the boundary cell increases by more than 200 % while the voltage decreases by approximately 16 %.

Poster No. 7

New type monoclinic-Li($Li_{0.08}Ni_{0.34}Mn_{0.50}Co_{0.08}$)$O_2$ phase for Li-battery material

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During the past decade, layer-structured lithium insertion materials have been investigated to find alternatives to hexagonal-$LiNiO_2$ (*h*-$LiNiO_2$) which is widely used in Li-battery industry. The *h*-$LiNiO_2$ is usually mixed with $LiCoO_2$ and $LiMnO_2$ in unit cell level by applying solid-state chemistry and electrochemistry of solid solution hexagonal-Li(CoMnNi)O_2 (*h*-$LiMnO_2$) to achieve a higher rechargeable capacity and to stabilize its thermal structure while charge-end voltage is restricted above 4.15 V. However, this material is still criticized for its deficient charge capacity and high cost.

In our recent research, the series of $Li_{1/2}M_{1/2}O$ (*m*-$LiMO_2$, M equals $Li_{0.08}Ni_{0.34}Mn_{0.50}Co_{0.08}$) was synthesized using simple chemical and solid state synthesized techniques. The rechargeable test, over 100 cycles of charging-discharging process, shows that our new type monoclinic material have 5 % higher capacity than any commercial material. The high resolution X-ray diffraction (XRD, NSRRC) and Rietveld refinement show that, rather than traditional hexagonal phase, the as-synthesized structure turned into a new type monoclinic symmetry (Figure 1). Also, the phase definition is different because the gamma angle of *m*-LiMO expend to 120.46 ° from 120 ° of *h*-LiMO (Figure 2). Several studies pointed out the monoclinic $Li_{1/2}Mn_{1/2}O$ phase (*m*-$LiMnO_2$) could be synthesized by an ion-exchange technique from -$NaMnO_2$ (-$NaFeO_2$ structure) [1,2]. Also, the *m*-$LiMnO_2$ was obtained from Mn_2O_3 using a hydrothermal reaction technique in $LiOH{\cdot}H_2O$-KOH or LiCl-KOH aqueous solution under pressure of 25-30 MPa [3]. The above studies [1-3] indicate that the *m*-$LiMnO_2$ phase is hard to remain or form by normal solid synthesized process.

Moreover, the XRD refinement data show that during recharging process *m*-$LiMO_2$ phase transformed into *h*-$LiMO_2$, while the charge capacity decreases. During the charging-discharging process, the Jahn-Teller effect can be explained that the oxidization of Mn^{3+} ion to Mn^{4+} results the loss of the monoclinic distortion. Besides, the refinement data show the large values of c and β, indicating large distance between two slabs in *m*-$LiMO_2$ lattice, i.e., *m*-$LiMO_2$ phase can offer a larger tunneling path for Li transportation. In short, this study present *m*-$LiMO_2$ phase as a novel, powerful material to enhance the performance of Li-battery.

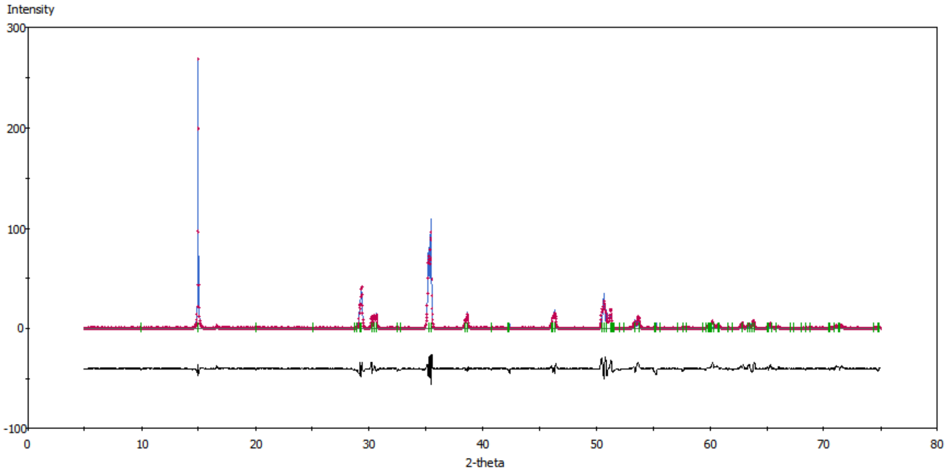

Figure 1: High resolution X-ray diffraction result of monoclinic Li($Li_{0.08}Ni_{0.34}Mn_{0.50}Co_{0.08}$)$O_2$ and Rietveld refinement data

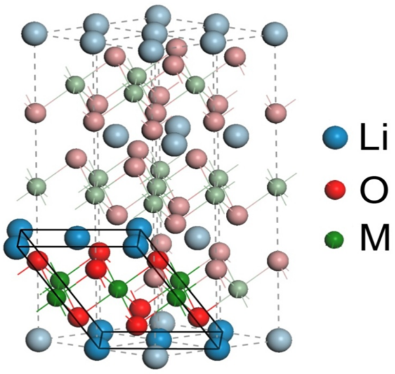

Figure 2: The unit cell structure of *h*-$LiMO_2$ (dash line) and *m*-$LiMO_2$ (solid line).

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Poster No. 8

Discrete, fiber-based modeling of liquid water transport in gas-diffusion layers for PEM Fuel Cells

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Water management is still an important topic for the optimization of power density, efficiency and durability of PEM Fuel Cells. The challenge is to maintain high ionomer water content to ensure a proper protonic conductivity, while keeping the porous structures of the electrodes and gas diffusion media free from liquid water.

For successful optimization of the fuel cell components and the control of the operation conditions, modeling is an important tool. However, the relevant processes like the electrochemical reaction, liquid water capillary transport and water vapor diffusion are very complex and highly coupled.

The most common way to model the liquid water transport in the porous structures of fuel cell models is by continuum modeling. Darcy's law which was developed for describing the liquid water transport in porous structures with low porosity and low contact angle as in soils is most often applied to porous structures in fuel cells. These models are not able to capture the fingering effects as observed in the highly hydrophobic and highly porous materials in fuel cells[1]. Newer, discrete models of the liquid water transport in gas diffusion transfer the fibrous structure into a pore network by dividing the space between the fibers into pores which are interconnected by throats. These models seem to model the liquid water transport quite realistic but are based on significant simplifications of the real GDL structure.

In this work, we present a discrete 2-dimensional model which represents the next step from the strongly simplified pore-network-modeling towards a model which is based on the true structure of the fibrous gas diffusion layer. The water movement does no longer take place along interconnected pores but along discrete paths between fiber pairs. The 2-dimensional fibers are randomly distributed with a defined distribution of size, orientation and contact angle. The input parameters are derived from SEM imaging of cross sections of commercial gas diffusion media.

The resulting saturation distribution (Figure 1) shows a distinct fingering effect as expected from literature [1]. Furthermore, the results of the model is compared to measured capillary pressure /saturation curves derived from recent literature [2] and shows good agreement.

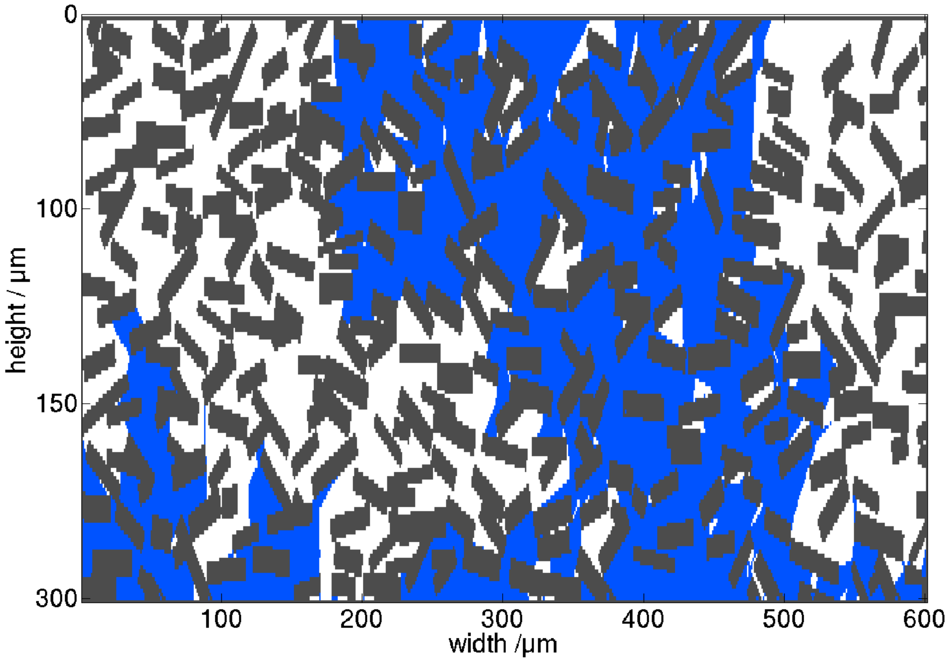

Figure 1: Liquid water distribution within the cross section of a carbon paper gas diffusion layer with porosity of 0.67. The water is pressed into the domain from the lower boundary.

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Poster No. 9

A Multi-Scale Thermal Model of a High-Power $LiFePO_4$ Lithium-Ion Cell

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The thermal stability of lithium-ion batteries is critical for high performance and safe operation especially in hybrid electric vehicle (HEV) applications. For efficient and safe operation there has to be a balance between heat generation and heat dissipation, that is, the amount of heat generated electrochemically inside the cell should not exceed the amount dissipated thermally. Therefore it is essential to comprehend the coupled behavior of these two mechanisms. A coupled electrochemical-thermal model can form the basis for devising an effective thermal management and cooling system.

We present a multi-scale thermal model of a lithium-ion battery. A 2D (1D+1D) electrochemical model, developed at German Aerospace Center (DLR), and a 3D finite element (FE) heat transfer model, developed at Institute of Chemical Process Technology (ICVT), were coupled using direct and indirect coupling methods. Indirect coupling of the two models involves heat sources varying only in time and not in space, while direct coupling involves spatial as well as temporal variations in heat generation, as well as feedback between temperature and heat sources.

The 1D+1D electrochemical model was validated using commercial high power lithium iron phosphate cells (A123) and represents multi-component transport (mass, charge, heat) within a cell repeat unit (anode, separator, and cathode) as well as solid-state diffusion within the active material [1].

In the 3D FE model, all the finer details of the cell geometry were captured. Natural convection conditions were assumed at the cell exterior. The 3D model treats the electrode layers as a composite body with experimentally determined values of anisotropic thermal conductivity and heat capacity. Temperature distribution and heat flow patterns inside the cell were studied at different discharge rates (1C, 2C, 3C, 5C).

Simulation results from the model provide a useful insight into the thermal behavior of the cells. Temperature versus time curves become steeper as we increase the discharge current. The model is found to be equally useful in predicting the thermal behavior of the cells under constant current loads as well as varying current.

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Poster No. 10

Influence of Liquid Saturation in Transient Bi-Domain 1D PEFC Model

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In PEFC technology, low dimensional cell models are used for performance prediction, parameter studies and system control. These applications are made possible due to the moderate computational effort. The 1-dimensional space discretization across the MEA is coupled with the mass transport in the channel and the models are termed 1+1 D. The core in these models is the 1D across the MEA sub-model. For *steady state* conditions these models can be tuned remarkably well to MEA components and operating conditions for predicting cell performance and local current densities [1,2]. However when the 1D (across the MEA) models are extended to the time domain significant differences between experimental and calculated temporal behavior are observed, which cannot be matched with parameter adaptation within reasonable physical domains.

One of the main reasons for this is the different boundary conditions of the MEA under channel and rib with respect to liquid saturation in the GDL as observed experimentally [3]. The difference can be parametrized into a single value for the steady state case, an approach which is not possible with a single parameter set for the entire time domain. The influence of the difference in liquid saturation of the GDL under channel and rib has led to a modified bi-domain 1D approach for the through MEA direction as shown in Figure 1, termed 1D^2. Rib and channel domain are treated as iso-potential parallel domains.

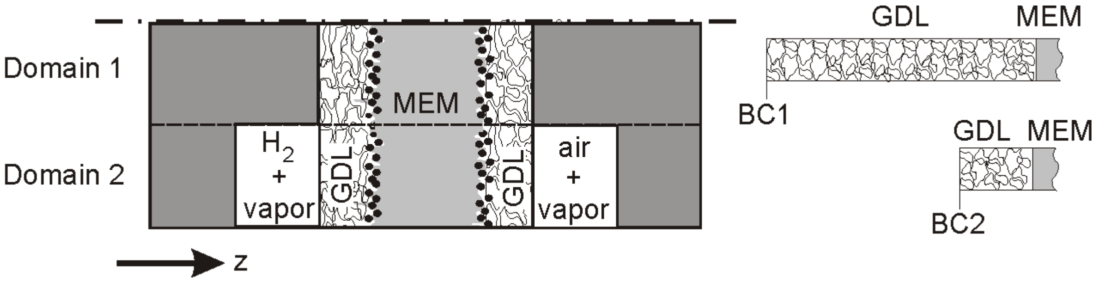

Figure 1: Schematic of the bi-domain 1D^2 concept for the 1D model approach (domain 1: rib; domain 2: channel), taking into account the different boundary conditions at the GDL/plate interface and diffusion length of the channel and rib domains of the cell.

Figure 2 shows the temporal behavior of the cell potential for an experimental differential cell (no gradients along the channel) and the 1D (after parameter fitting [4]) and 1D^2 models. It can be clearly seen that while the long term (> 1 s) temporal behavior fits well for both model approaches, the short term potential drop is much better reproduced by the 1D^2 model. Influential parameters for the transient cell behavior are the GDL saturation, the saturation boundary condition and the subsequent characteristics of the gas diffusion path. The different liquid saturation in the channel and rib domains also leads to differences in the membrane resistance in the two domains. A fact which has also been observed experimentally [5].

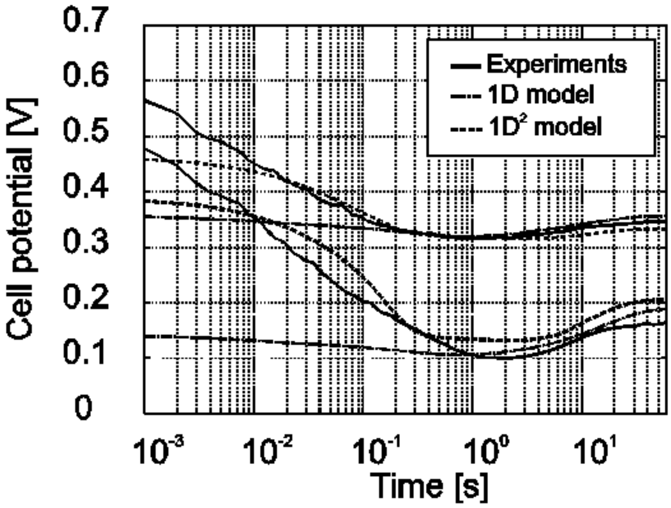

Figure 2: Experimental and modeled temporal cell potential for a current step of 0.3 to 0.8 A/cm^2. Two experimental conditions with different rel. gas humidities: top $RH_{an/cat} = 0.8/0.3$; bottom $RH_{an/cat} = 0.3/0.3$.

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Poster No. 11

Challenges in measuring low magnetic field changes for magnetotomography

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Magnetotomography is a promising tool to provide a non-invasive way to measure current densities spatially resolved inside an electrochemical device via the magnet field surrounding the device. High requirements must be fulfilled to measure reliable and reproducible data in non-perfect laboratory environments. For a detailed and highly resolved current density reconstruction – as provided in the oral contribution *Possibilities and Limits of Magnetotomography for Fuel Cells* – several measurement optimizations were successfully implemented. The major problems and the related fixing strategies are presented.

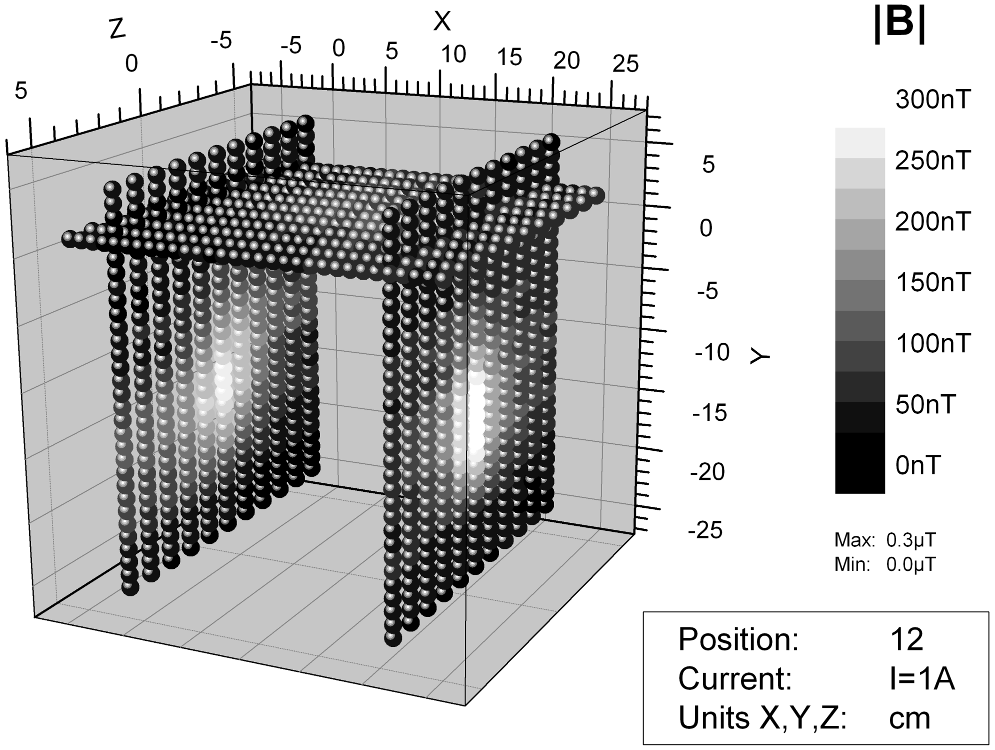

Figure 1: Measured magnetic field strength of a contact site in the middle of the measurement volume supplied with $I = 1\,\mathrm{A}$ ($j \sim 3\,\mathrm{A/cm^2}$).

Poster No. 12

Transmission Line Model of Water Fluxes in the Cathode Catalyst Layer of a Polymer Electrolyte Fuel Cell

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The cathode catalyst layer (CCL) is a crucial component in polymer electrolyte fuel cells (PEFCs) for vaporization exchange, water transport and the resulting water distribution [1,2]. In developing the model, we exploit a 1-1 correspondence of the problem of two-phase water fluxes in the nanoporous, composite CCL to the classical transmission line model of electrical charge fluxes in porous electrodes [3,4]. The model relates external conditions (pressure, relative humidity, temperature) and CCL porous structure to the distributions of liquid saturation and pressure as well as to the emitted water fluxes in liquid and vapour forms. We apply this model to the isolation and extraction of relevant transport parameters of water in the CCL from water flux measurements.

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Poster No. 13

Pore-scale Modeling of Ultrathin Catalyst Layers in Polymer Electrolyte Fuel Cells

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Recently, ultrathin catalyst layers (UTCLs) have shown promising potential to lower the Pt loading of PEFCs. We have developed steady-state and impedance pore-scale models of UTCLs, which examine the impact of pore geometry and metal|solution interfacial properties on UTCL performance. A UTCL nanopore is modeled as a cylinder with charged platinum walls. The surface charge density of the metal phase is related to the applied potential using a Stern double layer model. Proton and oxygen transport are governed by the Nernst-Planck equation and Fick's law, respectively. The steady state model found the potential of zero charge of the metal phase to have a crucial impact on performance; the impedance model allows for the separation of electrostatic and kinetic contributions to the overall current density.

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Poster No. 14

Model-Based Evaluation of Pt Loss Mechanisms and Evolution of the Particle Size Distribution in Polymer Electrolyte Fuel Cells

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The cathode catalyst layer in a conventional polymer electrolyte fuel cell (PEFC) contains a distribution of Pt nanoparticles dispersed on a nanoporous carbon support. The Pt particle radius distribution (PRD) defines the amount of electrochemically active surface area (ECSA) available to catalyze the oxygen reduction reaction and the effective rate of this reaction determines the performance of the PEFC. Over time, the PRD changes and correspondingly the ECSA changes, thus causing adverse effects on performance. We develop a physical-mathematical modeling methodology to rationalize the relationship between Pt dissolution, ripening, and coalescence and observable changes in PRD, ECSA, and Pt ion concentration in solution. Our work integrates classical mean-field type theories for these phenomena of Lifshitz, Slyozov and Wagner (LSW) for PRD evolution as well as Smulochowski's coalescence equations. Thereby, we establish a straightforward approach for the deconvolution of ECSA loss curves. Various limits of the model are solved, studied parametrically and compared with a wide range of available experimental data.

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Poster No. 15

Molecular Modeling of Interfacial Proton Transport in Polymer Electrolyte Membranes

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The performance of PEFCs depends on the efficient and selective transport of protons from anode to the cathode via a polymer electrolyte membrane (PEM). Nafion and similar ionomeric materials are best suited to fulfill the exacting requirements on stability, durability, and transport properties [1,2]. In these PEMs, hydrated side chains of the ionomer form charged and flexible interfacial layers relative to which protons move in water-filled nanopores; sulfonic acid head groups of the side chains release protons into water-filled channels. At high levels of hydration, protons move via the well-studied mechanism of structural diffusion in bulk-like water. The aim of our project is to study proton transport through the membrane under minimal hydration using first principles molecular simulations methods [3,4,5]. In our model, we have mapped the random arrangement of polymeric side chains onto a regular 2D array. A shortest sidechain, CF_3SO_3H, with one H_2O molecule per side chain is used. Interfacial structure, proton dissociation, strength of water binding and dynamics of proton and water transport at the interface are determined as functions of the side chain spacing. Transition pathways and free energy profiles of interfacial proton transitions are calculated using Car-Parinello molecular dynamics and Metadynamics methods [6]. The structure of the array of surface groups changes from an upright to a tilted conformation at the surface group spacing of $\sim 6.7\,\text{Å}$, which is found to be a critical value for long range proton transport; this finding is in agreement with experimental results for proton mobility at lipid monolayers. For the dense array of minimally hydrated side chains, we have discovered an ultra-efficient, highly concerted mechanism of interfacial proton transport.

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Poster No. 16

Validation of Current Distribution Diagnostics for Fuel Cell Stacks

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For the development of fuel cells and fuel cell components a uniform current distribution is important to achieve high efficiencies. There are different techniques known to measure the current distribution with more or less impact on the cell construction. Most of them use contact plates that have to be integrated into the stack. The whole stack current must be conducted through these plates and with a digital measuring and evaluation system the current distribution can be determined [1,2]. Another method is to measure the magnetic flux of a single fuel cell or a fuel cell stack by special sensors and to recalculate from this magnetic field the currents inside a stack. This technique needs no additional plates inside a stack, but the development of this ambitious technique is now at the beginning and the resolution is presently not as high as necessary [3-6].

In this contribution the validation of another technique determining the current density inside a stack with a small impact on the construction of a fuel cell stack will be presented. The idea is to determine the current distribution in fuel cell stacks by measuring electric cross-currents in bipolar units. With the measured cross-currents and the knowledge of the absolute current it is possible to calculate the location and the dimension of defects [7].

In [7] and [8] a method was described to simulate the current distribution in fuel cell stacks and it was shown that a blockage in one cell may have an influence on other cells of a stack [8], the same effect was numerically investigated by Kulikovsky [9]. The idea to minimize the influence of an uneven current distribution in one cell on the neighbor cells, is to integrate highly conductive metal plates into the bipolar plate, to enhance the conductance for homogenizing cross currents.

If such plates are splitted and connected over a connection link or a wire, cross currents are forced to flow through that wire and can be measured there. The electrical resistance of this connection is the crucial quantity determining the magnitude of the currents and the quality of the current density homogenization. To reduce this resistance, it is possible to measure the currents inductively. It is also possible to change the orientation of the gap in neighboring cells. Then it will be possible to identify failures not only in upside or downside but in a rectangular mesh, whose resolution is determined by the number of gaps. See in figure 1 on the left side the setup of a sample stack. From left to right it starts with the end plate, the cathodic flow field, the highly conductive plates, the anodic flow field, the MEA and so on. On the right of figure 1 a horizontal segmented inlay for the bipolar unit is shown.

To assess the function of this idea and to validate the results from the simulation, a single bipolar

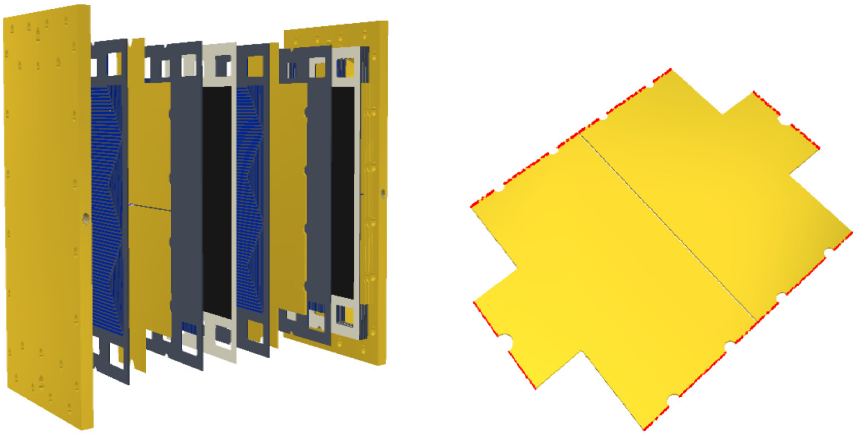

Figure 1: Setup of a five cell stack with segmented inlays in bipolar plates at a glance (left), highly conductive segmented inlay for bipolar unit (right)

unit with the integrated highly conductive metal plates is built up. This plate is integrated into a test setup with special electric contact plates. The contact plates consist of eight contact elements with a contact area of four square centimeters each. It is possible to control the currents in these contact elements and to measure the crosscurrents in the bipolar unit. In figure 2 the circuit diagram is shown on the left side. Number one is marking the highly conductive inlay plate, number two are the endplates with the integrated contact elements (number 3). The graphite bipolar plates are labeled with number four. Number five is marking the current source.

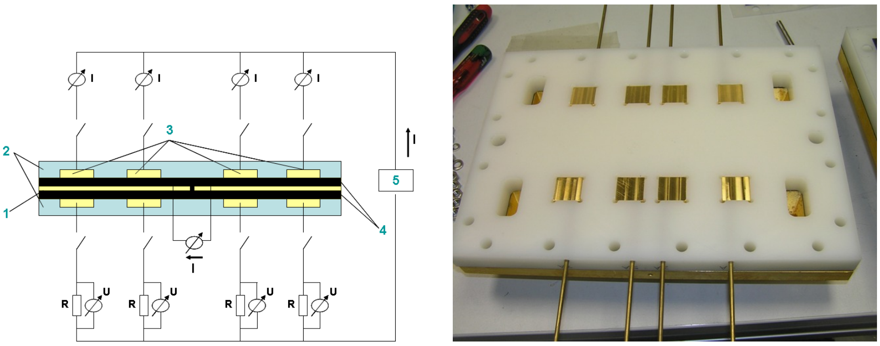

Figure 2: Circuit diagram of the measurement setup (left), contact plate to induce the current into the bipolar unit (right)

At the bottom of the circuit diagram (figure 2, left) you can also find resistors (R). These resistors are not only sensing resistors for the current, they have also the function to represent the resistance of the MEA, to achieve a representative current flow in the whole setup. The resistance of the whole setup including contact resistances is adapt to fuel cell stacks by measuring the conductivity of all materials and components and by adjusting the resistors (R). With this tool it is now possible to investigate the resolution limits of the measurement setup. It is also possible to adapt the segmented bipolar units onto the demands of practical current distribution measurements inside stacks.

To test the function of the setup and to compare results from the measurements with the simulation, the cross current and the absolute current were measured. In figure 3 the results of the measurements of the electric cross current in relation to the absolute current when a single contact is disconnected were shown. When using different bipolar plate materials the result is always in the same manner. This indicates that the contacts in the experimental set up are working reproducible even after mounting and dismounting with different materials.

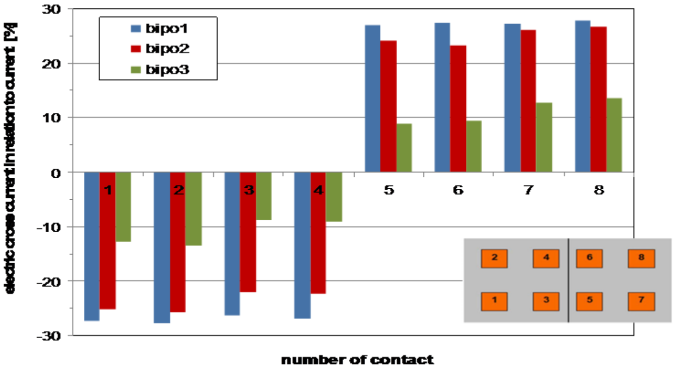

Figure 3: Electric cross current in relation to absolute current when disconnecting single contacts

With the same configuration the contacts (starting with contact one) one after another were disconnected and the cross current was measured and simulated. The correlation between measured and simulated values is obviously very satisfying (see in figure 4).

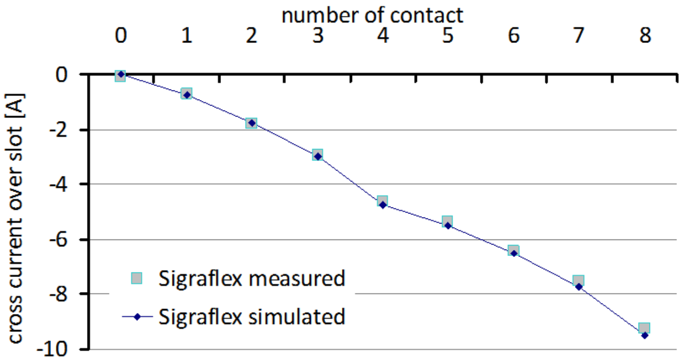

Figure 4: Electric cross current when disconnecting contacts

The measurements with the described setup have shown, that it is possible to calculate the current distribution of a fuel cell stack by measuring the cross currents in a bipolar unit. There is a good correlation of the measured and calculated values. The advantage of this method is that there are no big constructive modifications at the stack setup necessary. By integrating the highly conductive segmented elements the impact of an inhomogeneous current distribution on neighboring cells is reduced and additionally it is possible to get information of the current distribution in a fuel cell stack. Further measurements are now necessary to improve the resolution and to carry out first measurements in a working fuel cell.

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Poster No. 17

1-D Phenomenological Model for the Water Flooding in the Cathode Gas Channel of PEFCs

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In an operating PEM fuel cell, probably liquid water emerges from the GDL into the GC in form of small droplets and flow film, which would cover the GDL surface and block the GC. This, in turn, influences the levels of flooding inside the electrode [1]. In order to capture this physical phenomenon, the interactive mechanism of water transport between the GC and GDL should be incorporated into a full fuel cell model. However, due to the difficulty in the description of complicated water dynamics, two-phase flow in the GC has been commonly neglected in other numerical studies replaced by a mist flow assumption [2].

In this work, we proposed a phenomenological model for the water movement inside the cathode GC. As shown in Fig.1, the water distribution in the GC is assumed to have two different configurations, film flow at two corners due to the hydrophilic sidewalls, and droplet at the center of hydrophobic GDL surface. In order to avoid dynamic tracking of droplet movement [3] inside the GC, we introduced the following reasonable assumptions:

1. The movement of droplets in the GC can be described by the following sequential processes: emergence, growth, coalescence and final wicking onto the sidewalls of GC.
2. Based on the assumption 1, we presume that droplets solely influence the configuration of GC crosssection, which can be pre-described.
3. The liquid water coming from the GDL is removed out of the GC only via the film flow at the corners.

Based on above assumptions, we have two-phase flow in the GC, namely, gas flow and film flow. The existence of droplets is pre-described by a droplet distribution function. For 1-D model, gas flow and film flow both can be approximated by means of Hagen-poiseuille law [4] associated with proper flow conductivities. Moreover, pressures of two phases are coupled through capillary pressure.

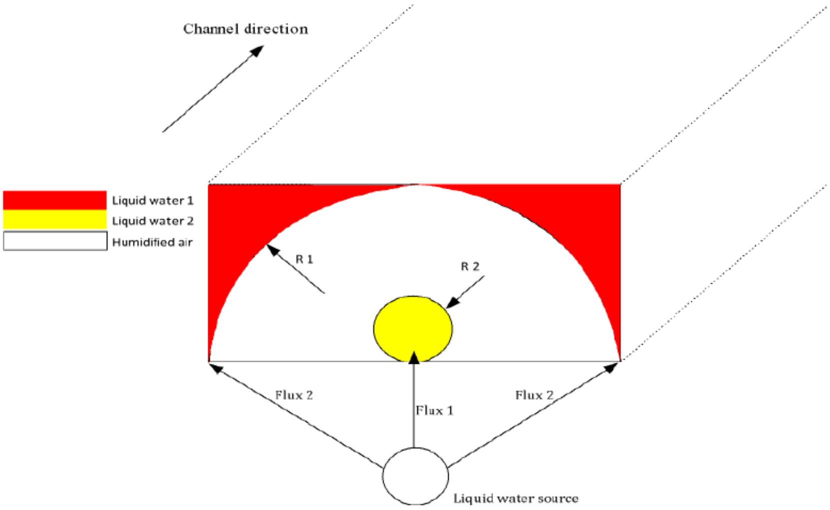

Figure 1: Idealized water distribution in the cross-section of GC (red color represents film flow at corners, while yellow one represents droplet flow above the GDL surface).

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Poster No. 18

Impact of Synchrotron Radiation on Fuel Cell Imaging Experiments

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On the way to fuel cell commercialization one of the key challenges is durability. Here product water and its movement in the porous fuel cell materials play a significant role. Various visualization techniques have been applied to gain information about liquid water movement and distribution, such as neutron and synchrotron radiography, nuclear magnetic resonance tomography as well as several optical methods. X-ray synchrotron radiography (SR) provides spatial and temporal resolution appropriate to investigate the fundamental transport mechanisms in operating fuel cells on the scale of the pores of the porous materials. Therefore, a special micro fuel cell with $7\,\mathrm{mm}^2$ active area was designed capable of application-relevant fuel cell operation within an SR beam line to obtain highly resolved tomography data sets. During cell operation under x-ray exposure, though, rapid cell performance degradation has been observed. Apparently the SR beam energy leads to mechanisms which degrade fuel cell materials quickly. However, the time constants of possible material degradation effects necessarily have to be much longer than the time constants of the transport mechanisms to justify such imaging experiments. Hence, understanding the beam/material interaction and mitigating the degradation effects by appropriate material selection, imaging conditions and test protocols are essential preconditions for reasonable studies and subject of ongoing work.

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