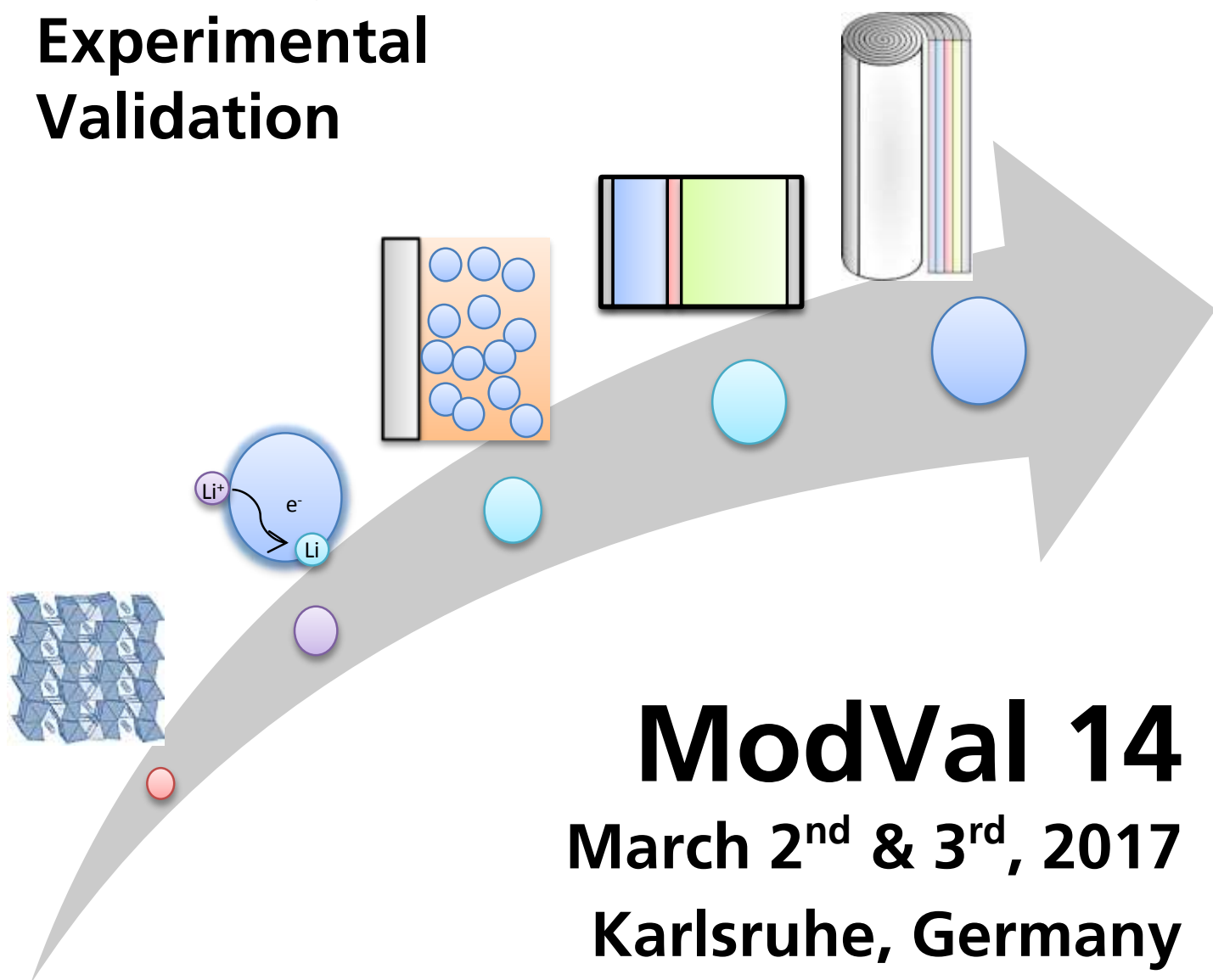# 14th Symposium on Fuel Cell and Battery Modelling and Experimental Validation

# ModVal 14

## March 2nd & 3rd, 2017

## Karlsruhe, Germany

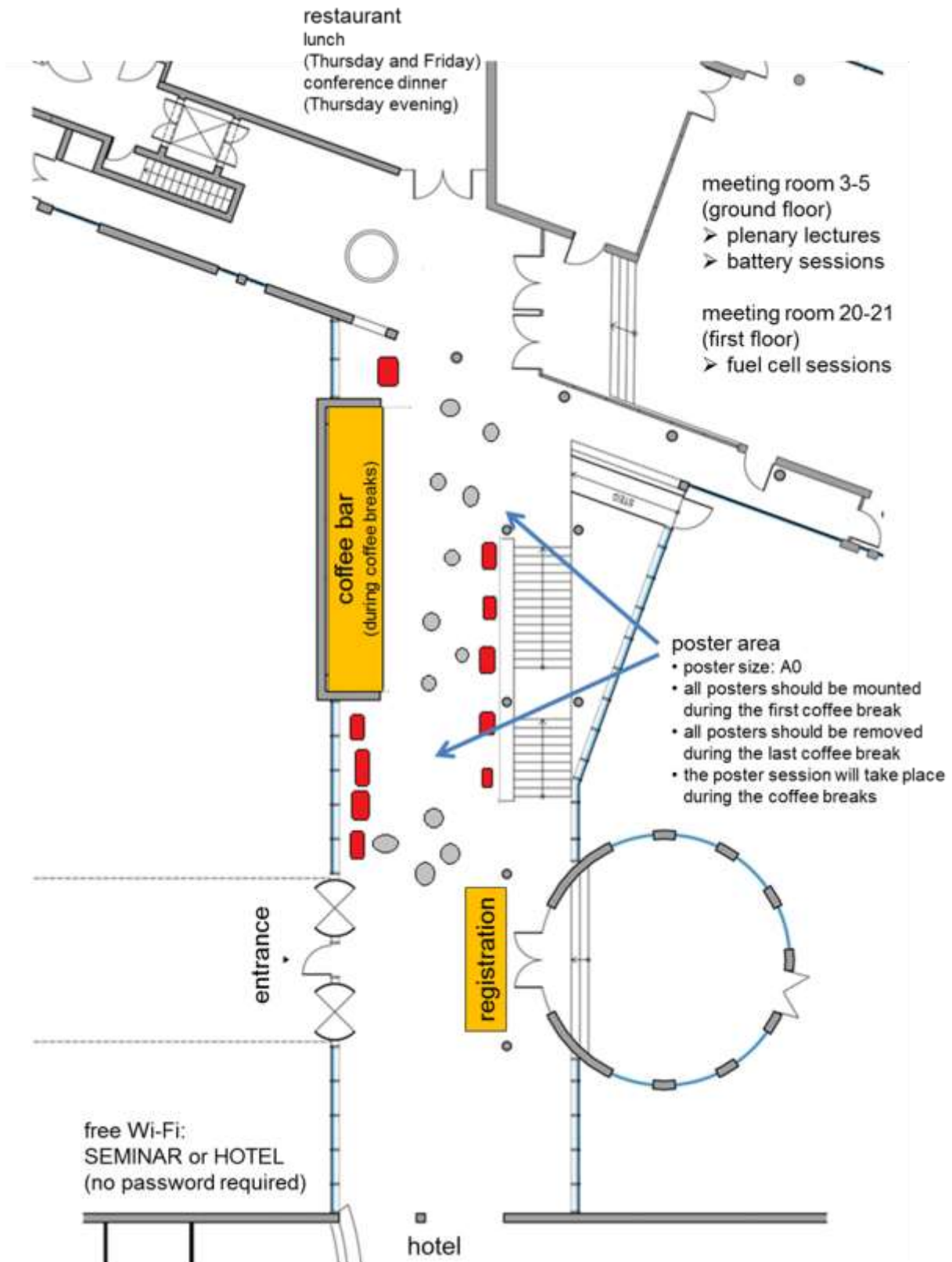# Book of Abstracts

# AkademieHotel Karlsruhe

Am Rüppurrer Schloss 40, 76199 Karlsruhe
phone: +49 721 98 98-0, http://www.akademiehotel-karlsruhe.de



restaurant
lunch
(Thursday and Friday)
conference dinner
(Thursday evening)

meeting room 3-5
(ground floor)
➢ plenary lectures
➢ battery sessions

meeting room 20-21
(first floor)
➢ fuel cell sessions

coffee bar
(during coffee breaks)

poster area
• poster size: A0
• all posters should be mounted
  during the first coffee break
• all posters should be removed
  during the last coffee break
• the poster session will take place
  during the coffee breaks

entrance

registration

free Wi-Fi:
SEMINAR or HOTEL
(no password required)

hotel

# Travel Information

Karlsruhe is located in the southwest of Germany close to the French border.

## Train

Karlsruhe has hourly ICE-services in the direction of Frankfurt/Cologne and Freiburg/Basel.

## Airport

It takes about 60 minutes by train from Frankfurt- (direct ICE-connection), Stuttgart- or Strasbourg-Airport to Karlsruhe.

## Car:

from Munich/Stuttgart via A8 direction Karlsruhe, change to A5 direction Basel at the motorway junction Karlsruhe and take the next exit no. 47 Karlsruhe Ettlingen
from Frankfurt (airport) via A5 direction Basel, pass the motorway junction Karlsruhe and take the next exit no. 47 Karlsruhe Ettlingen
from Basel via A5 direction Karlsruhe, leave the motorway at exit no. 47 Karlsruhe Ettlingen
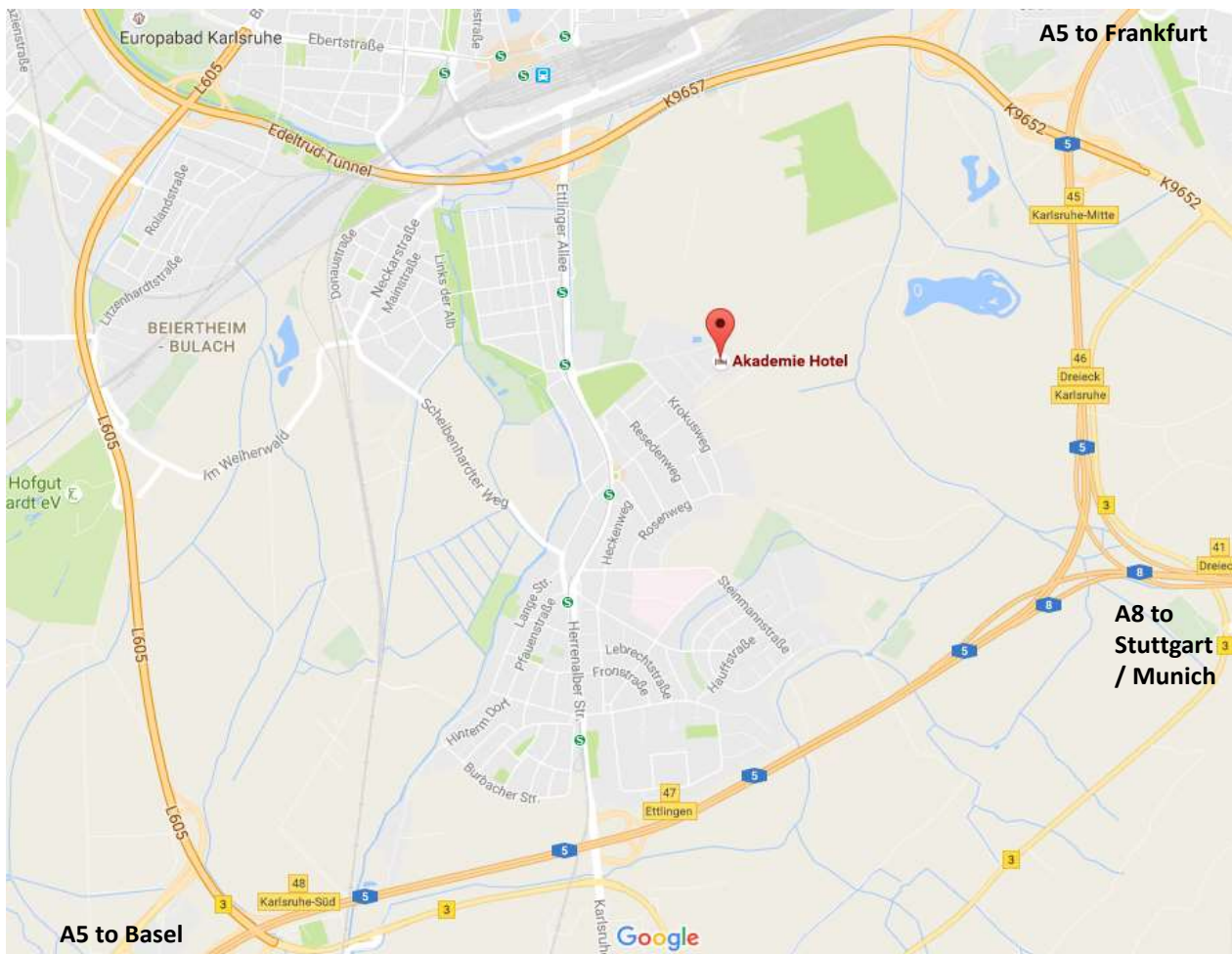
# Session Overview

| Wednesday, March 1st, 2017 | |
|---|---|
| 17h00 - 23h00 | Arrival, hotel check in |
| 19h00 - 21h00 | Possibility for dinner in the hotel, 1st stay overnight |

| Thursday, March 2nd, 2017 | | |
|---|---|---|
| 06h30 - 09h00 | Breakfast, Hotel Restaurant | |
| 08h00 - 09h00 | Registration & Welcome Coffee, Hotel Lobby | |
| | Meeting Room 3 - 5 | |
| 09h00 - 09h10 | Welcome, Prof. Dr. Oliver Kraft, Vicepresident for Research of KIT | |
| 09h10 - 10h10 | **Invited plenary talks** | |
| 10h10 - 10h40 | Poster mounting & Coffee Break, Hotel Lobby | |
| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
| 10h40 - 12h20 | **Fuel Cells: PEMFC I** | **Lithium Ion Batteries: System Aspects** |
| 12h20 - 13h50 | Buffet Lunch, Hotel Restaurant | |
| 13h50 - 15h50 | **Fuel Cells: Cell and Stack Modeling** | **Lithium Ion Batteries: Electrodes I** |
| 15h50 - 16h20 | Poster Session & Coffee Break, Hotel Lobby | |
| 16h20 - 18h00 | **Fuel Cells: PEMFC II** | **Lithium Ion Bat.: Alternative Chemistries** |
| 19h30 | Conference Dinner, Hotel Restaurant | |

| Friday, March 3rd, 2017 | | |
|---|---|---|
| 06h30 - 09h00 | Breakfast, Hotel Restaurant | |
| | Meeting room 3 - 5 | |
| 09h00 - 10h00 | **Invited plenary talks** | |
| 10h00 - 10h30 | Poster Session & Coffee Break, Hotel Lobby | |
| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
| 10h30 - 12h10 | **Fuel Cells: Materials Modeling** | **Lithium Ion Batteries: Cell Modeling I** |
| 12h10 - 13h40 | Buffet Lunch, Hotel Restaurant | |
| 13h40 - 15h00 | **Fuel Cells: Microstructure Modeling I** | **Lithium Ion Batteries: Electrodes II** |
| 15h00 - 15h30 | Coffee break, Hotel Lobby | |
| 15h30 - 16h50 | **Fuel Cells: Microstructure Modeling II** | **Lithium Ion Batteries: Cell modeling II** |
| | Meeting room 3 - 5 | |
| 16h50 - 17h00 | Closing remarks & Announcement of ModVal 2018 | |

# Conference Program

| Thursday, March 2nd, 2017 | | |
|---|---|---|
| 06h30 - 09h00 | Breakfast, Hotel Restaurant | |
| 08h00 - 09h00 | Registration & Welcome Coffee, Hotel Lobby | |
| | Meeting Room 3 - 5 | |
| 09h00 - 09h10 | Welcome, Prof. Dr. Oliver Kraft, Vicepresident for Research of KIT | |
| 09h10 - 09h40 | Invited plenary talk: Prof. Jon Pharoah, Queen's University: The Eternal Golden Braid: Modelling and Experiment | |
| 09h40 - 10h10 | Invited plenary talk: Prof. Robert M. McMeeking, University of California, Santa Barbara: The Generation of Stress and Fracture in the Storage Particles of Lithium-Ion Batteries | |
| 10h10 - 10h40 | Poster mounting & Coffee Break, Hotel Lobby | |
| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
| 10h40 - 12h20 | **Fuel Cells: PEMFC I** Chairs: Steven Beale (FZJ) Jürgen Schumacher (ZHAW) | **Lithium Ion Batteries: System Aspects** Chairs: Oleg Borodin (U.S. Army Research Lab.) Dong Kyu Kim (KIST Europe) |
| 10h40 | Martin Andersson (Lund University / FZJ): Volume-of-Fluid Modeling in Microscale Channels relevant for PEFCs | Marco Heinrich (PTB/TUBS): Ageing induced changes of charge distributions in a LIB analysed by correlating EIS simulations and experiments |
| 11h00 | Ivan Pivac (University of Split): Modeling of inductive phenomena at low frequencies in electrochemical impedance spectroscopy of PEM fuel cell | Kotub Uddin (University of Warwick): The impact EV power electronics on battery degradation |
| 11h20 | Guillaume Serre (CEA (Grenoble)): A multi-physic PEM Electrolyzer code for cell design optimization | Carlos Ziebert (KIT): Challenges for electrochemical and thermal characterization of Li-ion cells to improve parametrization for modelling |
| 11h40 | Denis Kramer (University of Southampton): Enhanced ORR Electrocatalysts Through Electronic Metal-Support Interactions between Pt and Boron Carbide | Nan Lin (TUBS): Parameter Sensitivity Study of a 3D Multiphysics Model of Large-format Li-ion Batteries |
| 12h00 | Matthias Messerschmidt (ZSW): CFD Modelling as a Validated Tool to Understand and Develop PEMFCs | Johannes Sturm (TUM): Modelling the Electrochemical-Thermal Behaviour of Cylindrical Lithium-Ion Cells during Internal Short Circuit Scenarios |
| 12h20 - 13h50 | Buffet Lunch, Hotel Restaurant | |

| Thursday, March 2nd, 2017 | | |
|---|---|---|
| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
| 13h50 - 15h50 | **Fuel Cells: Cell and Stack Modeling**<br>Chairs:<br>Aimy Bazylak (University of Toronto)<br>Guillaume Serre (CEA) | **Lithium Ion Batteries: Electrodes I**<br>Chairs:<br>Bob McMeeking(UCSB)<br>Thomas Carraro (Uni Heidelberg) |
| 13h50 | Steven Beale (FZJ):<br>Stability Issues for Three Dimensional Fuel Cell Models | Tobias Hofmann (FHG ITWM):<br>Stress simulation of phase-separating cathode materials |
| 14h10 | Denis Gryaznov (University of Latvia):<br>First principles calculations of perovskite cathode materials for protonic ceramic fuel cells | Peter Stein (TUD):<br>Mechanically coupled modeling of ionic transport and electrochemical reactions in Li-ion battery electrodes |
| 14h30 | Peter Urthaler (AVL):<br>3D Modeling of HT-PEMFC and Validation on an Industrial Cell | Yixiang Gan (University of Sydney):<br>Universality of the Emergent Scaling in Finite Random Binary Percolation Networks |
| 14h50 | Thomas Strohbach (Sunfire):<br>Homogenized 3D SOC model and validation | Georg Bauer (BMW):<br>Modeling of mechanical effects in lithium ion batteries |
| 15h10 | Shidong Zhang (FZJ):<br>An Open-source Code for High Temperature Polymer-electrolyte Fuel Cells | Timo Danner (DLR, HIU):<br>Thick electrodes for Li-Ion batteries: A model based analysis |
| 15h30 | Roman Kodým (University of Chemistry and Technology Prague):<br>Concept of 3D Mathematical Modeling of HT PEM FC Stack Degradation and Single Cell Model Experiments | Fabian Single (DLR, HIU):<br>Theory-based Investigation of SEI Formation |
| 15h50 - 16h20 | Poster Session & Coffee Break, Hotel Lobby | |
| 16h20 - 18h00 | **Fuel Cells: PEMFC II**<br>Chairs:<br>Peter Urthaler (AVL)<br>Felix Büchi (PSI) | **Lithium Ion Bat.: Alternative Chemistries**<br>Chairs:<br>Carlos Ziebert (KIT)<br>Bartosz Protas (McMaster University) |
| 16h20 | Georg Futter (DLR):<br>A Physics-based Model for PEMFCs: Process Identification from EIS Simulation | Wolfgang Bessler (HS Offenburg):<br>Electrochemical pressure impedance spectroscopy (EPIS): A promising tool for model parameterization and validation |
| 16h40 | Tasleem Muzaffar (Simon Fraser University):<br>Water Phenomena in PEFC Catalyst Layers as the Origin of the Pt Loading Effect: A Modelling Study | Tobias Gerber (FHG ICT):<br>Measurement method for locally resolved current density measurements in redox flow cells and stacks |
| 17h00 | Sven-Joachim Kimmerle (Universitaet der Bundeswehr Muenchen):<br>Mathematical Modelling of Hydrogen Nanobubbles in PEM Electrolysers | Dong Kyu Kim (KIST Europe):<br>Investigation of mass transport through Nafion® 115 in the vanadium redox flow battery |
| 17h20 | Jürgen Schumacher (ZHAW):<br>Influence of pore-scale material properties on the performance of proton exchange membrane fuel cells | Ismail Celik (West Virginia University):<br>Modeling of porous media effects on transport processes in sodium sulfur batteries |
| 17h40 | Victoria Manzi-Orezzoli (PSI):<br>Towards Patterned Wettability in Gas Diffusion Media for PEFCs | Manik Mayur (HS Offenburg):<br>Two-dimensional multiphysics simulation of Li-air button cells for electrolyte choice and electrode design |
| 19h30 | Conference Dinner, Hotel Restaurant | |

| Friday, March 3rd, 2017 | |
|---|---|
| 06h30 - 09h00 | Breakfast, Hotel Restaurant |
| Meeting room 3 - 5 | |
| 09h00 - 10h00 | **Invited plenary talks** |
| 09h00 - 09h30 | Invited plenary talk: Prof. Aimy Bazylak, University of Toronto: Modeling and validation for designing porous materials for PEM fuel cells and electrolyzers |
| 09h30 - 10h00 | Invited plenary talk: Dr. Oleg Borodin, US Army Research Lab: Modelling Lithium Battery Electrolytes and Solid Electrolytes Interphases |
| 10h00 - 10h30 | Poster Session & Coffee Break, Hotel Lobby |

| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
|---|---|---|
| 10h30 - 12h10 | **Fuel Cells: Materials Modeling** Chairs: Andreas Häffelin (Bosch) Adrien Lamibrac (PSI) | **Lithium Ion Batteries: Cell Modeling I** Chairs: Wolfgang Bessler (HS Offenburg) Clemens Guhlke (WIAS) |
| 10h30 | Eugene Kotomin (MPI-FKF): Large scale first principles modeling of non-stoichiometric complex perovskites for fuel cell applications | Thomas Carraro (UHD): On the charging behavior of a multi-radii Newman-type battery model |
| 10h50 | Bolahaga Randrianarizafy (CEA Grenoble): Cathodic carbon corrosion: from a 1D-model to a full 2D-model | Markus Ganser (Bosch): A Fully Coupled Electro-Chemo-Mechanical Model for Ion Transport in Solid Electrolytes at Large Strains |
| 11h10 | Julian Szász (KIT): Secondary Phases at Cathode/Electrolyte Interfaces | Michael Kespe (KIT): Numerical simulation and optimization of lithium-ion batteries on the microscale |
| 11h30 | Felix Büchi (PSI): Evaporation of water from gas diffusion layers | Christian Merdon (WIAS): A novel concept for the discretisation of the coupled Nernst-Planck-Poisson-Navier-Stokes system |
| 11h50 | Fabio Greco (EPFL): Parameter estimation of the elastic and creep properties of Ni-YSZ anode based on four-point bending measurements | Teng Zhang (Imperial College): Understanding the performance bottleneck in Li-S batteries: a model-informed approach |

| Friday, March 3<sup>rd</sup>, 2017 | | |
|---|---|---|
| 12h10 - 13h40 | Buffet Lunch, Hotel Restaurant | |
| | Meeting Room 20 - 21 | Meeting Room 3 - 5 |
| 13h40 - 15h00 | **Fuel Cells: Microstructure Modeling I** Chairs: Lorenz Holzer (ZHAW) Eugene Kotomin (MPI-FKF) | **Lithium Ion Batteries: Electrodes II** Chairs: Peter Stein (TUD) Hermann Nirschl (KIT) |
| 13h40 | Antonio Bertei (Imperial College): Quantification of Ni coarsening in infiltrated SOFC anodes by combining 3D tomography, impedance spectroscopy and mechanistic modelling | Reiner Mönig (KIT): Measurements of Stress and Strain in Electrode Materials of Lithium-Ion Batteries |
| 14h00 | Henrik Ekström (Comsol / KTH): A model for analysis of the porous nickel electrode polarization in the molten carbonate electrolysis cell | Herman Lemmens (ThermoFisher Scientific): Battery electrode imaging in 3D: Field of View or Resolution ? |
| 14h20 | Jochen Joos (KIT): Microstructure Modelling of Porous Cathodes for Solid Oxide Fuel Cells (SOFCs) | Bartosz Protas (McMaster University): Mathematical Model of Binder Distribution During Drying of Lithium-Ion Battery Electrodes |
| 14h40 | Roswitha Zeis (HIU): Pore network modelling of phosphoric acid distribution in high temperature PEM fuel cells | Janina Costard (KIT): Combined Impedance Study (EIS) and microstructure analysis (FIB/SEM) of intercalation electrodes: Determination of charge transfer parameters |
| 15h00 - 15h30 | Coffee break, Hotel Lobby | |
| 15h30 - 16h50 | **Fuel Cells: Microstructure Modeling II** Chairs: Antonio Bertei (Imperial College) Jochen Joos (KIT) | **Lithium Ion Batteries: Cell modeling II** Chairs: Jochen Zausch (FHG-IWTM) Reiner Mönig (KIT) |
| 15h30 | Lorenz Holzer (ZHAW): Microstructure limitations for relative permeability and liquid drainage in fibrous GDL (PEFC): The importance of the 'short range effect' | Andrea Falconi (Renault): Transient Lithium Ion Battery Behavior Simulations Through Electrochemical Modelling |
| 15h50 | Marie-Dominique Baum (DLR): Analysis of local heterogeneities and their effect on DMFC performance with a physical 2D cell model | Johannes Landesfeind (TUM): Parameters Controlling the Fast-Charging Limitations for Lithium Ion Batteries and their Temperature Dependence |
| 16h10 | Hamza Moussaoui (CEA Grenoble): 3D morphological modeling and validation for optimization of SOCs electrode microstructures | Jonas Keil (TUM): Modeling capacity fade due to SEI formation in Li-ion cells validated by neutron diffraction data |
| 16h30 | Matthias Neumann (UUlm): Big data for microstructure-property relationships: a case study of predicting effective conductivities | Bartosz Protas (McMaster University): Inverse Modelling Approach to Determine Material Properties of Electrolytes: Effects of Faradaic Convection |
| Meeting room 3 - 5 | | |
| 16h50 - 17h00 | Closing remarks & Announcement of ModVal 2018 | |

# Table of Contents

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## FUEL CELLS: POSTER PRESENTATIONS

**Roman Vetter\*[1], Philip Marmet[1], Jaka Dujc[1], Lorenz Holzer[1], Jürgen O. Schumacher[1], Adrien Lamibrac[2], Felix N. Büchi[2]**

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## LITHIUM ION BATTERIES: ORAL PRESENTATIONS

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## LITHIUM ION BATTERIES: POSTER PRESENTATIONS

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# The Eternal Golden Braid: Modelling and Experiment

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# The Generation of Stress and Fracture in the Storage Particles of Lithium-Ion Batteries

## Robert M. McMeeking

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**Abstract**   Models are developed for the transport of Li ions in the electrolyte of lithium ion batteries, their diffusion through storage electrode particles, and their kinetics through the surface of the particles between the electrolyte and the particles.  As a consequence of the Li ion intercalating in the storage particles, their lattices swell, leading to elastic stress when the concentration of Li ions in the particles is not uniform.  The models of transport are based on standard concepts for multi-component diffusion in liquids and solids, but are not restricted to dilute solutions, or to small changes in the concentration of the diffusing species.  The approach is used to compute the processes of charging and discharging the battery to assess the parameters that influence the development of stress in the storage particles, and to deduce the likelihood of fracture of the storage particle material.  Phase-field methods are also utilized to predict the process of cracking in the storage particles.  The objective is to assess designs of electrode microstructures that permit rapid charging and discharging, but obviate the likelihood of fracture and other mechanical damage that limit the performance and reliability of the battery.
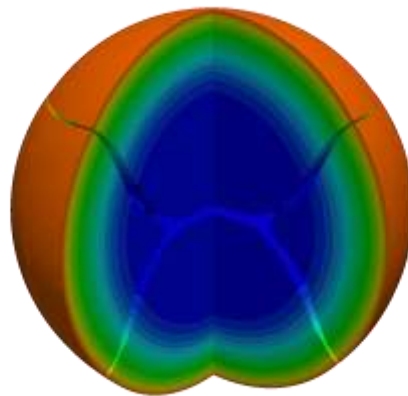
Computational results for the lithium distribution and cracks generated in a storage particle.

# Modeling and validation for designing porous materials for PEM fuel cells and electrolyzers

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The hydrogen polymer electrolyte membrane (PEM) fuel cell and electrolyzer provide enormous potential for a clean energy infrastructure. However, due to cost and inefficiency barriers, PEM fuel cells and electrolyzers have not yet reached widespread commercial adoption. Mass transport limitations such as liquid water flooding in the PEM fuel cell and oxygen gas bubble accumulation in the PEM electrolyzer lead to inefficiencies. If these issues become resolved, smaller and more reliable devices could be produced at a lower cost. Mass transport limitations can be minimized through the development of optimized materials, which have tailored pore structures, connectivities, conductivities, and surface wettabilities. Currently, the porous materials in PEM fuel cells and electrolyzers have not been customized for mass transport, due to the lack of information about their structure and the dominating mass transport mechanisms. In this talk, I will discuss my TEAM's techniques for analyzing the three-dimensional structure of the PEM fuel cell and electrolyzer gas diffusion layers (GDLs) and the microporous layers (MPLs). I will also discuss how we combine numerical models along with experimental validation to investigate and design next generation porous materials for advanced performance.

# Modelling Lithium Battery Electrolytes and Solid Electrolytes Interphases

## Oleg Borodin

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Tailoring electrolyte electrochemical properties is critical for stabilizing the electrode – electrolyte interfaces and enabling novel electrochemical couples in lithium batteries. The rational design of an electrolyte requires not only the knowledge of the limits of electrolyte electrochemical stability and electrolyte decomposition reactions that might or might not occur at the surface of the electrode but also understanding of the structure and transport properties of the passivation film formed at the anode and/or cathode surfaces. I will discuss application of the molecular modelling methodologies to predict electrolyte electrochemical stability, decomposition reactions at electrodes, initial stages of the passivation layer formation and its properties.

When combined with accurate predictions of the electrolyte structure, such calculations provide tremendous insight into the mechanism of the in-situ formation of a highly beneficial passivation layer on electrodes that enable a wide range of electrode couples from lithium metal to conversion cathodes in non-aqueous electrolytes. Molecular modelling of the electrolyte structure and SEI formation mechanism enabling high energy density electrode couples in electrolytes will be discussed.
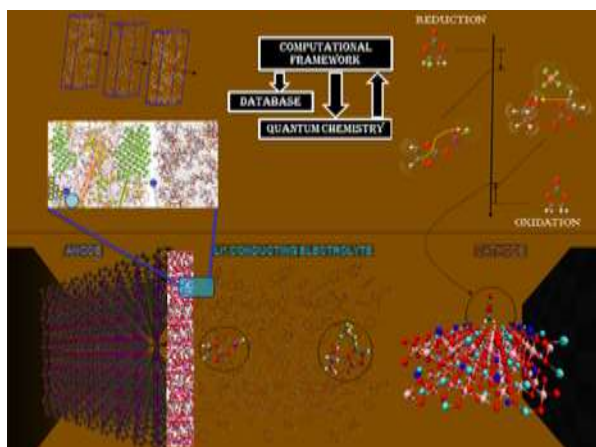
# Volume-of-Fluid Modeling in Microscale Channels relevant for PEFCs

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Regardless of scientific advances over the last few decades, the commercialization of polymer electrolyte fuel cells (PEFCs) remains unrealized, mainly due to: economic viability associated with the high material prices and components; as well as technical problems relating primarily to liquid water. PEFC modeling has advanced significantly over the last decades. Increased computational power and improved techniques have allowed problems of larger complexity to be solved with improved reliability [1-2]. The volume-of-fluid (VOF) approach is an interface-resolving method and has become a suitable methodology for solving two-phase flow phenomena within PEFCs. With the VOF approach, the interface between the phases is tracked by the volume fraction of liquid water at the computational cell volume schemes. In each cell of a mesh, it is customary to use only one value for each dependent variable defining the state. The use of several points in a cell that specifies the region occupied with liquid and gas, respectively, seems unnecessarily computationally expensive. Instead, the function $a$ is introduced whose value is zero at any location occupied by gas phase phase, and otherwise unity [1,3].

The influence of the contact angle, different contact angles on the membrane side and the wall sides, size of the liquid inlet (located at the membrane side), the ratio of liquid-to-gas velocities and the gas velocity are investigated by VOF with the software OpenFoam. The liquid/gas distribution for a case with 120° contact angle (left), 150° contact angle (middle) and 150/90 (right) when time equals 0.07 seconds are presented in Figure 1. It should be noted that the higher contact angle for the right figure corresponds to the membrane side.
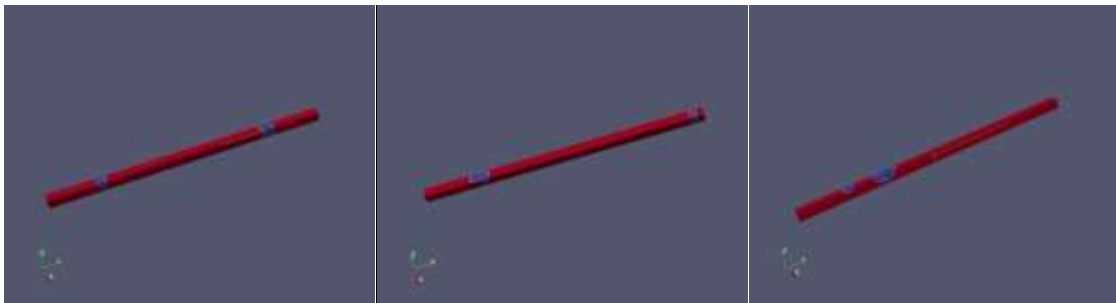


Figure 1. Liquid distribution at 0.07 seconds. (red is air and blue is liquid water)

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# Modeling of inductive phenomena at low frequencies in electrochemical impedance spectroscopy of PEM fuel cell

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Inductive phenomena at low frequencies have been already noticed in the results of electrochemical impedance spectroscopy (EIS) of proton exchange membrane (PEM) fuel cells [1] as an additional loop crossing on the positive side of the Im($Z$) axis in the Nyquist plot, Fig. 1. In literature, two generalized explanations with their variations have been imposed as possible causes of inductive phenomena at low frequencies: side reactions with intermediate species and water transport characteristics [1]. Additionally, carbon monoxide poisoning can also be a cause when reactant gases are not used rated ultrapure [1]. However, different interpretations and diverse models of this phenomena have given us a new motivation to use EIS for a better

understanding and identification of inductive loop processes, which are obviously occurring within the fuel cell, but are apparently still missing. In this paper, a novel 11-element impedance model with two resonant loops, shown in Fig. 2 [2], has been validated via detailed EIS measurements at different current densities, cell temperatures, gas humidities, air flow stoichiometries and backpressures. The simulation results show very good agreement with those from the experimental measurement data, including the low-frequency capacitive loop followed by the inductive loop and the trends of changes of the extracted model element values are mainly consistent with the expectations based on their physical interpretation.
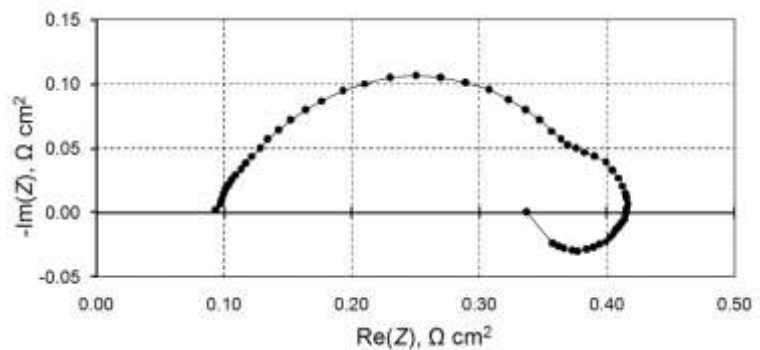


**Figure 1**. Typical Nyquist plot of the measured impedance data of a PEM fuel cell (50 cm$^2$, 65 °C, 0.5 bar(g), 0.3 A cm$^{-2}$, H2/Air stoichiometry 2/4, 100% RH)
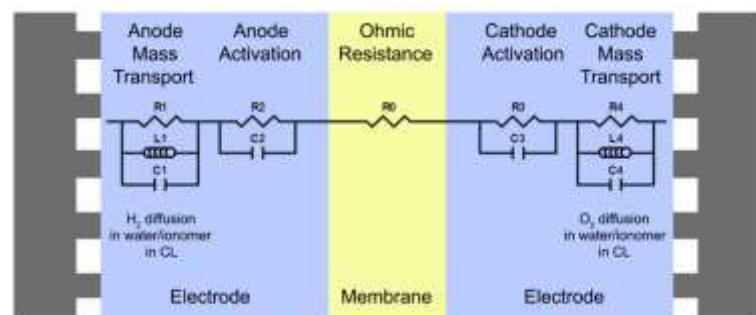


**Figure 2.** A novel 11-element impedance model [2]

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# A multi-physic PEM Electrolyzer code for cell design optimization

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*Keywords*: PEM water electrolysis, modelling

The performance of an electrolyzer highly depends on its key components. Moreover, the physical behaviour of them are strongly coupled: the two-phase flow that takes place in the porous transport layer is strongly coupled with the chemical reactions inside the catalyst layers which brings the water and evacuates the gases) and with the water flow through membrane, temperature strongly influences all the physical and electrochemical phenomena… Thus, the prediction of an electrolyzer's performance is greatly facilitated by the use of a numerical tool, a code, that calculates together all the phenomena which impact the electrochemical answer of a cell. This is why, in the frame of the European project MEGASTACK, an original multiphysics code for PEM electrolyzer has been developed at CEA.

The code has been developed on the bond-graph approach in the Matlab/Simulink platform. It calculates the two-phase flows in the components of the elementary cell such as the distributors, the PTL and through the membrane. The cell components can be nodalized in 2D along the cell surface and in 1D through it, giving access to the local variations of the mean quantities such as temperatures, pressures and thus activities. An electrochemical law provides the potential as a function of the current, the temperatures and the activities in the active areas. All the physical laws are coupled in order to capture the physical coupling between electrochemistry, heat transfer and gas and liquid flows.

The physical and electrochemical laws used in the code have been developed based on the results of an important experimental work. For example, ex-situ studies have given electric resistances and porous transport layer properties, in-situ experiments have provided EIS and polarization curves at various operating conditions that have been used to develop an electrochemical law.

The first simulation results obtained have been successfully validated against polarization curves as illustrated below.
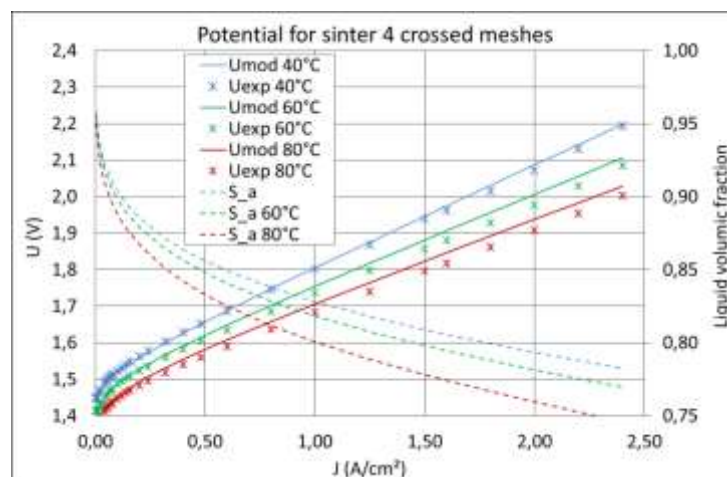


*Polarization curves (left scale): measurements (Uexp) and simulation (Umod). Liquid fraction in the anodic electrode (S_a, right scale).*

# Enhanced ORR Electrocatalysts Through Electronic Metal-Support Interactions between Pt and Boron Carbide

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Supported catalyst technologies are key for achieving economically viable precious metal loadings in PEMFCs. High surface area carbons are commonly employed as support material due to low cost and reasonable stability under harsh, strongly acidic, conditions. However, PEMFCs using this technology achieve only 50% of the lifetime required by the US DOE's target[1] with the oxidation of carbon supports at the cathode identified as a major lifetime limitation during typical load cycles[2]. Significant emphasis has been placed on increasing the activity of supported cathode catalysts and preventing the loss of catalyst surface area due to support corrosion during automotive use[3,4]. Research currently focuses on less defective allotropes of carbon, transition metal oxides and carbides as substitutes for high surface area carbons.

Boron carbide (BC) is an attractive alternative to high surface area carbons. This refractory compound[5] exhibits high chemical inertness[5,6] and electrochemical stability[7,8]. BC has, however, not yet attracted substantial interest within the fuel cell community.

Using standard deposition techniques, we have catalysed high surface area BC powders with Pt nano-particles and characterised them for ORR activity and stability. Electrochemical characterisation includes ORR activity as assessed by RDE measurements and durability testing in aqueous electrolyte.

RDE measurements provide evidence that Pt@BC shows roughly twice the activity towards ORR at high potentials when compared to Pt@C, whilst simultaneously showing significantly improved cycle stability within the operational voltage window of a PEMFC.



Figure 1: ORR Tafel plots

Advanced x-ray characterisation (XANES, EXAFS, XPS) and supporting DFT calculations were utilised to further elucidate the increase in ORR activity for Pt@BC. EXAFS measurements confirmed that the morphology of Pt@BC is similar to Pt@C, while XPS unveiled a relative shift between C 1s and Pt 4f core levels, which indicates a stronger dipole interaction between catalyst and support. Changes in electronic equilibration between catalyst and support might lead to different surface charge on the nano-particulate Pt catalysts with beneficial implications for activity and stability.
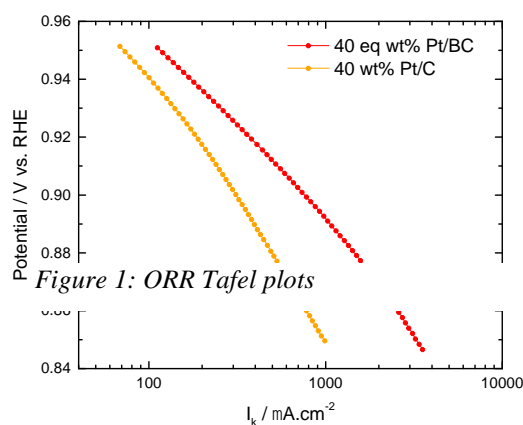
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# CFD Modelling as a Validated Tool to Understand and Develop PEMFCs

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Advanced CFD techniques can serve as very valuable tool both in the design phase of PEMFC development and to understand processes within the cell which are not easily accessible by experimental methods. Specifically full-cell simulation approaches provide high explanatory power because they aim to represent the physically relevant processes within the cell as far as possible. The phenomena covered by the models range e.g. from the electrochemical reactions or proton conduction in the membrane to the heat, gas and electron transport processes through the porous media and the flowfields (e.g. [1]). Furthermore, specific problems as e.g. the minimum pressure difference over the flowfield needed for proper condensate removal can be tackled by particular models, e.g. appropriate for two-phase flow. Nevertheless, these models are still numerically and computationally demanding and their general applicability can be challenged.

Thus, in this work we present full-cell modelling results obtained for a large (100 cm²) active area cell design which is relevant for application and illustrate how these results can contribute to understand cell behaviour and thus help to systematically improve the cell design. Furthermore, we will demonstrate how sophisticated experimental techniques as neutron imaging or current scan shunt measurements can be applied to validate the simulation results obtained.
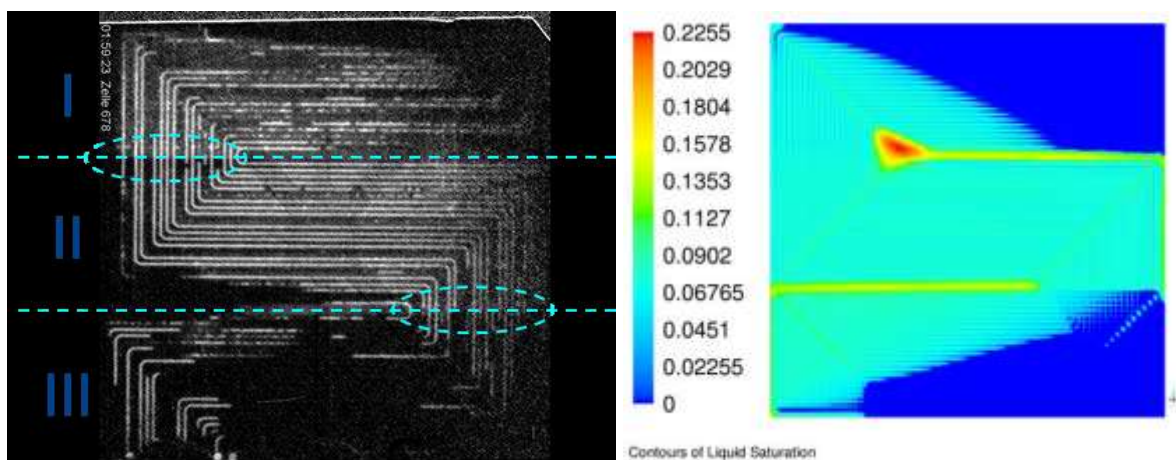


*Figure 2: Comparison of neutron imaging (left) and contours of liquid saturation for the anode GDL substrate from CFD simulations (right).*

References:
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# Stability Issues for Three Dimensional Fuel Cell Models

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The authors are developing generic open source fuel cell models. Originally applied to solid oxide fuel cells (SOFCs) and subsequently high temperature polymer electrolyte fuel cells (PEFCs), the current focus is low temperature PEFCs. The method is based on the solution of the Nernst, Kirchhoff-Ohm, and Butler-Volmer equations together with species, momentum, and energy balances. Depending on fuel cell type, numerical instabilities can occur in models at high current densities, and at low current densities if activation losses are large. However, in a mathematical idealisation of a fuel cell, it should be possible to transition from open circuit, $V = E$, to short circuit, $V = 0$.

At high current density, the local mass fraction, $y_i$ (the subscript $i$ denotes individual reactant/product species, $H_2$, $O_2$, $H_2O$ etc.) can approach but never reach zero, resulting in a mass transport limitation. Whether this occurs depends on geometry, transport and kinetic properties, flow conditions etc. Species boundary conditions/source terms are obtained [1] by summing products of the individual species mass fluxes, $\dot{m}_i''$, and mass fractions, $y_i$, to obtain the diffusion fluxes, $j_i''$, at the electrodes which are prescribed as unbounded fixed-flux Von Neumann conditions with cross-species terms. Computational fluid dynamics (CFD) codes typically restrict mass fraction values to be greater than a small number. This is not always sufficient to avoid oscillations and divergence. Other stability issues are associated with the highly non-linear nature of the Nernst and Butler-Volmer equations.

Four numerical techniques were employed to achieve unconditional stability; (i) Relax the calculation for current density, for example, $i'' = (1 - \alpha) i''_{old} + \alpha i''_{new}$.

(ii) The theoretical 'ideal' Nernst potential can become small or even negative. It is unlikely this would happen in a real fuel cell, therefore limit the solution so that $E \geq V$, always.

(iii) Write the species boundary as a linear (Robin) condition $j_i'' = \dot{m}'' (y_T - y_i)$. The value, $y_T$, is the transferred substance state [2] and the problem is now bounded. The coefficient, $\dot{m}''$, is just the net mass flux based on mixture velocity, and now there are no unnecessary cross-terms in the individual species equations.

(iv) Limit the mass flux at the electrode, $\dot{m}'' \leq \dot{m}''_{lim}$, so $y_i$ can never become zero or negative.

A previously considered geometry [1] was employed for both SOFC and PEFC. The fuel and air inlet velocities were adjusted to obtain a desired stoichiometric number. By employing the above 'best practices', it is possible to operate a 3-D CFD fuel cell model from open circuit to short circuit, and obtain a complete polarization curve, thereby correcting the limitations of previous models, for all current densities.

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# First principles calculations of perovskite cathode materials for protonic ceramic fuel cells

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Amongst ceramic fuel cells, protonic ceramic fuel cells (PCFC) attract growing interest. Proton-conducting ceramic electrolytes offer a higher ionic conductivity compared to standard zirconia or ceria oxide ion conductors, in particular at intermediate temperatures of 300-600°C. The two main limiting factors are (i) the manufacturing of a dense, thin electrolyte membrane with non-blocking grain boundaries, and (ii) finding optimum cathode materials for application on a proton-conducting electrolyte. For cathodes on oxide ion conducting electrolytes, it has been shown that the cathode should be conducting for oxide ions to allow the oxygen reduction reaction to extend beyond the gas/cathode/electrolyte three-phase (and that furthermore a high vacancy concentration and mobility is also beneficial for a fast surface reaction [1]). Analogously, for PCFC the cathode should exhibit a certain proton concentration and corresponding proton conductivity. So far, proton concentrations were reported only for few cathode materials such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (BSFZ [2]). These proton concentrations were found to be about one order of magnitude smaller than for electrolyte materials such as $BaZr_{1-x}Y_xO_{3-x/2}$ under comparable conditions.

In the present study, we performed first principles calculations (CRYSTAL14 computer code with hybrid functional [3]) for nonstoichiometric $La_{1-x}Sr_xFeO_{3-\delta}$ (LSF) [4] and $Ba_{1-x}Sr_xFeO_{3-\delta}$ (BSF) as a potential PCFC cathode material, with and without protons. These simulations yield detailed information on various possible point defect configurations. This makes it possible to look for correlations of their formation energies with other properties such as ion charges, local coordination, bond lengths etc. This allows us to obtain an atomistic understanding of the key parameters determining proton uptake in PCFC cathode materials. Proton migration and the comparison to proton uptake in other cathode materials will also be discussed.

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# 3D Modeling of HT-PEMFC and Validation on an Industrial Cell

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We present a three dimensional model for a high temperature PEMFC [1]. The fuel cell is modelled in 3D, including bipolar plates, current collector plates and additional cooling channels. The catalyst layer is modelled as a 2D surface, with the electrochemical reaction assumed to occur at the interface membrane/GDL or membrane/MPL.

The ionic conductivity in the membrane, which is typically a PBI (Polybenzimidazole) membrane doped with phosphoric acid, is modelled with an Arrhenius type approach [2]. Gas crossover is considered as a diffusive transport of the dissolved gases in a constant phosphoric acid concentration [2]. We assume that gas and porous solid share the same temperature field, and that water exists only in the gas phase, due to the high operating temperatures.

The model is verified with a single cell from Elcore GmbH [3]. The heating cartridges, which keep the cell at a constant temperature, are modelled with appropriate boundary conditions. Two voltage-current characteristics for pure hydrogen and a reformat are calculated. The exchange current density is calibrated for one operating point. All other operating parameters are either known or taken from literature. The resulting characteristics show a good agreement with the measurement data. Additionally, 3D results will be discussed.

Fig. 1 shows the temperature distribution throughout the single cell at an operating point of 0.6 A/cm$^2$. The heating of the gases, which enter the fuel cell at a much lower temperature than the operating temperature, is observable.

Furthermore, the model has been applied to a fuel cell stack. Some preliminary results will be presented.

Temperature [°C]
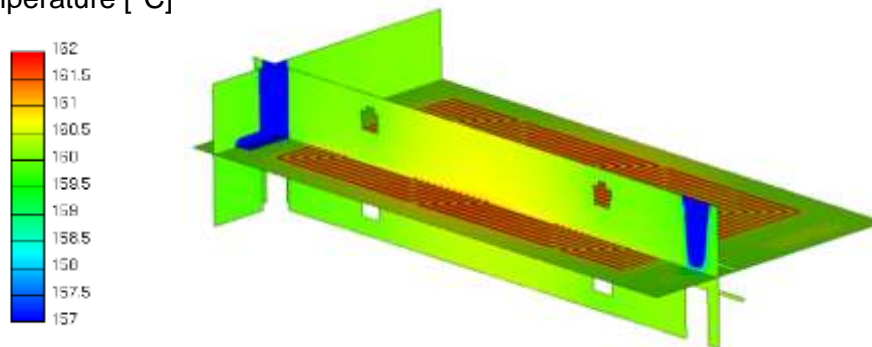


Fig. 1: Temperature distribution of the single cell from Elcore GmbH at 0.6 A/cm$^2$.

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# Homogenized 3D SOC model and validation

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Sunfire develops and produces high-temperature fuel cell (SOFC) and electrolyzer (SOEC) applications. Both processes can be combined in a single device: a reversible Solid Oxide Cell (rSOC) system. With these technologies, sunfire addresses a multitude of challenges in our energy systems. Due to the huge variety of possible operation points, stack tests have become more sophisticated. Therefore, not every operation point can be tested appropriately and simulation becomes more necessary.

Because of this, a SOC model has been developed. A homogenized 3D model approach in Comsol Multiphysics was chosen to ensure a simple and fast, but nevertheless adequate solution. Effective input parameters like heat conductivity, permeability or electric conductivity have been calculated or measured. Since the operation of the stack is heavily depending on the cell resistance, special attention has to be directed to the ASR(T)-curves of the different cells and operating regimes. The measured results of ASR(T) curves for different operation modes will be part of the presentation. An additionally important parameter is the thermal integration of the SOC stack. The local distribution of heat losses has to be considered to ensure proper results.

The presented model offers the possibility to simulate a three dimensional temperature distribution, current density distribution, gas flow distribution and gas composition by also considering the steam-reforming reaction and water-gas-shift reaction in SOFC and SOEC-mode. The model can either be used to solve stationary or time dependent problems to visualize the dynamic behaviour of a SOC stack, e.g. during rSOC cycles. Fig. 1 shows an exemplary temperature distribution of a SOFC stack operated with hydrogen. Comparisons of the temperature distribution and voltages of several SOFC and SOEC points have been used to validate the model and will be shown during the presentation.
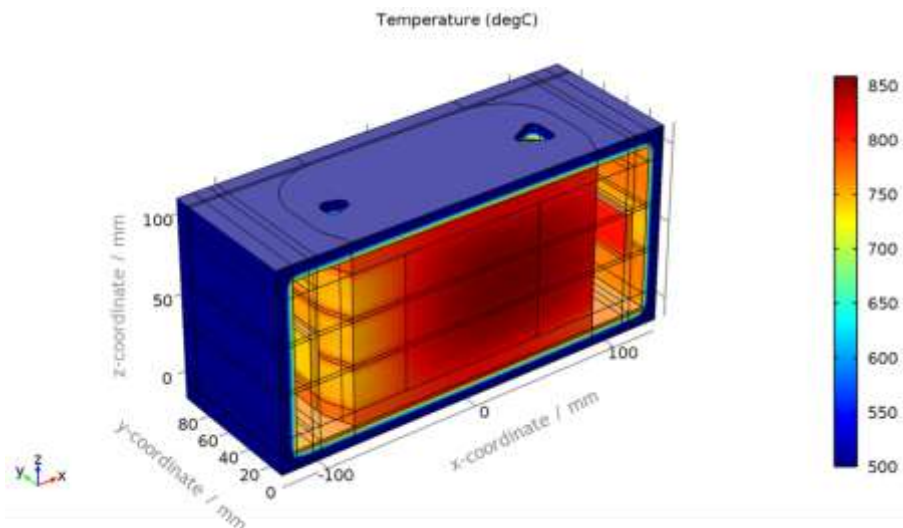


Fig. 1 temperature distribution of a sunfire stack operated with hydrogen

# An Open-source Code for High Temperature Polymer-electrolyte Fuel Cells

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The high temperature polymer electrolyte fuel cell (HT-PEFC) is a device that converts chemical energy to electricity. HT-PEFCs typically operate between 150-180℃, and feature certain advantages such as relatively simple water and heat management, as well as a high tolerance to carbon monoxide (CO). In the field of HT-PEFCs, a number of experimental and computational/numerical studies have been carried out, in the past. For computational work, commercial software suites have generally been employed; no open-source repositories capable of comprehensive, multi-physics, multi-scale calculations in the components of HT-PEFCs have been created, to-date.

An open-source code that allows for simultaneous consideration of flow phenomena in all HT-PEFC parts: membrane electrode assembly, gas diffusion layers, flow channels and bipolar plates is developed, based on a modified form of the previous work of Beale et al.[1]. The general approach is to solve the Darcy-modified Navier Stokes equations for momentum together with continuity (pressure) equations. Fick's/Fourier's laws are used as constitutive laws in the species mass fraction and enthalpy conservation equations. This approach, combined with the solution of the Nernst equation for the local open-circuit potential, the Kirchhoff-Ohm relationship for local current density, and Tafel equation for the activation overpotential, represents a closed system of equations.

Validation and verification is extremely important to understanding the scope and limitations of any model calculations. The authors compare numerical calculations obtained with the present code, with data gathered from physical experiments performed on three HT-PEFC prototypes, each with different flow configurations and active areas, and operating under a variety of current densities. Both polarization curves and current density distributions are compared, to quantify the predictive capability of the present code. Cell voltage predictions are within 27mV of experimental values in the activation and ohmic regions. Deviations in the concentration-overpotential region become somewhat larger, unless a transport limiting term is applied in the model equations. The model current density distribution predictions are also compared with an analytical solution[2] with acceptable agreement. Therefore, it is concluded that the open-source code is capable of performance prediction for HTPEFCs.

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# Concept of 3D Mathematical Modeling of HT PEM FC Stack Degradation and Single Cell Model Experiments

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Despite a rapid increase of performance and accessibility of the computational hardware during last three decades, a mathematical modelling of practical size polymer electrolyte membrane fuel cell (PEM FC) stack represents still a challenging task. It is due to the fact that the FC stack is typical representative of plate-and-frame multiple-layer set-up. Consequently, a detailed three-dimensional (3D) mathematical description of such device requires highly detailed spatial discretization of the system, which is very demanding on the hardware computational power and time. Solution of this problem is, however, highly practically important. Another issue, which has to be resolved, is an extension of this type of the 3D model about phenomena affecting a long-term behaviour and decreasing stability of the stack performance. A utilization of the 3D detailed mathematical model enables not only the prediction of the FC stack live time, but also an identification of local areas in the stack most susceptible to degradation processes.

Within this work a 3D modelling concept based on a volume-averaged (also called macrohomogeneous) approach is presented and used for mathematical modelling of large scale high temperature PEM FC (HT PEM FC) stack consisting of 100 cells [1]. An effect of basic types of flow-field geometry on a non-uniformity of distribution of various physical quantities is demonstrated. Last, but not least, an application of this 3D mathematical model for a simulation of the FC stack degradation on a local scale is presented. An attention is mainly paid at a degradation of the catalyst layer and decrease of the electrochemically active surface area during the FC stack operation. The model consists of mass balances, material balances and a charge balance. The system of partial differential equations was solved by finite element method in COSMOL Multiphysics environment.

For this purpose, a set of single cell model experiments was performed to provide necessary input data for the 3D mathematical modeling of HT PEM FC stack degradation. A single HT PEM fuel cell was polarized by constant voltage. Different values of the cell voltage and duration of the polarization test were studied. A Pt-based catalyst particle size distribution and electrochemically active surface was determined at the beginning and at the end of the experiment. A mechanisms and rate of the of the catalyst degradation are analysed and implemented into the model.

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# Physics-based Model for PEMFCs: Process Identification from EIS Simulation

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Within our new modeling framework called NEOPARD-FC we aim to develop a predictive, macroscopic fuel cell model which is able to describe the cell behavior under different conditions (e.g. temperatures, pressures, relative humidities,…). The model allows transient simulations in 2D or 3D taking into account electrochemical reactions, detailed membrane transport, gas cross-over, multiphase-flow in the porous domains, proton-, electron- and heat transport. The half-cell reactions are modeled with Butler-Volmer-kinetics in combination with an agglomerate model describing the oxygen transport to the active sites. Additionally, the formation of platinum oxides on the electrochemical active surface is considered.

A valuable tool for model validation, apart from polarization curve simulations, is the simulation of electrochemical impedance spectra (EIS). Based on the potential step method [1] the model is able to quickly simulate EIS over a large frequency range, which allows the detailed analysis of processes governing the cell performance.

Experiments often show a significant gap between the total cell resistance measured by EIS and obtained from polarization curves (Fig. 1). In a recent review [2], possible explanations for the occurrence of inductive features in the impedance spectra of PEMFCs at low frequencies (~0.01Hz) are discussed. However, the discussion is restricted to equivalent circuit models missing a clearly defined physical meaning. Our physical fuel cell model, allows inspection of the electrode processes giving new insights into the performance of a fuel cell. New explanations for the occurrence of the inductive feature will be discussed.
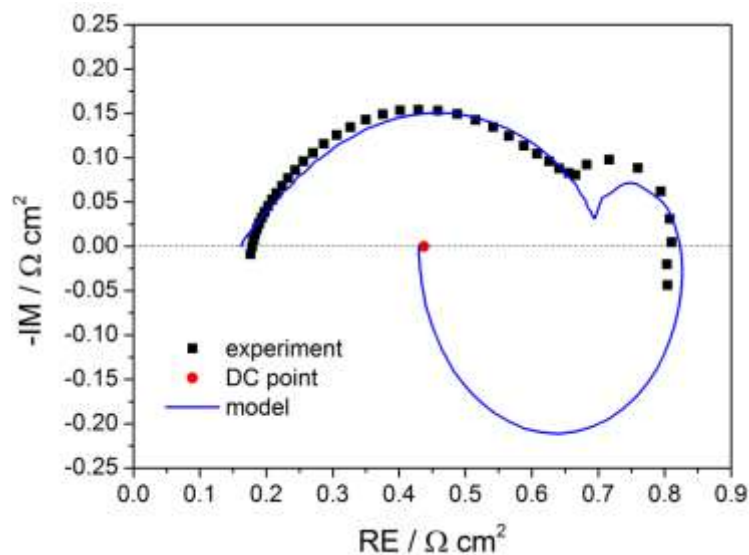


Fig. 1: Nyquist plot of an impedance spectrum at low relative humidity. The red dot denotes the total cell resistance obtained from the slope of the polarization curve

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# Water Phenomena in PEFC Catalyst Layers as the Origin of the Pt Loading Effect: A Modelling Study

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The foremost objective of research on polymer electrolyte fuel cells is to design and fabricate catalyst layers with high performance at drastically reduced platinum loading. Achieving this objective demands an understanding of the impact of composition and porous structure on the water balance in the layer [1–3]. Experimental studies have shown a marked increase in the resistance to oxygen diffusion when the Pt content and, correspondingly, the thickness of the catalyst layer were lowered [4–6]. We present a water balance model to explain these trends. Figure 1 illustrates the modeling domain and the processes considered. The set of 1D continuity and flux equations is formulated and solved for the liquid water pressure, vapor pressure, oxygen pressure, liquid water flux and vapor flux. Model solutions reveal the impact of composition, porous structure, and operating conditions on the aforementioned properties. Reducing the Pt loading (i.e. reducing the catalyst layer thickness) results in lowering of the liquid to vapor interfacial area and hence the vaporization capability. Liquid water builds up at the interface of catalyst layer and diffusion medium resulting in poor oxygen diffusivity. Findings of these model should be considered in the efforts to design and fabricate advanced catalyst layers and diffusion media with improved performance.
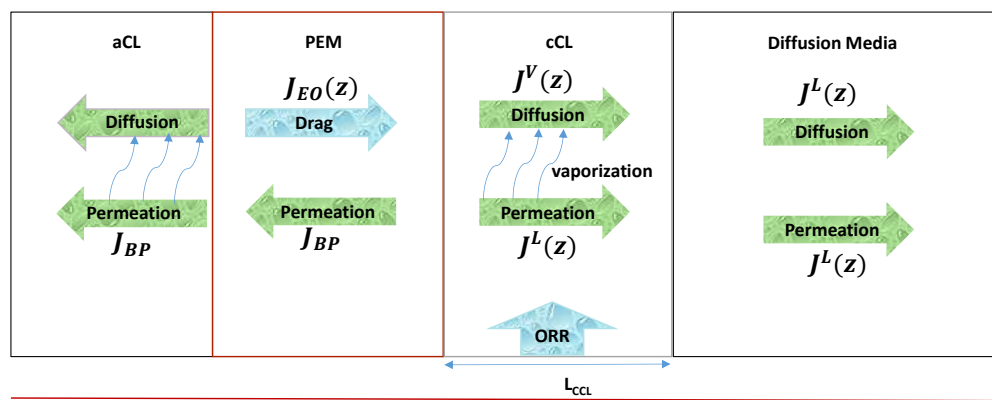


**Figure 3.** Schematic diagram of modelling domain and processes considered

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# Mathematical Modelling of Hydrogen Nanobubbles in PEM Electrolysers

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We present a mathematical model for nanobubbles arising from the hydrogen electrolysis in polymer electrolyte membranes (PEM). Near the cathode of the PEM electrolyser in operation hydrogen nanobubbles emerge in protonated water. At first surface nanobubbles in the form of spherical caps are generated that may finally detach and become spherical bulk nanobubbles. These nanobubbles may grow and shrink with time. On one hand this is due to the inflow of electrons into water at the cathode producing hydrogen, on the other hand the surface tension enhances the dissolution of the bubbles. Experiments show that these nanobubbles have a longevity that cannot be explained by classical theory. In the context of electrolysis the generation of large meta-stable surface nanobubbles is an undesired effect.
In our model surface and bulk nanobubbles may be both parametrized by their radii. Assuming a dynamical equilibrium this yields a coupled system consisting of a partial differential equation (PDE), namely an advection-diffusion equation for the hydrogen concentration in water, ordinary differential equations (ODE) for the radii evolution and an algebraic equation for the total conservation of hydrogen. We consider a steady-state model for a single bubble [1] and a many bubbles model, using a mean field approach [2].
For the single bubble model, we consider dynamic equilibria numerically. The coupled ODEPDE problem is solved by a fixed-point algorithm. For the many bubbles model [1], we derive macroscopic evolution equations by formal homogenization techniques exploiting typical scales. The resulting large dynamical systems are simulated. In our numerics, we have to pay attention to the unknown times when bubbles dissolve. Our results exhibit an interplay between surface and bulk nanobubbles similar to Ostwald ripening, where larger bubbles grow at the expense of smaller bubbles that eventually disappear. A problem with a similar mathematical structure applied to precipitation in galliumarsenide semiconductors has been modelled, analyzed and solved in [3].
Furthermore, we compute values for typical lifetimes of bubbles [2]. Our results indicate that the experimentally observed meta-stability of nanobubbles may be explained by interaction effects between many nanobubbles, surface as well as bulk nanobubbles.
The mathematical model and the single bubble problem [2] is joint work with Knut Sverstrup (U Cambridge, Cambridge, United Kingdom) and Peter Berg (U Alberta, Camrose, Canada).

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# Influence of pore-scale material properties on the performance of proton exchange membrane fuel cells

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We are working on the model-based characterization of porous layers used in proton exchange membrane fuel cells (PEFCs): the 3D morphology at different compression levels is acquired by X-ray tomographic microscopy. 3D-image analysis is performed to obtain the topological details of pores, fibres and binders in the GDL.

The microstructure characteristics of the porous layers are analyzed; this includes phase volume fractions, geodesic tortuosity, constrictivity and hydraulic radius. The latter two parameters include information from two different size distributions for bulges (continuous PSD) and for bottlenecks (MIP-PSD). Micro-macro-relationships are established for the in-plane and through-plane directions. Moreover, we extract new effective material transport parameters (diffusivity, permeability and conductivity). These relationships serve as input for macrohomogenous modeling to simulate microstructure effects of real GDLs.

We are developing macrohomogeneous models of PEFCs that take into account the liquid water and its influence on the cell performance. The main challenge is to predict the liquid water distribution and its effect on the transport processes at different operating conditions of the fuel cell. Appropriate boundary conditions and coupling conditions between the porous materials need to be used, e.g. the release of liquid water droplets to the gas channel need to be taken into account to improve the predictive power of the models.

For example, we established a macrohomogeneous model of a PEFC that takes into account the mechanical compression of the GDL, the two-phase flow of water, the transport of the gas species and the electrochemical reactions. Water removal of GDLs towards the flow-field is investigated to guarantee access of the gases to the electrodes under wet conditions. A new GDL design is simulated that includes a succession of hydrophobic and hydrophilic regions. This design is first characterized experimentally by measuring the local saturation as a function of the capillary pressure. Neutron radiography was used as imaging technique, allowing for quantification of the water thickness. The macrohomogeneous model confirms that the patterned GDL design liberates the pre-defined domains from liquid water and thus locally increases the oxygen diffusivity.
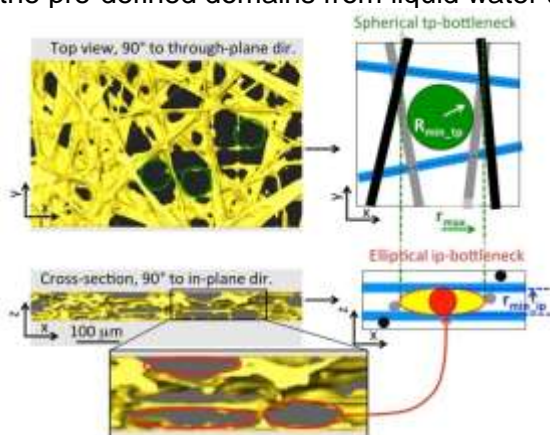


Fig. 1: Shape of the through-plane and in-plane bottlenecks in a gas diffusion layer (SGL 25 BA).
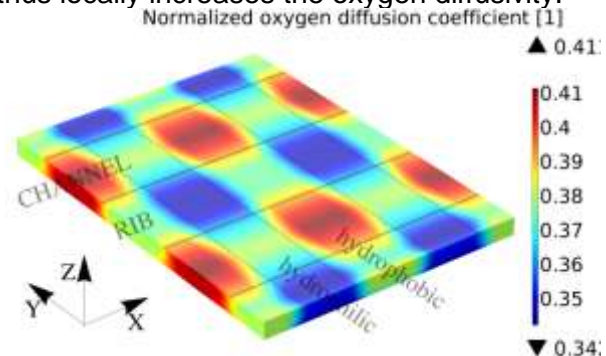
Fig. 2: Simulated distribution of the normalized oxygen diffusion coefficient in a patterned GDL.

# Towards Patterned Wettability in Gas Diffusion Media for PEFCs

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Polymer electrolyte fuel cells (PEFCs) require a well-balanced water management in order to have an efficient performance. The humidity needs of the polymer membrane must be satisfied without having liquid water blocking the access of the reactant gases to the catalyst. This process mainly takes place through the gas diffusion media (GDM), which is a highly porous network made of carbon fibers and a fluoropolymer coating, named gas diffusion layer (GDL), and a soft layer made of carbon particles and fluoropolymer, called microporous layer (MPL).

Our group has studied and developed a new method of enhancing water management in PEFCs by employing modified GDLs with patterned wettability. Using electron induced radiation grafting on the coating we are able to create hydrophilic regions which act as preferential pathways for water. Due to the partial separation between the gas and water pathways throughout the GDL, the fuel cell performance improves compared to the unmodified material [1,2]. Now we focus on further developing this modification and analyse its effect when incorporating a MPL.

In this presentation we will discuss the synthesis of an MPL which is well-performing and can withstand our modification. Also we will analyse selectively altering the GDL region, and not the MPL, by tuning the energy of the electrons used for activating the grafting. This method will be evaluated by electron energy simulations and experimental data that correlate the radiation dose with the penetration depth [3].
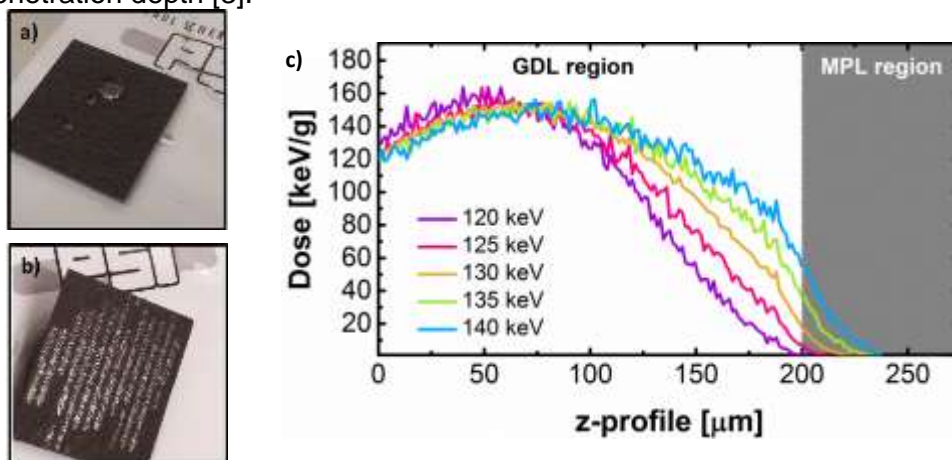


**Figure.** *Optical image comparing the interaction with water of, a) an unmodified GDL and, b) a GDL with patterned wettability. c) Simulation data for the Dose distribution along the GDM thickness for different electron energies.*

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# Large scale first principles modeling of non-stoichiometric complex perovskites for fuel cell applications

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Two types of ABO3-type perovskite solid solutions (BSCF: $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and LSCF: $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$), mixed ionic – electronic conductors, continue to attract a lot of attention because of a wide range of potential applications in modern technologies, e.g. gas separation membranes, solid oxide fuel cells (SOFC), etc [1,2]. The structural defects, first of all oxygen vacancies and antisite defects in perovskites, affect many properties and affect performance of the perovskite materials in specific applications.

In this talk, we present the results of first principles large scale computer calculations of defective BSCF and LSCF and thermodynamic stability of the cubic phase under different conditions [3,4]. We explored and analyzed in great detail the oxygen vacancy formation energies in the cubic and hexagonal phases of BSCF and demonstrated that a high concentration of vacancies (oxygen non-stoichiometry), in fact, serves as a stabilizing factor that governs the preference of the cubic phase over the hexagonal phase. We also discuss peculiarities of the oxygen vacancy diffusion in BSCF and LSCF. We observed considerable charge transfer between a jumping oxygen ion and B-type cation in the transition state of diffusion which is the main reason for the unusually low oxygen migration energy in BSCF [5]. The smaller size mismatch between A- and B-site cations in LSCF results in twice higher vacancy formation energy and higher migration activation barrier, which give rise to a smaller oxygen vacancy concentration and thus a slower oxygen exchange reaction, as compared to BSCF.

Based on the above-discussed results of first principles calculations of the defect formation and migration energies, as well as oxygen atom and molecule adsorption on perovskite surfaces, we calculated the diffusion-controlled kinetics of oxygen reduction reaction (ORR) as a function of adsorbed oxygen and surface vacancy concentrations [6].  This allowed us to determine the rate-determining steps (which is important for improvement of fuel cell and permeation membrane performances) and suggest interpretation of available experimental data. Special attention is paid to the role of surface termination in the ORR rate.

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# Cathodic carbon corrosion: from a 1D-model to a full 2D-model

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During startup and shutdown, carbon corrosion is identified as one of the most important phenomena of degradation inside the MEA of PEMFC [1][2]. We have developed a 1D through-thickness MEA model able to simulate startups and to observe the reverse-current mechanism [3], based on the carbon corrosion and platinum oxidation kinetics [4]. Mass transport in the porous media (GDL, MPL, CL) is described using a multi-component convective-diffusive model [5]. The model also takes into account proton and electron transport, water transport in the ionomer (CL and membrane), and gases permeation through the membrane. The local electrochemical response inside the CL is computed by implementing both ORR and HOR in both electrodes. Local mixed- potential then results from an equilibrium between the different reactions, including carbon corrosion.

Figure 1 shows the electronic and protonic potentials in the MEA at 1V under air/air operating conditions. An electrode potential of 1.6V appears at the positive electrode, leading to carbon corrosion and $CO_2$ production (Figure 2). Experiments are on-going to validate the model by measuring this $CO_2$ production. In parallel, a 2D along the channel cell model is under development in order to simulate the transient hydrogen-air front propagation and its impact on local ionic potential in the cell.
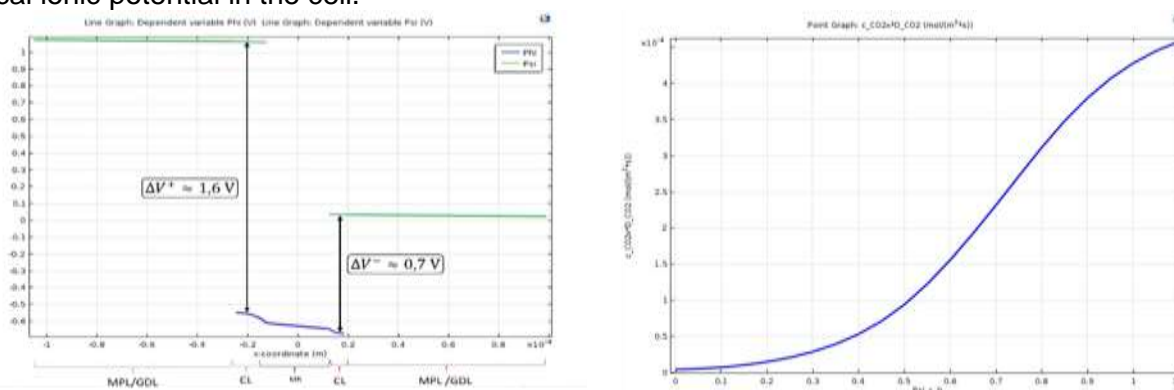
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# Secondary Phases at Cathode/Electrolyte Interfaces

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Understanding the nature of a cathode/electrolyte interface in solid oxide fuel cells (SOFC) is still a challenge, especially if this interface is composed of a mixed conducting cathode, i.e., $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), and a bilayer electrolyte, i.e., Gd-doped Ceria (GDC) interlayer and $Y_2O_3$ stabilized $ZrO_2$ (YSZ) electrolyte. The interface resistance can vary over more than two orders of magnitude [1], resulting from variable volume and local distribution of the poorly ionic conducting secondary phase $SrZrO_3$ (SZO) [2] and GDC-YSZ interdiffusion (ID) [3].

This contribution will introduce a *COMSOL Multiphysics* model, which simulates the performance characteristics of such heterogeneous cathode/electrolyte interfaces. The model is based on 3D-reconstruction data of an interface region, which was characterized (i) electrically by in-situ electrochemical impedance spectroscopy and (ii) by ex-situ elemental analysis using STEM/EDXS. Our model calculations quantify the contributions of both secondary phases, SZO and ID to the cathodic polarization resistance, but also a contribution of ID to the ohmic resistance, corresponding well to the performance measurements. Our results further reveal that interface morphology, i.e. volume and local distribution of secondary phases, plays a significant role. When GDC is sintered at high temperatures (see Fig.1 at 1300°C) to a continuous and dense ID layer (green color),  SZO formation is still significant (turquoise color), but a comparatively small area of "free" pathways for oxygen ions from LSCF→GDC→ID→YSZ can reduce the polarization resistance up to two orders of magnitude. On the contrary; when GDC is sintered at lower temperatures, a much thicker and continuous SZO layer blocks the diffusion of oxygen ions, corresponding to the highest polarization resistance.
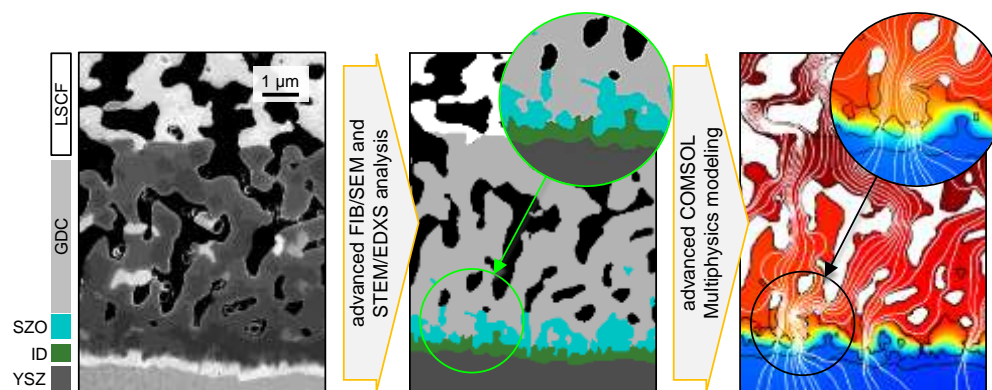


**Figure 1** *Cathode/electrolyte interface made of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), Gd-doped Ceria (GDC) and $Y_2O_3$ stabilized $ZrO_2$ (YSZ) after sintering GDC at 1300°C: FIB/SEM image (left), 3D-reconstructed and phase assigned image (middle) and visualization  of potential and current distribution (right) using a COMSOL Multiphysics model.*

The results of this contribution are fundamental for understanding the microstructure characteristics of secondary phases and their correlation to SOFC performance. They convey intuitive knowledge to fabricate high performance cathode/electrolyte interfaces for individual cell concepts.

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# Evaporation of water from gas diffusion layers

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On the one hand, evaporation of water from gas diffusion layers (GDL) is an important process for water management in polymer electrolyte fuel cells. At temperatures around 80 °C and locally under-saturated conditions, evaporation can have a significant impact on the GDL saturation. On the other hand evaporation from the GDL can also be engineered for evaporative cooling of the cell, such that the endothermic heat flux of the evaporation matches the exothermic flux stemming from the losses in the cell.

However, only little is known about the evaporation rates of water in gas diffusion layers. First results at room temperature and for low saturations have been reported in [1]. But for a better understanding of the evaporation rates under real operating temperatures, as well as for optimization of the evaporative cooling configuration, generic data is required at different temperatures and saturation levels.

Using a special set-up, which is applicable for X-ray imaging of the water saturation, water surface and GDL structure, evaporation rates are determined for different gas speeds (over the surface of the GDL) at temperatures of up to 80 °C and at relevant liquid saturations. Figure 1 shows data (including reproducibility) for Toray TGPH 060 material as function of temperature up to 80 °C, at a liquid saturation pressure of 10 mbar and gas velocity of 6 m/s.
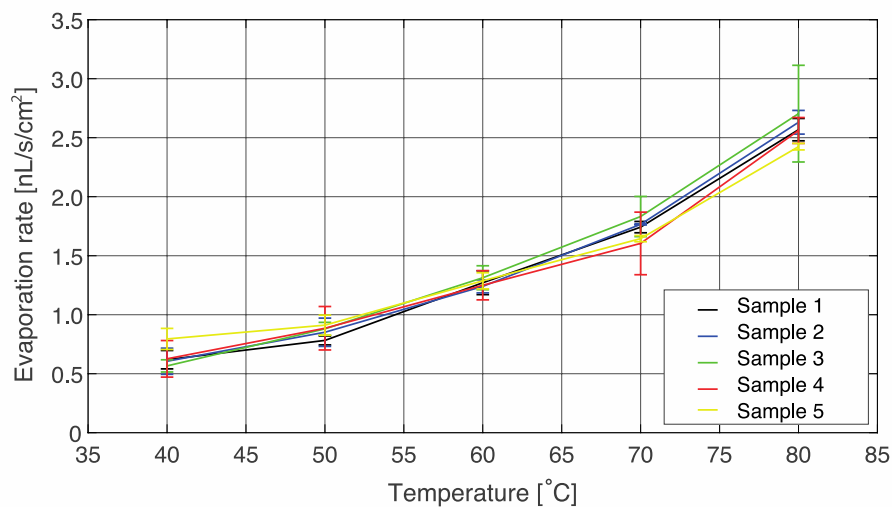


Figure 1: Evaporation rates from Toray TGPH 060 gas diffusion layer material as function of temperature at a water capillary pressure of 10 mbar and gas velocity of 6.0 m/s.

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# Parameter estimation of the elastic and creep properties of Ni-YSZ anode based on four-point bending measurements

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Thermo-mechanical issues in solid oxide fuel cells (SOFCs) must be understood and overcome to meet the reliability standards for market implementation. Attempts have been made to investigate the mechanical failures of SOFCs experimentally. Thermo-mechanical characterization by numerical analysis is relevant to post-process measurements from targeted experiments and/or for the detailed analysis of SOFC stack design. In this context, the measurement of the mechanical properties of the component materials is essential for the models. Ceramics are extensively used in SOFC stacks. The characterization of their mechanical properties requires specific precautions because of their brittleness: three/four-point bending, ring-on-ring (ROR), ball-on-ring (BOR) and ball-on-3-balls setups are widely used.

This study is focused on the four-point bending test design, which has several advantages. However, intrinsic errors, such as the friction between the sample and the rollers, anticlastic curvature, contact point shift and large deflection should be considered when analysing the experimental data obtained from this testing design. Analytical solutions used for post-processing do typically not account for these phenomena, affecting the accuracy of the measurements. Further, procedures based upon analytical solutions are available for the analysis of the secondary creep regime, but not for estimating primary creep parameters. Numerical model-based methods are required to overcome these limitations.

In this study, the model is a 3-D finite-element (FE) continuum model of the sample together with the testing fixture of the four-point bending setup. The experimental data are obtained by mechanical testing of Ni-YSZ anode samples. A metamodel approach has been developed to reduce the computation time of the parameter estimations. The workflow starts with a sensitivity analysis with the FE model to create a distributed metamodel of the four-point bending responses during elastic and creep testing. The discretization is here either the displacement at the inner roller or the time for the measurement of the elastic and creep properties, respectively. The optimisation problem is then solved using the metamodel, to identify the parameter values that minimize the discrepancy between the experimental data and the simulated responses.

The developed identification workflow is used to estimate firstly the elastic modulus and the friction coefficient between the sample and the testing fixture of the four-point bending setup, and secondly the primary and secondary creep parameters together. The robustness is tested using a set of numerical experiments and a variety of optimisation starting points. The measured elastic properties are then compared with results from 3-D imaging and computational homogenization. The experimental data from testing at room and high temperature is then analysed.

# Quantification of Ni coarsening in infiltrated SOFC anodes by combining 3D tomography, impedance spectroscopy and mechanistic modelling

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Nickel coarsening is one the main degradation mechanisms that affect the lifetime of solid oxide fuel cell (SOFC) anodes. In this study we present an integrated experimental/modelling approach to quantify the effect of the Ni microstructural evolution on the electrochemical performance of infiltrated anodes.

Symmetric cells made of a scaffold of scandia-stabilised zirconia (ScSZ) impregnated with different volume fractions of Ni were produced and annealed at constant temperature while recording the impedance every 30 mins. The microstructure of the fresh and degraded samples was reconstructed with focused ion beam SEM tomography and analysed to quantify the change in three-phase boundary (TPB) density, Ni percolation and Ni particle size upon annealing. A physically-based electrochemical model, based on conservation equations, was used to link the microstructural degradation to the evolution of impedance spectra. The model was able to decouple the microstructural contribution of Ni coarsening in impedance spectra and to interpolate the TPB density change with time, thus linking the microstructural evolution due to Ni coarsening to the increase in polarisation resistance.

The analysis reveals a high coarsening rate in the first few hours of annealing. The degradation gradually slows down and a stable polarization resistance is approached, provided that a sufficient volume fraction of Ni is present to guarantee electronic percolation. On the contrary, an insufficient Ni volume fraction causes a gradual decrease in Ni percolation, resulting in a dramatic reduction in current collection with corresponding increase in polarization and ohmic resistance. Thus, the combination of mechanistic modelling and 3D tomographic analysis allow for an insight into the mechanisms that control Ni coarsening in infiltrated SOFC electrodes.
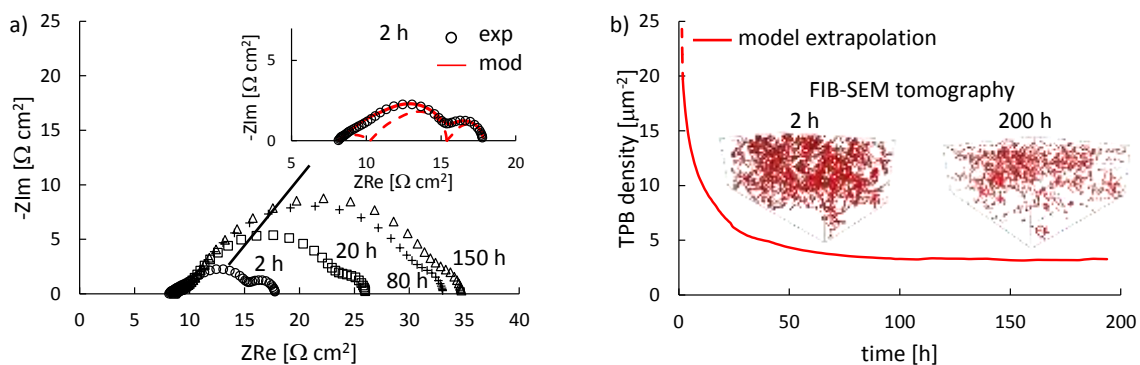


*Figure 1 – a) Impedance spectra of a symmetric infiltrated Ni:ScSZ anode as a function of time during annealing. The inset shows the fitting and deconvolution according to the mechanistic model. b) Extrapolation of TPB density vs time from impedance spectra according to the model. The insets show the rendering of TPB by using 3D tomography.*

# A model for analysis of the porous nickel electrode polarization in the molten carbonate electrolysis cell

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A promising option for producing hydrogen and/or syngas is by water electrolysis and/or co-electrolysis of water and carbon dioxide using the molten carbonate electrolysis cell (MCEC).

The molten carbonate electrolysis cell operates at high temperatures, 600–700 °C, which gives the potential to attain high overall efficiency and to require low applied voltage. Previous studies in our lab [1] proved that it is feasible to operate the molten carbonate electrolysis cell using the corresponding fuel cell (MCFC) catalysts, i.e., nickel-based porous electrodes. Moreover, lower polarization losses were found for the electrolysis cell than for the fuel cell, and the electrolysis cell also showed good durability in the long-term test using a conventional fuel cell setup [2]. The molten carbonate fuel cell is already commercially available and the possibility of operating both the electrolysis cell for fuel gas production and the fuel cell for electricity generation in a single device may be beneficial from an economic perspective.

In this study a one-dimensional model for the Ni electrode of a MCEC based on the Maxwell-Stefan transport equations was fitted using the method of least squares to steady state polarization data for various inlet gas compositions of $H_2O$, $CO_2$ and $H_2$ between 10 and 40%. Two separate sets of model parameters were fitted: for when including and not including the water gas shift reaction (WGSR) in the model. In both cases it was possible to get a good fit to the experimental data, but including the WGSR it gave a significantly lower value of the global least squares objective function, and a somewhat more reasonable estimate of the gas phase porosity.
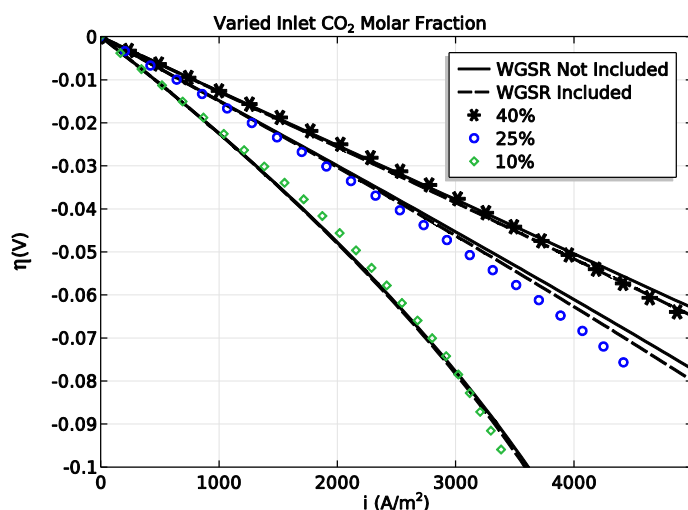


*Experimental polarization curves for varied inlet CO2 molar fractions, and corresponding modelling results, both for including and not including the water gas shift reaction (WGSR)*

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# Microstructure Modelling of Porous Cathodes for Solid Oxide Fuel Cells (SOFCs)

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Microstructure modeling of porous electrodes for solid oxide fuel cells (SOFCs) has rapidly developed over the last years. Advanced imaging techniques such as focused ion beam/scanning electron microscopy (FIB/SEM) tomography support this progress by enabling 3D reconstructions of µm- and sub-µm-scaled multiphase electrodes [1,2]. From these reconstructions microstructural parameters can be determined which form the basis for calculating electrode performance via homogenized microstructure models [3,4].

Even more desirable is a direct use the 3D FIB/SEM data in adequate performance models [4]. Therefore a 3D finite element method (FEM) model is presented, which calculates e.g. the area specific resistance (a performance index) of mixed ionic-electronic conducting cathodes by directly using the preprocessed 3D FIB/SEM data. The required size of the reconstructed volume (the



Figure 1: Visualization of the O2- concentration inside the porous cathode, calculated with different material parameters representing the cathode (a) at initial stage and (b) after 1000h of operation.
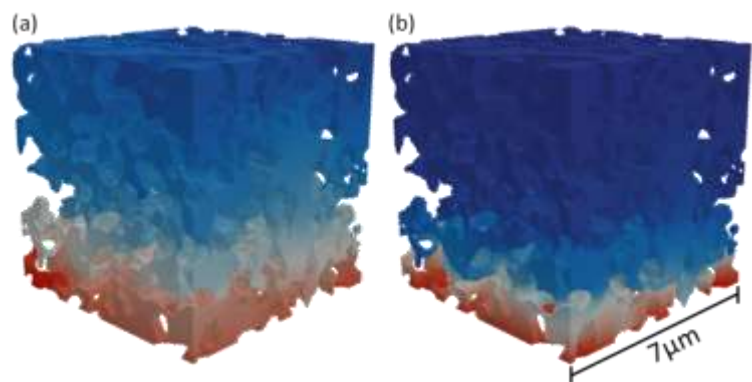
computational domain in the model) and the resolution of the 3D image data are investigated. A too small volume or a not accurately resolved structure leads to untrustworthy results. In contrast, large volumes which are highly resolved demand for high computational effort, notably enormous demands for memory and long computing times.

Model calculations were validated with experimental results obtained by electrochemical impedance spectroscopy. Combining experimental and modeling results is the key to predict cathode characteristics as a function of operating conditions and material configurations and thus enables a well-directed improvement of the SOFC performance.

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# Pore network modelling of phosphoric acid distribution in high temperature PEM fuel cells

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High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) operate at an elevated temperature (160°C). Therefore, Phosphoric Acid (PA) instead of water acts as a proton conductor in the Membrane Electrode Assembly (MEA). Controlling the PA distribution and minimizing its leaching out of the MEA, particularly the electrodes, is key for optimizing performance and extending the lifetime of the HT-PEMFC. In this work, pore network modelling is used to investigate the redistribution of phosphoric acid in the Gas Diffusion Electrode (GDE) of a HT-PEMFC. A GDE composed of a catalyst layer (sprayed in-house), Micro-Porous Layer (MPL), and fibrous substrate (GDL) was prepared [1] and its three-dimensional (3D) geometry was imaged using synchrotron X-ray computed tomography. The spatial distribution of pore spaces and their connections were identified based on the 3D geometry, and an equivalent pore network of the GDE was obtained for simulating the PA transport with an invasion percolation algorithm. The predicted mass redistribution of PA in the GDE is in excellent agreement with experimental values reported in the literature [2]. Our analysis spreads clarity on the role of the MPL in HT-PEMFC: the MPL acts as a barrier, which encourages the accumulation of PA content within the CL while simultaneously inhibiting the leaching of PA towards the channel [3]. The MPL serves in Low Temperature PEMFC an entirely different function, where it aids water management. In the present model, MPL cracks were defined as the only pathways for PA to reach the GDL, and this assumption led to realistic predictions of PA in the GDE. Therefore, we conclude that tuning the distribution and size of MPL cracks is an important design consideration for controlling PA redistribution within the GDE and improving the performance of HT-PEMFCs.

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# Microstructure limitations for relative permeability and liquid drainage in fibrous GDL (PEFC): The importance of the 'short range effect'

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Understanding microstructure-property relationships of fibrous gas diffusion layers (GDL) is an important condition for materials optimization in PE-Fuel Cells. In this study we investigate a commercial GDL (SGL 25BA) by injecting liquid water (non-wetting phase) from the bottom. The drainage of liquid water and associated breakthrough behavior is observed at the pore scale level by means of in-situ X-ray tomography experiments (at PSI) [1] and the relative permeability curves are determined based on 3D-simulation. New insight about the limiting effects from microstructure is obtained from detailed 3D image analysis and pore morphology modeling.

Quantitative relationships between microstructure characteristics and effective transport properties (diffusivity, permeability) were established in previous studies [2-4], which represent the basis for the present investigation. The relevant microstructure characteristics are pore and liquid volume fractions ($\varepsilon, \phi$), size distributions of pores and bottlenecks (c-PSD, MIP-PSD), constrictivity ($\beta$), tortuosity ($\tau$) and hydraulic radius ($R_h$). In fibrous GDL these parameters can differ significantly for in-plane and through-plane directions.

- Injection Experiments: In through-plane direction a 'pseudo-breakthrough' is observed, whereby local bubble-points on the surface evolve continuously over an extended pressure interval. In contrast, in the in-plane direction the breakthrough is an abrupt event. It is shown by pore morphology modeling, that the anisotropy of the drainage and associated breakthrough-behavior is mainly caused by a so-called 'short range effect', which is dominant for the through-plane direction.

- Steady state flow properties as a function of liquid saturation: The relative permeability curves in our 3D-analyses show complex 'S-shapes' with concave, linear and convex segments, which is in contrast to the findings of most existing literature. The shapes of these segments can be explained in the view of the anisotropic breakthrough behavior (at low liquid saturation influenced by the short range effect) and with the detailed information from quantitative micro-macro-relationships that help to identify limiting microstructure effects also at higher saturation levels. The presentation gives a summary of these complex micro-macro relationships, which are extensively descirbed in two recent papers [5,6]. The findings are considered as a basis for future purposeful optimization of GDL microstructure and associated flow properties of liquid and gas phases.

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# Analysis of local heterogeneities and their effect on DMFC performance with a physical 2D cell model

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In order to develop direct methanol fuel cells (DMFCs) with enhanced lifetime and performance, it is important to understand the physical phenomena inside the cell. During operation, the local conditions inside a DMFC can be very heterogeneous, leading to non-homogeneous performance and degradation. Together with experimental validation, physical modelling can help to understand the processes that are causing those heterogeneities.

DMFC exhibit a pronounced performance loss during operation, which can partially be recovered by adjusting the operating strategy, as Bresciani et al. have shown [1]. This temporary performance degradation is to a great extent dependent on conditions like the local potential and the species distribution. Those parameters are not easy to measure experimentally but can be studied in detail in numerical simulations.

We present a two-dimensional DMFC cell model, which allows transient simulation of a single cell, including the possibility to simulate impedance spectra. The model is implemented in *NEOPARD-FC,* a code developed at DLR based on the open source CFD-framework DuMu$^x$ [2]. It accounts for two-phase flow and multicomponent transport in channels and electrodes, as well as for electrochemical phenomena in the catalyst layers. All layers are spatially resolved. We use a multiphase Darcy approach to describe the behavior of gas and liquid in the porous media. Furthermore, the crossover of methanol and water through the membrane and the resulting mixed potential on the cathode are included. The model is validated using experimental data from segmented cells. The occurrence of local heterogeneities and their effect on cell performance is discussed.

# 3D morphological modeling and validation for optimization of SOCs electrode microstructures

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The manufacturing routes of Solid Oxide Cells (SOCs) are based on typical ceramic processing such as screen printing, tape casting or dip-coating. Thanks to the flexibility of these methods,   a wide range of electrode microstructures is liable to be produced and then adapted to fulfil the specific constrains of each SOC applications (fuel cell, steam electrolysis, co-electrolysis). Indeed, a strong correlation exists between the SOC electrochemical performances and the electrode microstructure. However, the basic relationships between the three-dimensional characteristics of the microstructure and the electrode properties are not still precisely understood. Thus, several studies have been recently proposed in an attempt to improve the knowledge of such relations, which are essential before optimizing the microstructure, and hence, designing more efficient SOC electrodes. In this frame, two complementary stochastic methods have been developed to generate a large variety of virtual 3D electrodes microstructures. The first one is an adaptation of the 3D truncated Gaussian random field model for multi-phases media while the second one is based on an original overlapping sphere packing algorithm. In order to validate the two methods, 3D electrode reconstructions have been obtained by X-ray nano-holotomography at the new Nano-Imaging beamline ID16A-NI of the European Synchrotron Radiation Facility (ESRF) (Fig. 1a). The model validations have been conducted on typical LSCF and Ni-YSZ materials for both electrode functional and diffusion layers (Fig. 1b). The validation step includes the comparison of morphological and physical parameters such as the phase covariance function and the effective conductivities (Fig. 2). The flexibility of the two validated methods enabled us to simulate different microstructures representative of impregnated electrode or graded structure for composite electrodes. Finally, this validated tool will be used, in forthcoming studies, to identify the optimal electrodes microstructures for steam electrolysis and co-electrolysis applications.
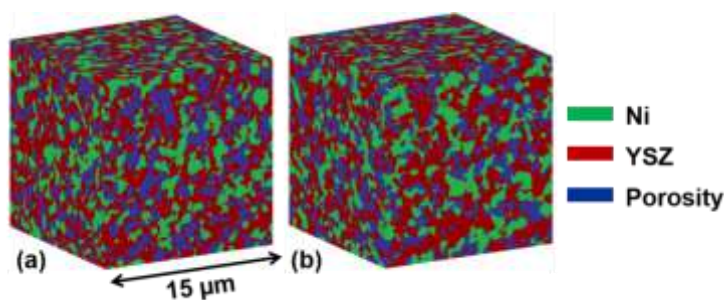


Figure 1: Visual comparison of the real microstructure (a) and the synthetic microstructure (b) by means of 'Gaussian Random Field Model'.
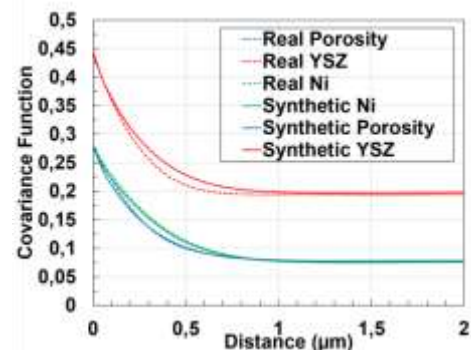
Figure 2: Quantitative comparison of the phase covariance functions between the synthetic and the real microstructures.

**Keywords**: SOC, Microstructure modelling, 3D Gaussian random field model, Overlapping Sphere Packing Algorithm, LSCF, Ni-YSZ, X-ray nano-holotomography

# Big data for microstructure-property relationships: a case study of predicting effective conductivities

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Data is the new oil. Analysis and modeling of big data is changing industries, businesses and research. One of the reasons that has contributed to this success is that large amounts of data are available nowadays. In the area of microstructures, however, acquisition of (3D tomographic image) data is difficult and time-consuming. It is shown that large amounts of data representing the geometry of virtual, but realistic 3D microstructures can be generated using stochastic microstructure modeling. Combining the output of stochastic microstructure modeling, which is a large amount of virtual microstructure data, with physical simulations and methods from statistical learning, microstructure-property relationships can be quantitatively characterized. As a case study, we aim to predict effective conductivity given the microstructure characteristics, which are relevant for transport (i.e. connected phase volume fraction $\varepsilon$, its mean geodesic tortuosity $\tau$ and constrictivity $\beta$). The quantitative relationship between these microstructure characteristics and effective conductivity has already been investigated based on 43 virtual microstructures in [1], where the following formula

$$\sigma_{eff} = \sigma_0 \, \varepsilon^{\,1.15} \, \beta^{\,0.37} \, / \, \tau^{\,4.39} \tag{1}$$

was derived. Here $\sigma_0$ denotes the intrinsic conductivity of the material.

Now we are able to analyze a total of 8119 microstructures generated by two different stochastic 3D microstructure models. This is - to the best of our knowledge - by far the largest set of microstructures that has ever been analyzed. Fitting artificial neural networks, random forests and classical equations, we validate the prediction formula from (1) by more than 8000 virtual microstructures and show that it is possible to predict effective conductivity more accurately using methods from statistical learning. The proposed concept leads to a better understanding of microstructure-property relationships and thus, it has the potential to generate recommendations for new, more efficient microstructures.

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# Advances in Multi-Scale Modelling of PEFCs

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Mathematical modelling of polymer electrolyte fuel cells on different length scales enables a better understanding and a systematic optimization of the complex processes involved. We report on some recent improvements for a more appropriate treatment of the microstructure properties in multi-scale models. Results from small-scale models are used for the parametrization of the next scale and results from the large-scale models are used to improve the lower scale processes to optimize the cell performance (Fig. 1).

The relationship between microstructure characteristics and effective macroscopic transport properties of the porous layers has been studied on the pore scale and implemented in a macro-homogeneous model of the membrane electrode assembly (MEA). Geodesic tortuosity, constrictivity and porosity can be combined to a single microstructure factor (M-factor) [1], with which the effective macroscopic diffusivity, permeability and conductivity can be determined [2]. From continuous phase size distribution and intrusion porosimetry measurements of thin porous media, we have observed a short range effect that gives rise to a liquid water saturation gradient across the gas diffusion layer (GDL) [3], which cannot be captured appropriately with the commonly used macro-homogeneous models for the water distribution. We implemented a MEA model that accounts for saturation gradients and their influence on the gas diffusivity via the M-factor. A fundamentally different behaviour is found for the liquid water and vapour fluxes through the GDL when saturation gradients are included.

Additionally, an interface model for the exchange of liquid water between GDL and gas channel has been developed inspired by a simplified view on droplet formation [4], to build the bridge between porous microstructure and appropriate boundary treatment in macro-homogeneous PEFC modelling.
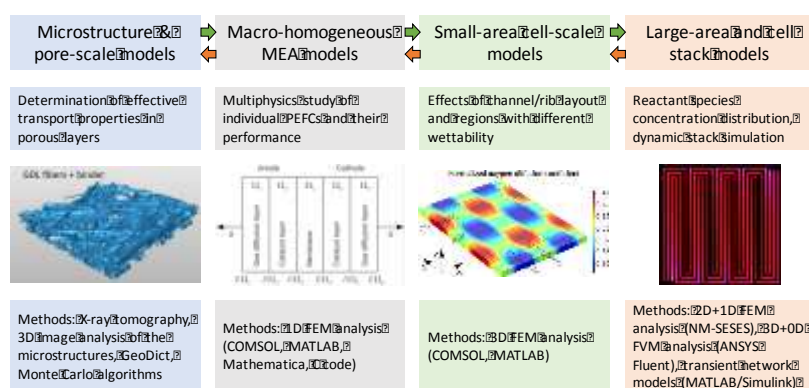


*Figure 4: Overview of multi-scale simulations.*

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# Toward predictive PEFC simulation: The importance of thermal and electrical contact resistance

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In computational models of polymer exchange fuel cells (PEFCs), thermal and electrical resistances between the different contacting material layers are commonly disregarded [1,2]. Various experimental conductivity measurements have shown, though, that the effect of interfacial resistance can have a significant share in the overall through-plane resistance and may even dominate over bulk resistance [3], such that they cannot be just neglected in numerical simulations that aim to be quantitatively predictive. Here, based on published experimental evidence, we argue that both thermal and electrical contact resistivities $R$ at the interfaces between catalyst layers, gas diffusion layers (GDLs) and bipolar plates (BPs) are governed by power law relationships with the applied clamping pressure $P$: $R \sim P^{-\alpha}$ with an exponent $\alpha$ lying in the interval [1/2,1] for typical materials such as SGL and Toray carbon papers and stainless steel or graphite. A selection of measurements in support of this is shown in Fig. 1.

We demonstrate the effect of taking thermal and electrical contact resistance into account in modelling by implementing them into a sophisticated, steady-state, non-isothermal, macro-homogeneous two-phase finite element COMSOL model of a single PEFC. Our simulations show that contact resistance is responsible for a significant voltage loss of the fuel cell even at high clamping pressures, and that this performance drop increases with current density, as shown in Fig. 2. These results challenge researchers in PEFC modelling not to neglect interfacial resistance in their computational studies.
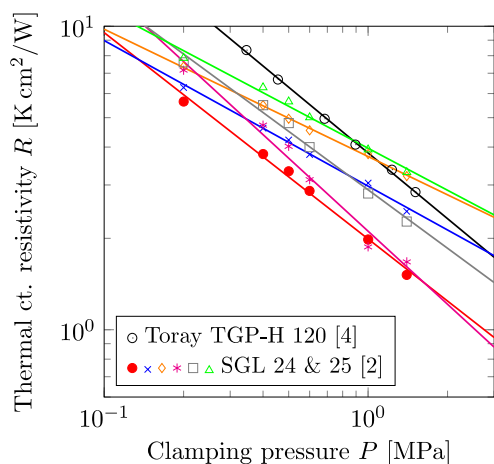


*Figure 5: Thermal contact resistivity between GDL and BP as a function of applied clamping pressure. Data points from experiments, lines represent power law fits.*

*Figure 6: Effect of thermal and electrical contact resistance (at 2 MPa clamping pressure) on fuel cell performance as computed with the finite element model.*

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# Segmented PEM fuel cell for verification of the variable temperature flow field concept

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Variable temperature flow field has been proposed and investigated in a previous study [1]. It is based on using internally generated water for reactant humidification. Close to 100% relative humidity along the cathode side was achieved by prescribing variable temperature profile extracted from Mollier's *h-x* chart. The computational fluid dynamics (CFD) model has been developed using ANSYS Fluent® PEM Fuel Cell Module in a previous study [2], and the simulation results of the polarization curve and relative humidity profile along the cathode channel length, Fig. 1, have shown good agreement with the experimentally obtained data. However, the experimental relative humidity profile was only available for the cathode side of the cell. In order to develop a credible CFD model for further investigation of the variable temperature flow field concept, the anode side relative humidity must also be investigated experimentally. The CFD simulation results have shown that the current density distribution along the cell with variable temperature flow field is quite different when compared to the isothermal case, and that the temperature of the reactants inside the channels is higher than the temperature prescribed at the current collector terminals. For this reason, a new segmented PEM fuel cell experimental setup, Fig. 2., is developed to enable measurements of temperature at the current collector terminals, relative humidity and temperature profiles along the reactant channels for the anode and cathode side, and operating electrical current on each segment. Each segment can be maintained at a different temperature by individually attached Peltier elements, so that a desired temperature profiles are achieved along the anode and cathode channels.
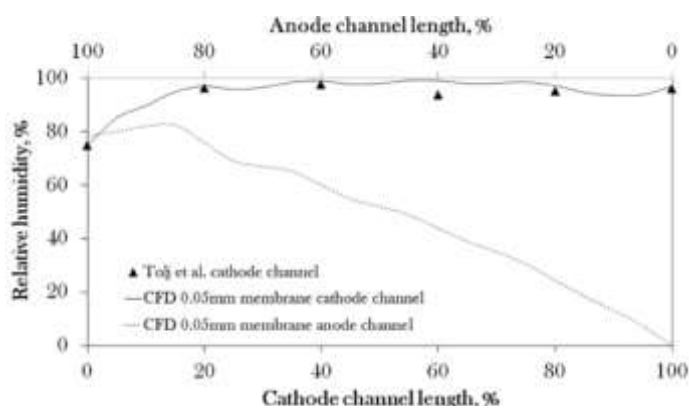


Figure 1. Comparison of experimental and simulated relative humidity profiles along the cell length [2]
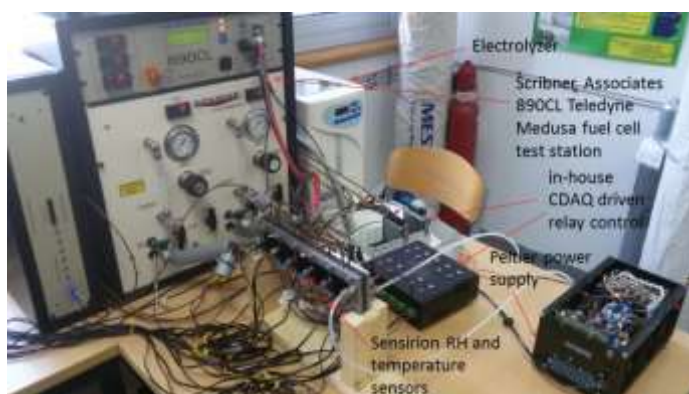


Figure 2. Segmented fuel cell experimental setup

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# Gas transport in PEFC gas diffusion layers and its analysis for upscaling

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In polymer electrolyte fuel cells of the type PEFC, DMFC and HT-PEFC, the gas diffusion layer (GDL) with its geometric structure on meso scale connects the electrodes with the feeding channels of the bipolar plate on the cell and stack scale. Efficient fuel cell operation requires that the electrodes are sufficiently supplied by fluid fuels from the channels. Also, reaction products must be transported away from the electrodes. The GDL also has to provide electric contact to the bipolar plates but its major task is the mass transport of these fluids. The GDL is typically composed of materials based on carbon fibers, e.g., paper, woven and non-woven textiles.

The structure of non-woven and paper-type GDLs in real fuel cells was analyzed by x-ray synchrotron under different local compressions [1]. The gas transport is simulated in compressed and uncompressed microstructures in through-plane and in-plane directions of the GDL, both in real structures and in stochastic equivalent geometries. In order to support multi scale simulation effective properties can be calculated from the meso scale simulation results to provide model parameters for homogenized approaches in cell scale simulations. Furthermore, the resulting gas flow is analyzed with statistical methods which were introduced in a previous study [2]. This approach provides the opportunity to detect quantitative relationships between functionality and microstructure and to design virtual GDL materials with improved transport properties [3]. The evaluation with stochastic methods provides substantiated properties suitable for connecting the meso scale to larger spatial scales. Figure 1 shows the simulation of through-plane gas flow at the exit layer of the GDL. 70 % of the volume flow is leaving the GDL at less than 30 % of the surface area.
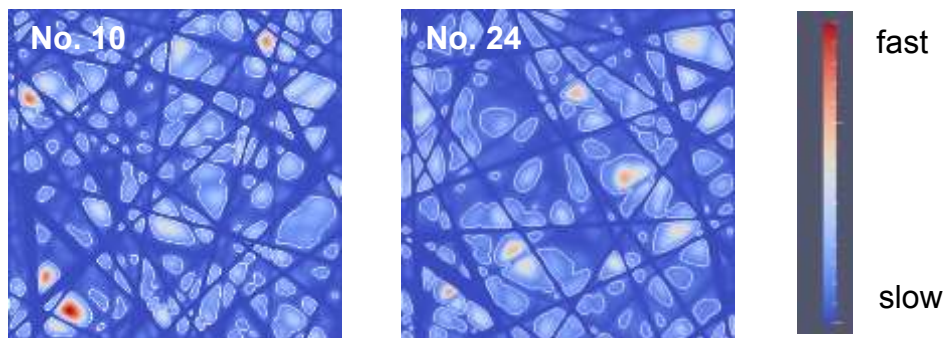


Fig. 1: Through-plane gas flow in two realizations of paper-type GDL

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# Microstructure Modeling and Optimization of Transport Properties of Gas Diffusion Layers in PEM Fuel Cells

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The Gas Diffusion Layer (GDL) is one of the determining factors for the performance of PEM Fuel Cells (PEMFCs). Hence, in order to improve the performance of the PEMFC, optimizing the transport properties, i.e. the gas diffusivity, electrical conductivity and flow permeability of the GDL, is crucial. In this work, the modelling and the simulation of the transport through the GDL's microstructure are presented enabling the optimization of the GDL microstructure.

First, a stochastic microstructure model of the non-woven GDL materials is created using the software GeoDict. The GDL is modeled at the micrometer scale as a fibrous porous medium composed of bent fibers and a binder material. In addition, a Micro-Porous Layer (MPL) is placed below the GDL to account for the transport resistance of the MPL. The MPL is modeled as a homogeneous medium, since its porosity cannot be resolved on the micrometer scale. The geometric model depends on several parameters, such as: fiber radius, fiber volume fraction, curvature of individual fibers, preferred fiber direction and porosity of the MPL. While fiber volume fractions and fiber diameters are known from the production process, parameters determining the curvature and the preferred directions of the fibers have to be fitted to measurements. To determine the free parameters, the transport properties of the fiber network, i.e. electrical conductivity, and the pore space, i.e. diffusivity and permeability, of the modeled structures are computed. Then, the free model parameters were fixed by fitting the calculated electrical conductivities to measurements taken on a reference GDL provided by Freudenberg FCCT. The model fitting was done by minimizing a distance function depending on the transport properties, using iterative stochastic optimization. This fitting method accounts for the stochastic nature of the geometric model and the resulting stochastic nature of the effective properties. Due to the potentially high number of iterations, it requires a fast and yet accurate computation of the transport properties.

The diffusivity and permeability of the pore space were computed using GeoDict. For the computation, the generated microstructure was voxelized, and the transport equations were solved in the pore space of the model. The MPL was modeled as a homogeneous medium with an effective diffusivity and permeability. Computation of the electrical conductivity of the fiber network using voxelized geometries is not very accurate, due to the inability to model the fiber-fiber-contact resistance. Also, the large size of the representative volume element requires simulating a large domain. To overcome the high computational costs, a graph theoretic method was employed. A weighted graph was created consisting of fibers as edges and contact points as nodes. The electrical conductivity can then be computed on the graph, using a graph-Laplacian approach.

After the model parameters were determined and an agreement of the transport properties with measurements was reached, simulation studies were done assessing the sensitivity of the transport parameters to changes of the model parameters. Finally, the stochastic optimization is used again, to find improved microstructures to meet future performance requirements.

# Evaluating force schemes in ShanChen multiphase lattice Boltzmann models in a flat interface test

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Lattice Boltzmann method intrinsically has some benefits to simulate multiphase / multicomponent fluid problems in porous media with a mesoscopic scale (micro meter scale) [1]. Concerning applications of polymer electrolyte membrane fuel cell (PEMFC), some porous media is commonly seen in components of it, such as gas diffusion layers. The D3Q19 ShanChen single component multiphase (SCMP) models is introduced which is one of multiphase lattice Boltzmann models [2]. Shift velocity and exact difference method (EDM) force schemes are implemented in the model with single relaxation time (SRT) approximation, while Guo and EDM force schemes are implemented with multi relaxation time (MRT) approximation. The Peng-Robinson (P-R) equation of state for water is included in the model and it confirms dynamic viscosity ratio of two phases. A 3D flat interface test is selected for comparison of the different approaches. The flat interface test is a validation platform for the capability of simulating immiscible flow by lattice Boltzmann method. All force schemes are checked with varied relaxation time. The accuracy of force schemes are evaluated by comparison between analytical and numerical density ratio of two phases. In a further step, the spurious velocity located in interface which is not observed in actual physical situation, as another error measure is also compared. We conclude that SRT-EDM and MRT-EDM are more accurate than other force schemes. MRT approximation is less relaxation time dependent than SRT. We conclude that MRT-EDM can be a good choice to simulate two phase flow in porous media of PEMFC with ShanChen multiphase lattice Boltzmann method.
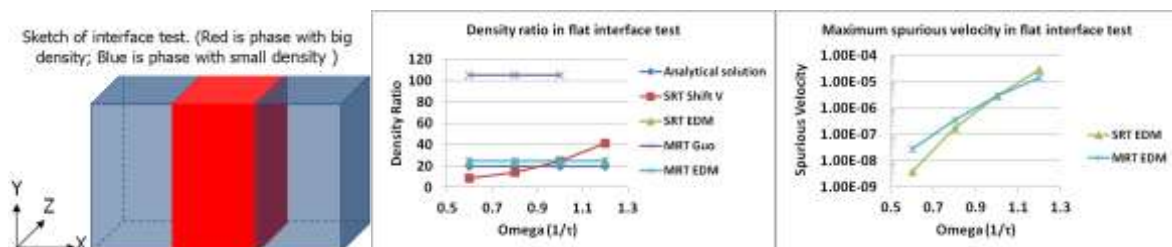
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# Anode Starvation Processes in HT-PEM Fuel Cell analyzed by Impedance Spectroscopy

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One of the major hurdles for complete market intrusion of high temperature polymer electrolyte fuel cells (HT-PEM FC) is their limited lifetime. Thus, within the German project QUALIFIX (funded by the Federal Ministry of Economic Affairs and Energy) different operation parameters shall be analyzed with respect to their influence on lifetime and durability of HT-PEM fuel cells. Hence, in this project, a tool to predict stabilities on FC single cell basis will be developed, with the approach to provide a lifetime prognosis based on the type of degradation occurring or expected.

An important tool to be used is electrochemical impedance spectroscopy (EIS) because this technique is noninvasive and allows separation of different degradation processes. Basis for lifetime prognosis is the deep knowledge and understanding of various degradation modes that reduce the durability of a fuel cell. A first approach to understand specific degradation mechanisms is fuel starvation, e.g. during start-up/shut-down procedures [1, 2], and its effect on FC performance.

By applying standard HT-PEM FC operation conditions (T=160 °C; p=ambient pressure; oxygen with $\lambda_C$=9.5), varying electrical load (0.4 A/cm$^2$; 0.5 A/cm$^2$) and reducing anode stoichiometry ($\lambda_A$=1.5-0.9 in 0.1 steps), fuel (hydrogen) starvation within a single cell has been provoked and its effects were determined by impedance spectra. The obtained spectra (Fig.1) were fitted to an electrical circuit model in order to describe the detailed degradation mechanisms. In the Nyquist plots (Fig.1), EIS measurements are shown. When stoichiometries decrease at a current density of 0.5 A/cm$^2$, impedance increases drastically. Such an effect was expected. By contrast, at 0.4 A/cm$^2$ a decreasing anode stoichiometry, i.e. fuel starvation resulted in slightly decreasing impedance. Possible reasons for this behavior could be phosphoric acid leakage and uncompleted activation of the FC.
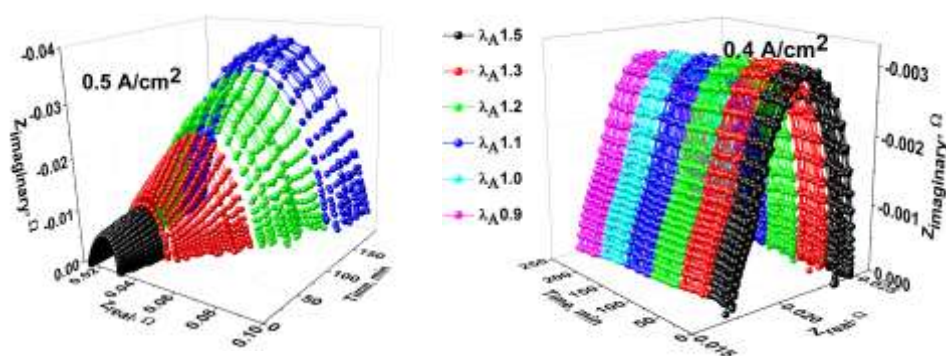


Fig.1: Impedance spectra for current densities 0.4 and 0.5 A/cm$^2$ at different anode stoichiometries

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# PEM Water Electrolysis Modeling and Simulation: A Comprehensive Review

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The growing concern over environmental pollution and diminishing fossil fuel reserves has prompted the move towards renewable energy sources. To achieve independence from the conventional energy sources it is essential to develop means of effective storage and transportation of energy from renewable sources. Electrolysis of hydrogen from water by using energy from these sources and using it to store energy is a promising solution. Among the available techniques, polymer electrolyte membrane (PEM) electrolysis is getting much attention recently. Compared to PEM fuel cells, research in PEM electrolysis domain is still in its early stages. As with any other engineering research, this also involves theoretical modeling and experimentation. Modeling and simulation of PEM elelctrolyser systems started nearly two decades ago and it has got significant traction in the past few years. This involves simple analytical equations to 3D flow simulation, steady state models to dynamic models, component level models to system level models or models integrating photo-voltaic systems. It is essential to have a good overview of the activities that have taken place over time. A comprehensive review of PEM electrolysis systems in general has been reported by Carmo et al. [1]. Bensmann and Hanke-Rauschenbach [2] have reported a brief review of modeling of PEM water electrolysis systems. The current review aims to provide further details into this subject. It compares activities carried out by different groups and provides insight to the current state of the art. It is found that Onda et al. [3] reported one of the earliest modeling approaches. Nie and Chen [4] reported three dimensional computational fluid dynamics simulation of flow in the flow field plates. On the other hand, Olivera et al. [5] have utilised micro and nanoscale models for porous electrodes and the catalyst layer modeling. It is observed that modeling of the processes inside the porous electrodes and catalyst layer still requires further development.

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# Physical Modeling of the Proton Density in Catalyst Layer Nanopores of PEM Fuel Cells

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In polymer electrolyte fuel cells, a primary objective is to design high performing catalyst layer with markedly reduced platinum loading. In this realm we present a model that explores the impact of ionomer structure and metal charging properties on the proton density distribution in a typical catalyst layer nanopore. The model consists of a cylindrical pore with a solid platinum coated core that is surrounded by an ionomer. The gap region between core and shell is filled with water. The density of charged side chains at the shell exerts a pronounced impact on the surface charge density at the Pt surface and thereby on the activity of the pore for the oxygen reduction reaction. The key parameter controlling the interplay of surface and bulk charging phenomena is the overlap of the Debye lengths of ionomer and metal surfaces in relation to the width of the gap. It allows distinguishing regions with weak and strong correlation between surface charge densities at ionomer shell and Pt core.
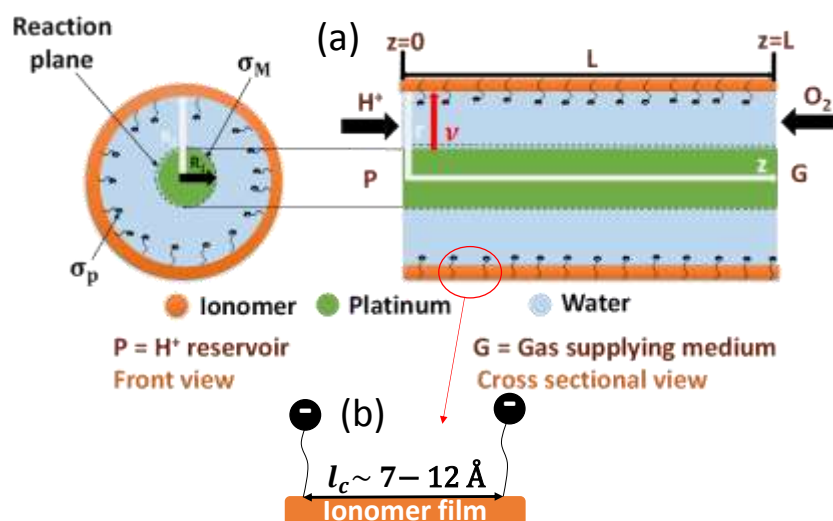
Figure 7. (a) Schematic of a single pore with both ionomer and metal charged walls. The pore space is bounded by a proton reservoir on one side and a gas transport medium on the other side. (b) Schematic of side chain separation at the ionomer skin.

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## Fast X-ray Tomographic Microscopy Imaging: Time Resolved Water Transport and Breakthrough in Gas Diffusion Layer

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Water, electrochemically produced in PEFC, is removed from the catalyst layer in vapor and liquid forms towards the flow field. The main component, responsible for water and reactant transport is the gas diffusion layer (GDL), which is sandwiched between the catalyst layer and the flow field where reactants are fed and water removed from the cell. Liquid water occupies GDL pores and hinders the gas supply to the catalyst. This results in a significant performance drop and may lead to failing of the process. The GDL is a thin porous material, based on carbon fibers with pore sizes of typically dozens of micrometers. This is large enough to be imaged using X-ray tomographic microscopy. Up to now the temporal resolution at the TOMCAT beamline was limited to about 10 s per scan and therefore water movement could not be resolved. Basic understanding about the interaction of water with the porous GDL structure was made in model in-situ experiments with well-defined boundary conditions by stepwise injection of water in the GDL and determining the local, steady saturation from the 3D reconstructed images [1]. The resulting saturation behavior is used as input for macro-homogeneous or pore network modeling [2]. The approach with steady water phases remains limited since dynamic behavior needs to be deduced from steady state measurements.

Recently, fast X-ray tomography development at the TOMCAT beamline has opened new possibilities for fuel cell characterization. Operando imaging has been performed with scan times below one second making possible to observe how water appears and moves within the porous structure [3]. However, the multi-physics of fuel cell, combining mass, heat and charge transports makes it difficult to decouple all the phenomena leading to water displacement. Therefore an ex-situ experiment with well-defined boundary conditions and dynamic water imaging has been developed, that allows to monitor the dynamics of water imbibition within the GDL until breakthrough, as well as droplet formation and droplet detachement in the gas flow channel.

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# Distinction of liquid water and ice with neutron imaging

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In order to address the challenge of fuel cell start-up at sub-zero temperatures, we apply time of flight (TOF) neutron imaging to investigate differences between liquid water and ice in-situ during fuel cell operation. TOF neutron imaging is a neutron wavelength resolved method that allows measurements of neutron transmission spectra in every pixel of the image by evaluating the velocity (which can be converted to wavelength) of each detected neutron. The velocity is measured by the time it takes the neutron to travel from the chopper disk to the detector over a known path length. The neutron attenuation between liquid water and ice differs at long wavelengths $\gtrsim$ 4Å as shown in figure 1. By using TOF or other wavelength selective neutron imaging techniques (e.g. dual spectrum method with beryllium filter [1]) the aggregate state of water can be determined. By applying the dual spectrum neutron imaging method for investigating a fuel cell with 50 cm2 active area, it was demonstrated that the first freezing events occur close to the gas outlets [2].

We will discuss our latest results from TOF neutron imaging experiments, performed on a water scale at the ESS test beamline at the Helmholz Zentrum Berlin (HZB) [3] with a neutron sensitive MCP detector (512 x 512 pixel, 55 µm pixel pitch) [4]. The results show that the contrast between liquid water and ice is increased by a factor of around 5 in images obtained with the TOF technique compared to the dual spectrum method. Figure 1 shows the neutron cross section of liquid water and ice (with a thickness of 1 mm in beam direction) that was measured with a very low wavelength resolution ($\Delta\lambda$ = 3.5 Å) and around 7 to 8 minutes exposure time. In this presentation, the experimental TOF results are compared to theoretical calculations, which will allow us to design an optimized chopper cascade for studying the phase change of water in fuel cells at the beamline BOA at SINQ (PSI).
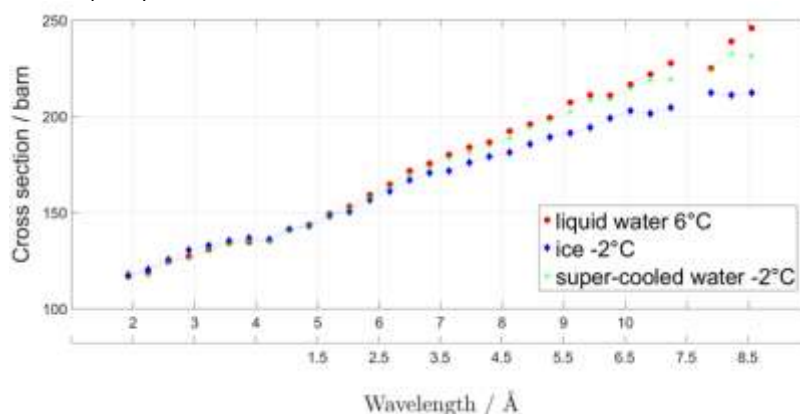


Figure 1: Neutron cross section averaged over 2 mm2 pixel area of liquid water at 6°C (red), super-cooled water at -2°C (green) and ice at -2°C (blue) as a function of neutron wavelength. The two x-axes show the $\Delta\lambda$ of 3.5 Å.

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# Signal to Noise Ratio Evaluation for X-ray Computed Tomographic Imaging of Water in PEFCs

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Over the past years, X-ray tomographic microscopy (XTM) has been intensively investigated for imaging of liquid water in the gas diffusion layers of polymer electrolyte fuel cells (PEFCs) [1-3]. For 4D XTM studies of the water distribution under transient operation conditions, increased temporal resolution with scan times clearly below 1 s are needed. In order to explore the consequences of reduced scan time on water segmentation, the influences of different imaging parameters on the of signal-to-noise ratio (SNR) of water versus void have been studied with an *ex-situ* XTM experiment at the TOMCAT beamline of the Swiss Light Source (SLS) at Paul Scherrer Institut (PSI). The cathode channels of a double channel XTM cell [1] have been filled with liquid water, while keeping the anode channels empty, as shown in Figure 1a. The $SNR(H_2O/Void)$ in the gas channels is quantified as an indicator for contrast between liquid water and void in gas diffusion layer (GDL) to derive imaging parameters for operando conditions. The consequences of decreasing scan time (Figure 1b), different beam energy (Figure 1c) and voxel size on $SNR(H_2O/Void)$ are discussed.
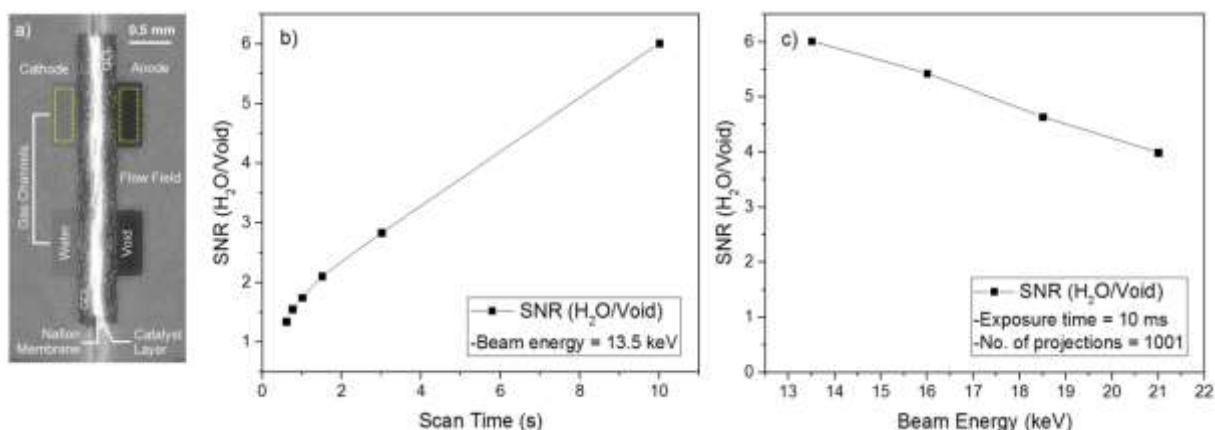


Figure 1: a) Tomographic 'through-plane' slice of a double channel PEFC with water filled cathode flow field; the dashed yellow rectangles indicate the sampling area for SNR calculation; b) Influence of scan time on $SNR(H_2O/Void)$ at a beam energy of 13.5 keV; c) Influence of beam energy on $SNR(H_2O/Void)$ with fixed scan time of 10 s.

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[3] J. Eller, F. Marone and F. N. Büchi, "Operando subsecond tomographic imaging of water in PEFC gas diffusion layers." ECS Trans. 69(17), 523–531, 2015.

# Temperature Dependence of Phosphoric Acid Invasion in GDLs: an X-ray Tomographic Microscopy Study

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High temperature polymer electrolyte fuel cells (HT-PEFC) are based on a polybenzimidazole membrane, doped with phosphoric acid (PA) as the electrolyte. Unlike in PFSA-type membranes, the electrolyte is not bound to the base polymer, but is more or less mobile within the pores of the membrane. As shown by Eberhardt et.al. [1], PA can therefore flood the gas diffusion layer (GDL), which plays a significant role for fuel cell performance and durability.

To better understand the interaction between PA and GDL, an *ex-situ* experiment was developed, which allows to use well defined boundary conditions (temperature, acid concentration, acid injection rate, acid and gas pressure), which are difficult to control in *operando* investigations. The setup described by Lamibrac et.al. [2] was adjusted to be used with PA and at temperatures up to 160 °C.

The invasion of PA is performed by stepwise increasing the PA pressure. To visualize the behavior of PA, X-Ray tomographic microscopy imaging is performed after each step at steady state. The resulting images are segmented into fiber, void and PA phases (Figure 1a), which are then used to quantify the PA invasion (Figure 1b) and the local PA saturation in the GDL (Figure 1c) as a function of the capillary pressure. This will eventually provide the structure dependent parametrization, which is required for model based material design.

Results for PA invasion into a Toray GDL material, tested at different temperatures from room temperature up to 160 °C, will be presented and compared with the water invasion into the same GDL.
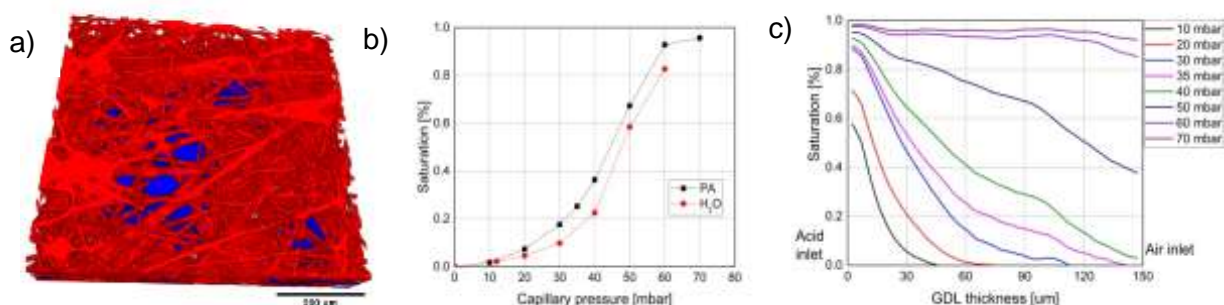


Figure 1a: 3D visualization of the dry GDL structure (red) and PA (blue) at 40 mbar capillary pressure. Figure 1b: Capillary pressure vs water and PA (85 w %) saturation at room temperature. Figure 1c: Local PA saturation in the GDL.

S.H. Eberhardt et.al., *J. Electrochem. Soc.*, **162** (3), F310-F316
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# Where does the PTFE end up in SGL gas diffusion layers:
## A multiscale morphological analysis

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While most GDL binders are solid, the binder of SGL GDLs is porous and its influence on gas phase transport is unclear [1]. In SEM surface images of SGL, GDL binder domains appear as flake like fine-structure with particles of about 100 to 300 nm. Here, we apply multi-dimensional X-ray imaging techniques, morphological analysis and multi-scale numerical simulations to clarify possible contributions of the sub-micron binder porosity to overall gas transport of SGL 24 gas diffusion layers with different PTFE content. The microstructure of the samples was quantified using X-ray tomographic microscopy measurements at the TOMCAT beamline and with a GE nanotom m laboratory X-ray CT-scanner, as well as with ptychographic nano-CT at the cSAXS beamline of the Swiss Light Source (SLS). The GDL pore structure was acquired with the lab-CT micro-CT data (resolution ~3 µm), whereas the sub-micrometer XTM data from TOMCAT (resolution ~0.3 µm) and the nano-CT from cSAXS (resolution ~50 nm) was used to capture the binder porosity. A predominantly accumulation of PTFE in the binder domains can be identified already by the different gray scale levels of the micro-CT data (see Figure 1) that is confirmed by an analysis of the pore space morphology. The higher resolution TOMCAT and cSAXS data additionally reveal the loss of binder porosity with increasing PTFE content. The influence of the PTFE-dependent binder porosity changes on overall GDL effective diffusivity was quantified using numerical transport simulations with GeoDict. A porous binder as observed in SGL 24AA and 24BA with an effective diffusivity of 0.2 results in about 100 % (50 %) higher overall GDL effective diffusivity compared to the solid binder of SGL 24 DA in through-plane (in-plane) direction. The findings are important to understand the performance losses of SGL 24DA compared to SGL 24BA at similar water contents observed by neutron radiography [3] and to derive further improvements of PEFC water management.
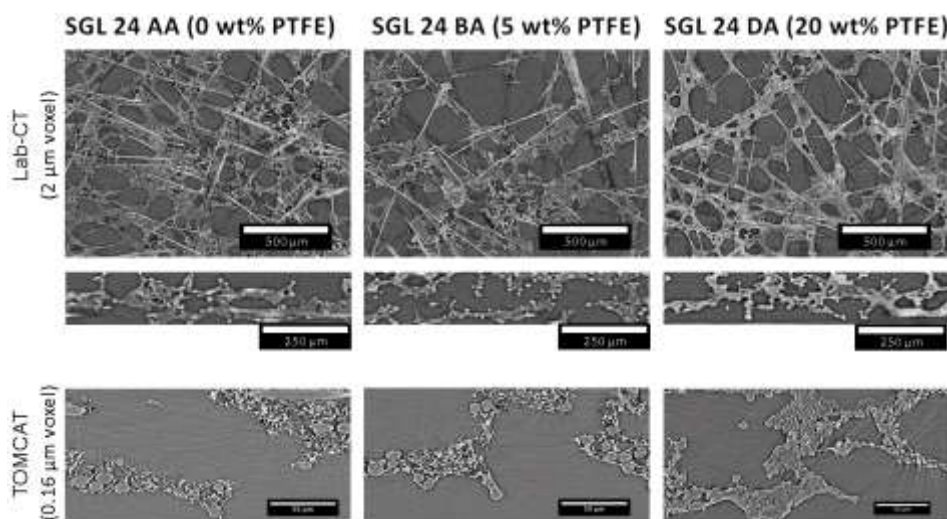


Figure 1: Micro-CT data (top, middle) and sub-micron XTM data (bottom) of SGL 24 with different PTFE content.

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# Analytics Platform Linking Materials Simulations and Characterization Data

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Similar to the advancements gained from big data in genomics, security, internet of things and e-commerce, new materials design processes can become highly efficient by combining multi-source experimental and computational data with predictive analytics capabilities [1,2]. In materials science, data sets are large, unstructured/heterogeneous and difficult to process and analyze from a single data channel or platform. New conceptual frameworks such as "Virtual Material Design" are able to solve problems and support industrial development of new products and processes by using state-of-the-art computer-aided simulations [3,4]. In combination with advances in data mining and predictive analytics, computer aided materials design can bring about reductions in development time and cost of new energy materials.

Focusing on fuel cell materials as a use case, we demonstrate a platform of materials performance and characterization databases with advanced user interface capabilities and relevant analytics and visualization features. The databank is created mainly with data from first principles and classical simulations. The platform employs big data analytics and management tools for secure data repository, data storage and data mining. It is essentially different from a typical big materials data repository [5,6] which is open to a multi-disciplinary group of users. Our platform can be customized and tailored for use by individual materials development projects and includes comprehensive tools for data discovery, collection, extraction, communication, and analysis. The advantage of our platform is to combine information originating from large data sets of different origins (for example, DFT, MD, experimental characterization of properties and performance). The data storage, data analysis and advanced analysis algorithms therein will enable efficient and secure dataflow between several different simulation and characterization activities. The cloud-base platform ultimately aims to manage all available materials databases and relevant modeling, simulation, performance, cost, and characterization data and how they can be communicated to materials fabrication and design teams.

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[3] Jan Hamaekers , Fraunhofer Institute for Algorithms and Scientific Computing SCAI
[4] Internal report, Eikerling's lab, Simon Fraser University, Canada
[5] Materials Genome Initiative, https://www.whitehouse.gov/mgi
[6] NOMAD Project, https://nomad-coe.eu/index.php?page=centre-of-excellence

# Simulated impedance of diffusive processes in tomographically derived microstructures

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Impedance spectroscopy is a powerful and widely used technique for characterising processes in electrochemical devices, such as batteries and fuel cells. The performance of these devices is closely related to their 3D microstructures; however, the elements used for representing them are typically either zero dimensional (resistors, capacitors etc.) or occasionally 1D. The most commonly used 1D elements are Warburg diffusion elements, which are particularly useful as they have analytical solutions and so can be easily incorporated into standard EIS fitting algorithms. However, the transport processes that these elements are used to represent are inherently 3D, and so Warburg diffusion elements must capture transport phenomena with bulk parameters such as tortuosity factors and porosities.

Details of the geometry of porous electrodes have recently become routinely available using microtomography. This technique typically represents the geometry as an array of cuboid volume elements (voxels) that must be segmented from greyscale to a phase labelled volume. In 2016, the authors published an open-source software package, *TauFactor*, which allows for the rapid calculation of tortuosity factors from segmented tomography data. An updated version of the software is here presented to efficiently calculate diffusive impedance spectra in the frequency domain, directly from segmented tomography data.

Numerical results show that the diffusion impedance may significantly deviate from the Warburg analytical solution for structures showing an inhomogeneous distribution of pores. In particular, multiple peaks may appear in the high-frequency region in the complex plane, which may be misinterpreted as separate electrochemical processes in real impedance data (see fig.1 for a simple 2D example). Two classes of structures, namely with increasing or decreasing porosity distribution, can be identified from the analysis of diffusion impedance. Thus, the software can be used to overcome the limits of conventional equivalent circuit analysis in modelling transport phenomena in porous electrodes.
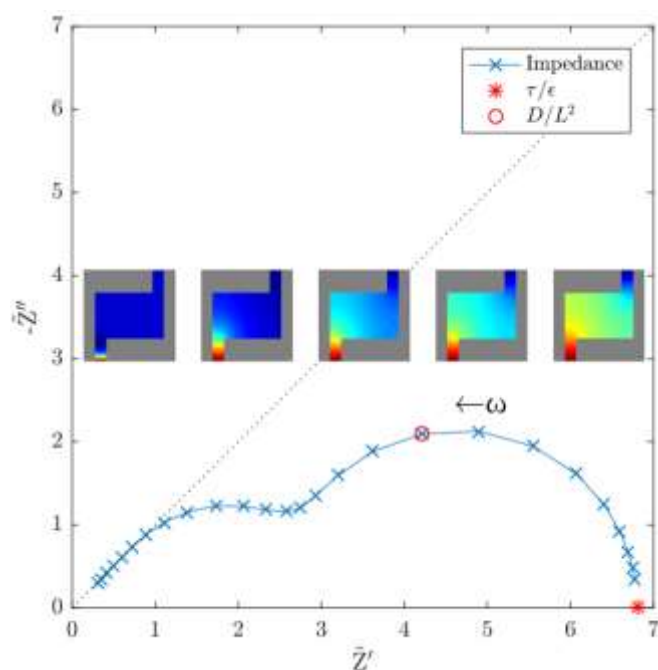


**Figure 1:** Simulated spectrum of a simple 2D structure with an open boundary at the upper surface and a fixed concentration stimulus at the lower surface. The five inset colourmaps indicate the distribution of the real component of the diffusing scalar going from high to low stimulation frequency (l-r). The spectrum shows two distinct peaks, which would not be possible for a uniform 1D system. The axes have been normalised such that the low frequency intercept is the obstruction factor ($\tau/\epsilon$) and the characteristic frequency ($D/L^2$) is also highlighted.

# A model-based analysis of the performance limiting factors in Ni/YSZ cermet anodes

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Electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate the polarization processes in complex electrochemical systems such as Solid Oxide Fuel Cells (SOFC). Generally the measured impedance spectra are analyzed by the distribution of relaxation times [1] and a subsequent Complex Nonlinear Least Square approximation to an equivalent circuit model [2] in order to identify and quantify the contribution of different loss mechanisms.

In high performance anode-supported SOFC the fuel electrode is realized with a porous two-phase composite Ni/YSZ cermet composed out of two layers. Both layers are characterized by specified microstructure properties, which are volume fractions, tortuosity and triple phase boundary length (fig. 1b)). The substrate layer close to the gas channel shows a high porosity in order to minimize diffusion losses, whereas the



Figure 8: a) Illustration of the reaction and transport processes in Ni/YSZ cermet anodes, b) SEM-image of the anode functional layer and substrate and c) modelling scheme of the TLM

functional layer between substrate and electrolyte shows low porosity but high triple phase boundary length, resulting in a large number of electrochemically actives sites. At these sites the electrochemical oxidation of hydrogen couples the (i) ionic transport through the YSZ-matrix, (ii) the electronic transport through the Ni-matrix and (iii) the gas transport through the pores (fig. 1a)).

In this study a physical meaningful modelling approach based on a three channel transmission line model (TLM) was developed in order to describe all electrochemical and physical processes occurring in such a two layer Ni/YSZ cermet anode (fig. 1c)). The required model parameters are obtained from EIS measurements on patterned model anodes [3], 4-point DC conductivity measurements on electrolyte bulks and microstructure properties extracted from FIB-tomography for both layers [4]. We will present a detailed study on the development and parametrization of the TLM model, as well as the validation of the model with measured impedance data for different cell configurations. This modelling approach is capable to correlate microstructure and geometry properties with the performance of Ni/YSZ cermet anodes.

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# Conceptual Design of Methane Synthesis
# Using Solid Oxide Electrolysis Cells

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Electrochemical methane synthesis from $CO_2$ and water is one of the means of storing intermittent renewable energy. It also attracts attentions because it can contribute to the fuel cycle which does not rely on fossil sources. In this study, methane synthesis in solid oxide electrolysis cells (SOEC) is investigated. The concept is shown in Figure 1. A novel point of this concept is that CO methanation reaction is integrated into well-known co-electrolysis. This reaction occurs at relatively low temperature (below 800$^{o}$C). It is reported that exothermic nature of the reaction leads to smaller heat loss which results in higher round-trip efficiency for energy storage in closed systems[1,2]. On the other hand, methane-synthesis SOEC (hereafter MS-SOEC) for open systems have not been seriously discussed. In open systems, methane-rich cathode outlet gas is utilized outside the system. Barelli *et al.* conducted a precise model analysis on hydromethane (methane with 5-30% hydrogen) production for transportation applications[3]. This is an example of open system analysis, but their system consists of co-electrolysis SOEC and subsequent methanation reactors, not MS-SOEC.
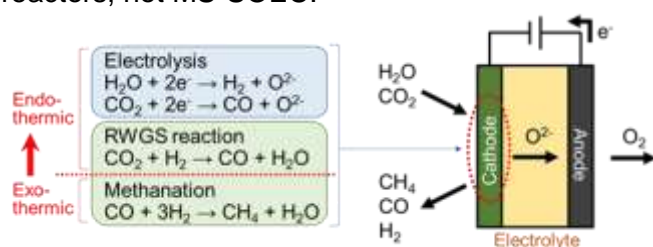


Figure 1. Concept of methane-synthesis SOEC

In order to quantitatively examine the advantages and limitations of MS-SOEC in open system, a process model was developed. Two-step methane synthesis (co-electrolysis SOEC followed by methanation reactors) was also modelled for comparison. Models were developed using Aspen Plus V3.7. In the MS-SOEC model shown in Figure 2, cathode reactions are modelled by three reactors. First one is for fast WGS equilibrium. Second one simulates water electrolysis and $CO_2$ electrolysis with specified conversions. Final one is for RWGS and CO methanation reactions. Equilibria of two reactions are considered. Open circuit voltage of the cell is calculated based on gas compositions of inlet and outlet flows. Activation and ohmic overpotentials are estimated to obtain *i-E* curves.
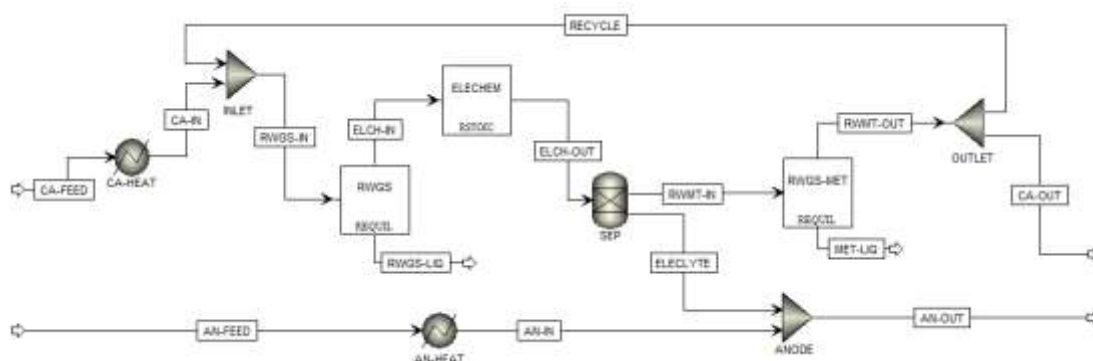


Figure 2. Process model for methane-synthesis SOEC.

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# Comparison of different approaches to analyse Electrochemical Impedance Spectroscopy data

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Electrochemical Impedance Spectroscopy (EIS) has been proven to be a powerful tool for reaction mechanisms and transport properties investigation and characterization of an electrochemical device. The application of this technique in the study of a Solid Oxide Fuel Cell (SOFC) allows the analysis of the different processes occurring during its operation. However these processes often overlap in the frequency spectrum rending their discrimination difficult. To overcome this problem, spectral analysis tools have been successfully applied yielding distribution of relaxation time constants (DRT), in which the different processes appear as distinct peaks. The number and position of these peaks are however sensitive to the DRT method used and the quality of EIS data. In this study different DRT approaches are compared. Experimental measurement of EIS is generally done in a frequency range that goes from mHz to MHz and can present some anomalies, due to noise and to the high frequency inductance loop resulting from cabling, that have to be corrected before processing the data. The first step in data analysis is to check the consistency of a recorded spectrum by verifying that its real and imaginary part satisfy the Kramers-Krönig relations. The linear Krönig-Kramers transformation test proposed by Boukamp [1] is used for this purpose. It is shown that this technique can yield not only the verification of the interdependence of imaginary and real part of the spectra but also the DRT in specific conditions. Another way to obtain the same results is to pass through the Discrete Fourier Transformation (DFT) of the imaginary spectrum [2]. For both techniques, smoothing of the spectrum, inductance correction and high/low frequency extrapolation, are necessary steps for a successful application. The Tikhonov regularization technique is also used to solve the same problem [3]; it has the advantage to be less sensitive to noise and limited frequency range. Moreover, the study shows how to couple DRT techniques with a curve fitting procedure (Complex Non Linear Square Fitting) to propose a meaningful equivalent circuit model.
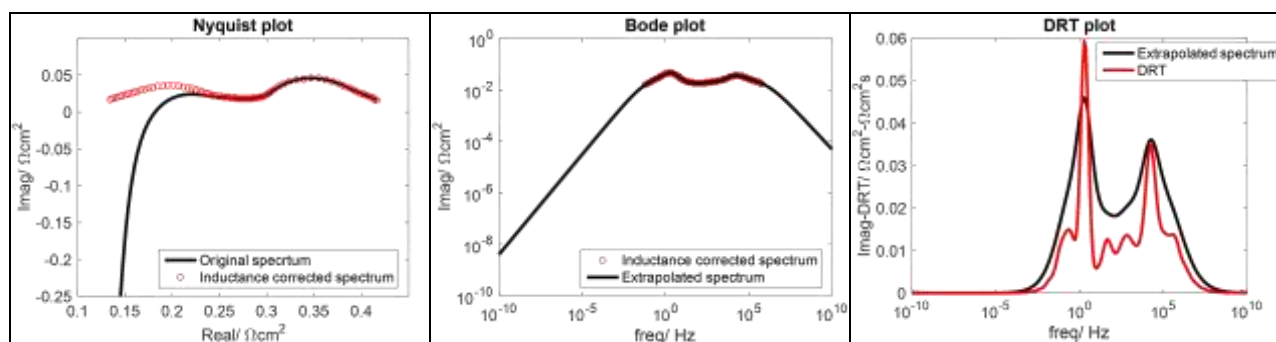


Figure 9. Process chain: from the original spectrum (left), through inductance corrected/extrapolated spectrum (centre), to peaks separation/DRT (right).

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# Locally resolved microstructure investigation of an anode-supported solid oxide fuel cell stack

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In this research a 100 W solid oxide fuel cells stack was tested. After 3700 hours of continuous operation a subsequent post-test analysis of the anodes' microstructure was conducted using a combination of focused ion beam and scanning electron microscopy. The obtained data was reconstructed into three-dimensional images, based on which the microstructure parameters were obtained. The microstructure parameters were quantified at different locations in the stack and different locations in a cell. Additionally, microstructure of a supplementary sample called the reference cell was investigated. The reference cell did not participate in the aging test and macrostructure analysis was conducted at an as-received cell. The analysis covers the critical spots including upstream, center, downstream and the vicinity of sealing. The obtained results indicate strong non-homogeneous microstructure morphology changes after long-term operation. The most vivid change is the drop of triple phase boundary length. In the open literature a cell power generation is generally proportional to triple-phase boundary. Therefore, it could be expected that when TPB drops significantly during long-term operation, the cell performance should also drop. However, the presented research unravels an opposite tread. The stack performance increased slightly during first few hundreds hours of the operation. A careful microstructure analysis unravel that multiple changes in microstructure morphology could cause overlapping degradation and optimization effects that could lead to the improvement of the stack performance.
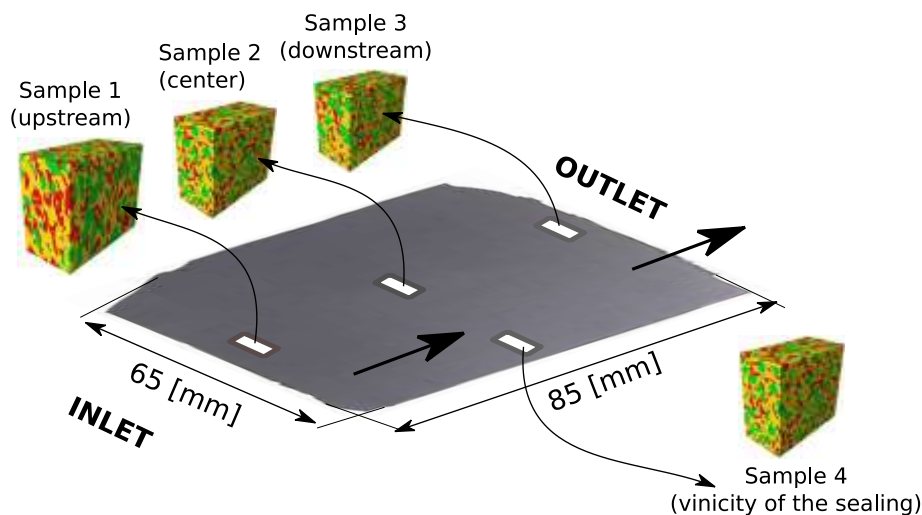
Fig. 1 - An example of samples location in a single cell

# Multiscale model of solid oxide fuel cell using real microstructure information

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Solid Oxide Fuel Cell (SOFC) models in the literature can be divided into two main categories – macroscale models and microscale models. The macroscale models are focused on heat and mass transfer while the electric behaviour of electrodes and electrolyte and mass transport phenomena in porous parts are simplified. These models give important feedback for the SOFC stack developers and allow heat and mass transfer management. On the other hand, the microscale models investigate effect of microstructure parameters on the cell performance. Microscale models punctuate important aspects of charge transport and mass diffusion processes inside the porous microstructure and allow microstructure-oriented optimization. There is insufficient number of studies that focuses on both scales simultaneously. Calculating those phenomena together require microscopic/macroscopic scale transition. It is aimed to calculation of system behavior on one scale using information from different scale. Mathematically it is obtained by applying more or less complex averaging process to these equations. Such models provide more information than strictly macroscopic models since they include the concept of average microstructure parameters and the associated behavior. The most accurate information about average microstructure parameters can be derived from real structure analysis, followed by quantification. Recently, the combination of a focused ion beam and scanning electron microscope tomography (FIB-SEM) as well as the X-ray tomography techniques brought a breakthrough in the direct 3D observation of porous structure. In current work the information about electrodes microstructure was obtained using FIB-SEM coupled with 3D reconstruction technique. A sample taken from SOFC stack was virtually reconstructed and its average microstructural parameters were quantified. The obtained microstructure parameters were introduced into the two-dimensional mathematical model that couples micro- and macro-scale, so called multiscale model. The model takes into account mass, energy and charge transport within the cell. The results from numerical calculations based on presented model was compared with experimental results obtained from 300 W SOFC stack and the good agreement was found. It is shown that the microstructure is an crucial parameter in SOFC modeling and the change of microstructure parameters strongly impact model performance.

# Beyond Common Practices in Experimental Characterisation and Model Validation of Solid Oxide Cells

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Performance and reliability of state-of-the-art solid oxide cells (SOCs) need to be further improved so as to outperform, in terms of cost-effectiveness, the more traditional power and substance generating technologies, incentiving in this way their public acceptance and hence boosting market penetration.

In order to achieve the aforementioned ameliorations, the use of more application-specific analysis tools, techniques and testing protocols is regarded as a crucial step. It must be noted that among these, computational modelling is especially gathering the attention of the scientific community, as it complements the more traditional analysis areas (experimental and theoretical), enabling to use hypothesis for extrapolation of their application. An exhaustive validation campaign is needed in order to ensure the soundness of the model and bounding its applicability. Yet, there is a growing feeling in the fuel cell modelling community that commonly used validation practices (basically confronting current-voltage curves) are not enough to assess the validity of the model. In order to tackle these issues, the High Temperature Fuel Cell Laboratory (HOTLAB) of ENEA has developed an in-house set-up for testing SOC single cells allowing to measure *in-operando* the gas composition and the temperatures in eleven spot-sampling points distributed throughout the negative electrode side of the cell.

The innovative set-up has demonstrated to be an extraordinary analysis tool, mapping the distribution of temperatures and gas compositions when in stationary and transient conditions. Moreover, the geometrical characteristics of the housing enable characterising unambiguously the electrical and electrochemical performances of cell, obtaining current-voltage curves and EIS measurements barely affected by parasitic resistances. One one hand, the innovative set-up can be used to generate statistical multivariate models correlating localised conditions with global settings; and on the other hand it can be used to fully validate two or three dimensional CFD models. The synergy of both approaches can lead to more powerful monitoring methodologies and also to the generation of models capable of predicting degradation based on the operating conditions.

# Artificial Ageing of PEMFC GDL

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The Gas Diffusion Layer (GDL) of a Polymer Electrolyte Fuel Cell (PEMFC) is one of the components which age during PEMFC operation. In comparison to the ageing of other PEMFC components as for instance the Membrane Electrode Assembly (MEA) the GDL ageing is slower and during long operation times may have less, but finally similar effects on the power of the PEMFC. Because of this in operating fuel cells the GDL ageing effect is hard to separate from other ageing effects. Therefore to examine the GDL ageing mechanisms artificial ex-situ experiments were performed. To get information about the influence of hydrophobic coating and Micro Porous Layer (MPL) on ageing, a ready to use GDL with MPL and its pre-stages the pure substrate and the hydrophobic coated substrate were investigated. The GDL was kept in 35 % $H_2O_2$ solution at elevated temperature of 90°C for defined times. During the ageing the $CO_2$ emission was detected. Before and after the ageing, the surface contact angle was measured. Beside this, also the inner contact angle was measured. These parameters, including the Leverett function parameters currently elaborated, will be used in further PEMFC modelling (CFD and Monte Carlo) to describe the GDL wetting behaviour. The poster presented shows experimental results and changes of the wetting parameters surface and inner contact angle as function of the ageing time.

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# Ageing induced changes of charge distributions in a LIB analysed by correlating EIS simulations and experiments

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**E**lectrochemical **I**mpedance **S**pectroscopy (EIS) is a widely used measurement technique to analyse properties of **L**ithium-**I**on **B**atteries (LIBs), since impedance spectra are sensitive to changes of battery parameters like surface layer thicknesses, material conductivities and reaction rate constants. Physico-chemical models of LIBs are a useful tool to correlate changes of measured impedance spectra to changes of LIB parameters. We will present a model based on Doyle and Newman [1] extended with double layers and aging processes to simulate EIS during degradation of a LIB. The model has been used to simulate impedance spectra and fit them to measured impedance spectra with a linear least square fitting tool.

Achieving reliable results is only possible if measured and simulated impedance spectra meet linearity, causality and stationarity requirements for EIS. Therefore we will also present a set of pre-measurements and calculations to ensure low noise, linear, causal and stationary conditions. Initial values of state variables have been adjusted and Fourier transformed output signals have been analysed.

Finally, various ageing induced changes in the charge distributions at the anode surface interphases have been assumed and compared under the preconditions mentioned above. Each of these ageing models aims to describe the effect of the **S**olid **E**lectrolyte **I**nterphase (SEI) on the impedance spectrum during cyclical ageing. It is assumed that the charge distribution providing the best possible fits for all spectra of a cycled LIB is also the best approximation of the real physical charge distribution. We will show that the SEI influences the reaction and the double layer at the anode/SEI interphase as well as the reaction at the SEI/electrolyte interphase. Figure 1 shows fits to the cycle aged cell assuming the described charge distribution. Relative deviations between measurement and simulation, e.g. in the second semicircle, can be reduced to $10^{-6}$.

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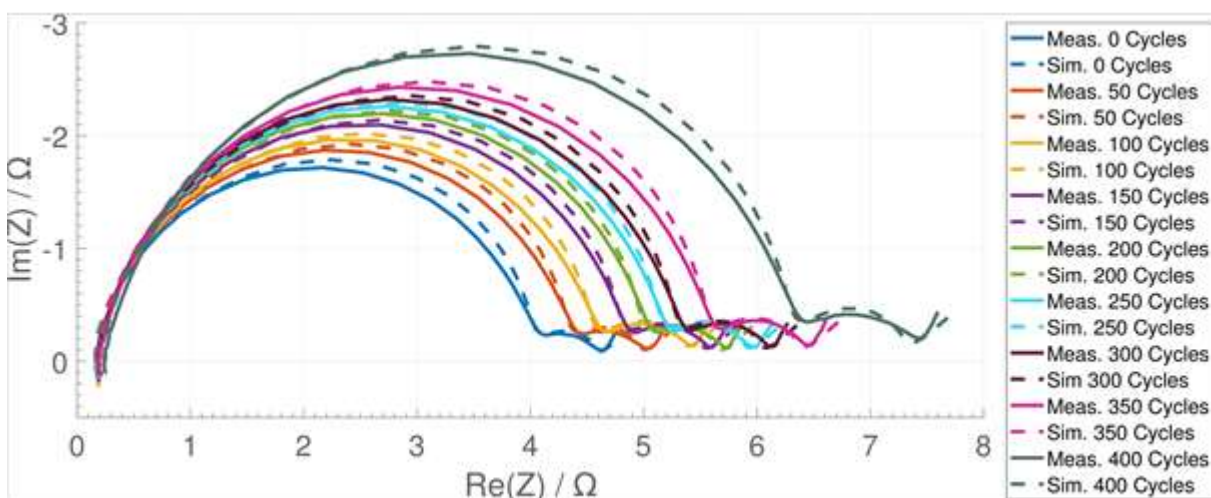
Figure 1: Fit to measured EIS for the cycled Lithium-Ion battery

# The impact EV power electronics on battery degradation

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High resolution measurements of the harmonic content on the DC link on EVs reveal the existence of high-current high-frequency current perturbations generated by the power electronics subsystems used to manage the flow of energy within the EV. Little is reported about the rate of degradation associated with exposing the battery to coupled direct current (DC) and alternating currents (AC). Based on the Real-world measurements of current on the high-voltage bus of a series hybrid EV, a long-term ageing experiment involving fifteen 3Ah $C_6$/$LiNiCoAlO_2$ batteries are subjected to coupled AC and DC cycles with various AC frequencies is carried out. The results highlight that both capacity fade and impedance rise progressively increase with AC frequency; the spread of degradation for cells cycled with a coupled AC-DC signal is also considerably larger than a pure DC cycle. To understand the underlying causality of this frequency-dependent degradation, XPS of the negative-electrode surface was carried out which showed that high-frequency AC perturbations lead to the increased formation of passivating film. A heterogeneous electrochemical model coupled with governing equations for the electrical double-layer and solid-electrolyte-interface film growth is developed. Simulation results suggest that the increased growth of surface film is attributed to frequency dependent heat generation. This is due to ion kinetics in the double layer governed by the Poisson-Boltzmann equation. Additional thermal and reference cell relaxation experiments further corroborate the conclusion that heat generation within the battery is a function of the AC excitation frequency through resistive dissipation and the entropy of the cell reaction.

# Challenges for electrochemical and thermal characterization of Li-ion cells to improve parametrization for modelling

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The thermal behaviour of lithium-ion cells and their active materials depend on a large variety of internal and environmental physicochemical parameters, which are still not deeply understood. Therefore thermal characterization of the cells, batteries and their individual active and passive materials is required in combination with multiscale modelling to obtain quantitative and reliable thermal data. Combined electrochemical-thermal characterization techniques will be presented, which are needed in order to study the influence of ageing phenomena on different modes of heat generation, to collect data that can be used in battery management systems and for parametrization of models. It will be shown that accelerating rate calorimeters (ARC) can be used for in-operando thermal investigation of Lithium-ion cells and battery packs during electrochemical cycling under isoperibolic and adiabatic environmental conditions, respectively. The results for cylindrical as well as prismatic-type pouch cell Lithium-ion batteries indicate a significant increase of their surface temperatures under adiabatic conditions (s. Fig. 1) [1]. Additionally, the careful calibration of the ARC allows the quantification of heat generation and dissipation in different operation modes. One central point in the operation of LIB is the aspect of cell safety, because several exothermic reactions can occur inside a cell during operation as its inner temperature is increasing. If the heat generation is larger than the dissipated heat to the surrounding space, this may cause heat to accumulate inside the cell and the chemical reactions will be accelerated, which leads to a further temperature increase, until a thermal runaway is reached. Therefore it will be described how thermal runaway behaviour and the related reaction mechanisms of the cells and materials can be investigated quantitatively using ARC (s. Fig. 2) and how these data can be used to parametrize models for electrochemical-thermal simulations in COMSOL Multiphysics® and Matlab®.
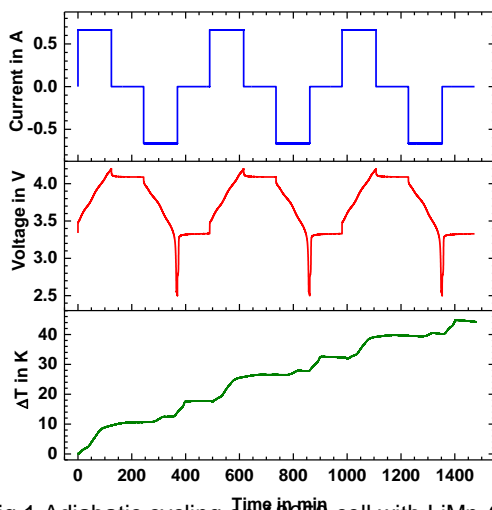


Fig.1 Adiabatic cycling on 18650 cell with $LiMn_2O_4$ cathode at C/2 rate: Current profile (upper curve), voltage profile (middle curve) and temperature difference (lower curve).
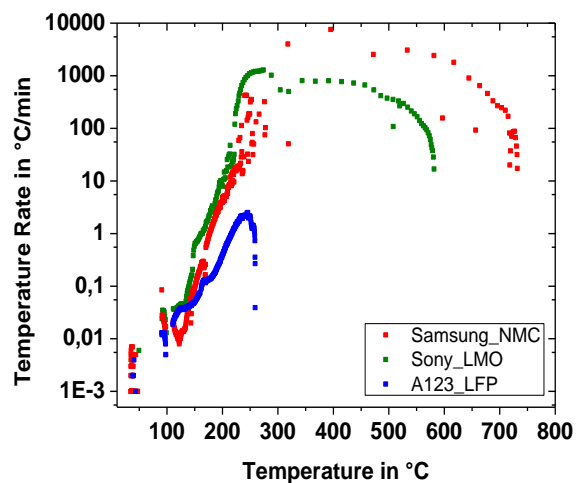


Fig. 2 Comparison of temperature rate vs. temperature plots during thermal runaway of 18650 cells with different cathode materials.

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# Parameter Sensitivity Study of a 3D Multiphysics Model of Large-format Li-ion Batteries

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The thermal behaviour of large-format cells is crucial for commercial cell designs and thermal management systems (TMS) in terms of cell performance and safety [1]. Individual and joint effects of these parameters on the cell performance are typically non-intuitive and difficult to quantify empirically. Here, an extensive model-based parameter sensitivity study might be beneficial for industrial cell designs, cell testing, and TMS control optimization issues [2]. To ensure an optimal performance the most relevant cell parameters have to be identified and adapted deliberately. In this work, based on our developed 3D Multiphysics model, parameter effects onto multidimensional thermo-electrochemical performance were studied. To this end, a global sensitivity study using Sobol' indices with a polynomial chaos expansion (PCE) approach [3] was performed for the cell voltage and the local maximum temperature under normal and high applied currents. Here, the most challenging part was to reduce the computational burden for the analysed model. Thus, a least angle regression based PCE concept was identified as an optimal trade-off between the approximation power and computational complexity. In doing so, the sensitivity study revealed the most relevant parameters and parameter interactions regarding thermal and electrochemical aspects as indicated in Fig. 1. These findings are a valuable source of information to improve manufacturing processes of high-performance large-format cells systematically.
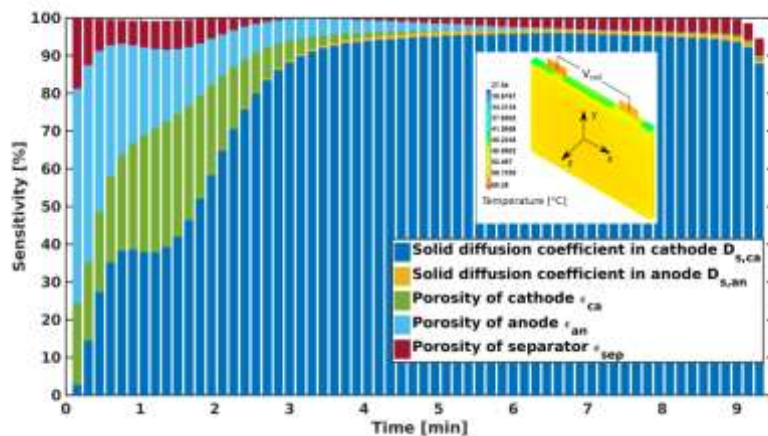


*Figure 10: Sensitivity analysis of cell voltage at 4C discharge*

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# Modelling the Electrochemical-Thermal Behaviour of Cylindrical Lithium-Ion Cells during Internal Short Circuit Scenarios

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Recent incidents such as fire and explosion of lithium-ion batteries were caused by internal short circuits (ISC) which therefore pose a severe safety threat. As the experimental analysis of Li-Ion battery ISCs requires special testing equipment and thorough test, modelling and simulation [1] can provide a safe and efficient alternative.

As electrochemical, electrical and thermal mechanisms can be assigned to different length scales [2], a geometrically simplified model can be established in order to reduce computational costs.
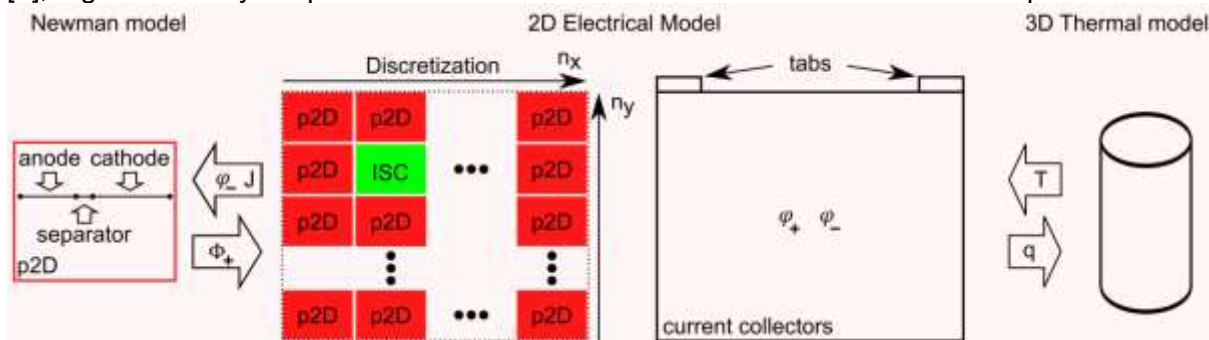


Fig. 1 Modelling and simulation of Li-Ion battery ISC on varying length scales via FEM

The basic modelling approach is shown in Fig. 1 consisting of several pseudo-two-dimensional (p2D) Newman-models [3], representing the electrochemical behaviour of the cell between the current collectors. The two-dimensional (2D) electrical potential field within the current collectors is modelled via Poisson's equation which is coupled either to a representative Newman-model or to a specific ISC section. The short circuit is implemented by calculating an electrical current due to the potential difference between the current collectors and varying electrical resistances representing the electrically shorted area of the ISC. Temperature and heat generation rates are transferred between the 2D electrical and the three-dimensional (3D) thermal model in order to account for temperature dependency of physical parameters and electrochemical processes as well as for the resulting thermal behaviour of the cell.

The simulation scenarios considered in this work include different locations of the shorted areas (ISCs) within the 2D electrical model in order to investigate local thermal load effects within the 3D thermal model and the electrochemical / electrical behaviour within the p2D Newman and 2D electrical model, respectively. The calculated temperature distribution shows a dependency on the local occurrence of ISCs which reveals insights into the mechanisms taking place during these field failures and may reveal potential improvement for enhancing the cell's intrinsic safety. Furthermore, the presented model allows for a first-principle evaluation of a possible electrical soft-short detection which is also discussed here.

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# Stress simulation of phase-separating cathode materials

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Some cathode materials in lithium-ion batteries show phase-separation during usage. The imbalanced intercalation of the lithium ions into the lattice causes large concentration gradients. The stresses resulting from these gradients can damage and destroy the battery cell. The computer simulation of the stresses during charging and discharging can support the development of battery cell structures.

In this talk, a method coupling lithium-ion diffusion to the electric potential, Butler-Volmer interface currents and linear elasticity is shown. A phase-field method with the Cahn-Hilliard equation is used to model the phase-separation of lithium-rich and lithium-poor phases. The complex three-dimensional microstructure of the anode and cathode material in the liquid electrolyte is resolved. The phase separation dynamics of lithium ions is described based on a micromodel [1]. It is coupled to the electrolyte phase by Butler-Volmer interface currents [2]. Additionally mechanical stresses resulting from concentration-dependent strains [3] are computed.

A fast immersed boundary method is presented. A three-dimensional finite-volume discretization on a periodic regular voxel mesh is used in combination with fast elliptic solvers. The domain decomposition uses the explicit jump method [4]. The semi-implicit time discretization is stable and enables larger time steps [5] in the time integration.

Different examples of periodic grids of spheres as microstructures are simulated for different charging rates. The process of spinodal decomposition, the effects on the cell voltage and the occurring stresses in the electrode material are discussed. The figure below shows the Von-Mises stresses occurring in an electrode microstructure consisting of spheres located at the grid points of a HCP lattice.
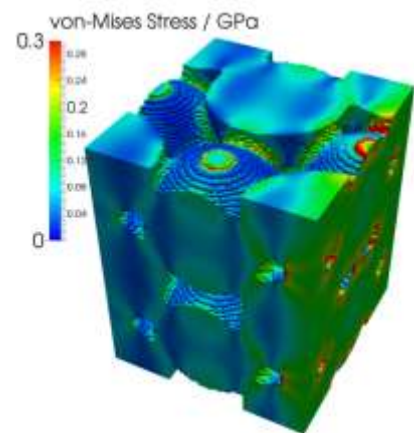


The simulation results are interpreted to allow for qualitative and quantitative prediction of damage and fracture resulting from multiple charge cycles by extension of the linear elastic model to e.g. include large deformations.

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# Mechanically coupled modeling of ionic transport and electrochemical reactions in Li-ion battery electrodes

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Lithium-ion batteries are the primary power source for mobile devices. Wider application, e.g. in (hybrid) electric vehicles is currently hindered by their gradual capacity fade over cycle lifetime. Main factors for this degradation are electrochemical side-effects and mechanical damage. The latter is due to the cyclic insertion and extraction of Li ions, resulting in high stresses and large deformation of the electrodes, leading to delamination of the electrode and to fracture of particles. The freshly cracked surface is then exposed to further chemical reactions. Experimental evidence however suggests, that nanostructured electrodes exhibit a higher resilience against this diffusion-induced mechanical degradation.

In this talk, we report on our efforts towards modeling the chemo-mechanical processes taking place in free-standing electrode particles at the micro- and the nano-scale. We describe two models used to study the interaction of phase segregation and crack growth, as well as the interaction of chemical reactions and surface tension in nanoparticles.

We show that surface tension provides mechanical stabilization in nanoparticles, allowing, in principle, for higher charge/discharge rates. This effect is size-and shape-dependent. However, the usable capacity of a particle shrinks with its size. We further demonstrate how the rate of surface reactions can affect phase separation, and that the interface evolution can drive the propagation of pre-existing cracks.

# Universality of the Emergent Scaling in Finite Random Binary Percolation Networks

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The bulk behavior of complex systems comprising disordered multi-phase components is of importance in various applications including characterization of super-capacitors, batteries, and dielectric materials. Electrical networks of randomly distributed resistors and capacitors have been observed to exhibit intrinsic electrical characteristics that show power law behavior with respect to the frequency of the electrical signal applied [1-3].

To examine these scaling laws, we apply lattice models of finite binary percolation networks to examine the effects of network configuration on macroscopic network responses. We consider both square and rectangular lattice structures in which bonds between nodes are randomly assigned to be either resistors or capacitors. Results show that for given network geometries, the overall normalized frequency-dependent electrical conductivities for different capacitor proportions are found to converge at a characteristic frequency. Networks with sufficiently large size tend to share the same convergence point uninfluenced by the boundary and electrode conditions, can be then regarded as homogeneous media. For these networks, the span of the emergent scaling region is found to be primarily determined by the smaller network dimension (width or length). Moreover, the numerical simulations are compared with our experimental investigation of the stress-dependent electrical properties of randomly packed spheres of stainless steel, subjected to various conditions of compressive force.

This study identifies the applicability of power-law scaling in random two-phase systems of different topological configurations. The comprehensive understanding of this emergent scaling can guide the design and testing of disordered systems in terms of determining testing conditions (e.g., testing location, fixture shape and size, etc.), boundary conditions, and system dimensions.

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# Modeling of mechanical effects in lithium ion batteries

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Over the past decades, several computational approaches for the simulation of batteries in general and lithium ion cells in particular were developed (e.g. see [1]). Electrochemical models for lithium intercalation batteries, based on continuum hypothesis and porous electrode theory, were initially introduced in [2]. Further extensions towards multi-physics models were made by coupling the electrochemical part with additional thermal and/or lifetime models. In recent years, it is observed that an increasing effort is made to include in these models different mechanical effects that occur inside cell components. This enables to study mechanical influences on cell properties such as performance, lifetime and safety. However, the complex interaction of electrochemistry and structural mechanics is still far from being completely understood today. Therefore, further intensive research, that combines theoretical, numerical and experimental methods, is required in order to develop a consistent, fully-coupled mechanical-electrochemical-thermal cell model.

This presentation starts with an overview of situations where the consideration of mechanical effects in simulation models plays an important role. Besides standard operational conditions, this includes also certain safety-related situations. After this brief introduction, recent results of two different research activities that consider mechanical effects inside lithium ion cells will be presented.

First, diffusion induced stress in a graphite lithium cell anode is investigated numerically [3]. An electrochemical-thermal simulation approach is extended to compute the mechanical stress in both radial and tangential direction inside graphite particles. Transient simulations of cell discharge reveal a sinusoidal stress evolution inside the anode, which is attributed to the staging behavior of graphite. The presented results are important contributions for a better understanding of local mechanical effects in the anode during cell operation. This is especially true concerning the lifetime of lithium ion batteries, since mechanical breakdown of graphite materials is considered as one of the key aging mechanisms (e.g. see [4]).

As a second example, recent results on the modeling of mechanical effects in all-solid-state cells are summarized. Due to the application of a solid electrolyte instead of a liquid one, mechanical aspects are much more critical for a successful realization for these kind of future cell concepts. This work establishes a three-dimensional model, which accounts for the volume change of cathode particles as well as the volume change of the lithium metal anode. Since a pure mechanical approach does not lead to realistic results, a multi-physics approach is used that includes both electrochemistry and structural mechanics. Modeling assumptions, the numerical solution approach as well as several three-dimensional simulation results will be discussed in this contribution.

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# Thick electrodes for Li-Ion batteries: A model based analysis

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Li-Ion batteries are commonly used in portable electronic devices due to their outstanding energy and power density. A remaining issue which hinders the breakthrough e.g. in the automotive sector is the high production cost. Going 'giga' is one solution which is currently pursued by Tesla but requires large investments. Recently, novel battery concepts were presented as an interesting alternative[1]. Batteries with thicker electrodes (>300 µm) allow to attain high energy densities with only a few electrode layers which reduces production time and cost[1,2]. However, mass and charge transport limitations can be severe at already small C-rates due to long transport pathways[2,3]. Novel design and operation strategies of the battery and its components are needed to mitigate these issues.

In our contribution we present 3D micro-structure resolved simulations of thick (electrodes > 300µm) Graphite-NMC batteries based on our thermodynamically consistent modeling framework BEST[4]. The parametrization and validation of our model is presented in a recent publication[3] and simulation results agree favourably with experimental data[2]. Electrode micro-structures are either taken from tomography data provided in the literature[5] (NMC) or virtual electrode realizations generated with a stochastic approach[6] (graphite). Based on the validated model we evaluate the influence of inhomogeneities in electrode composition and structure. Furthermore, we investigate the effect of different solvents and Li salt concentrations on battery performance. In our simulations we find improved energy densities at elevated concentrations which is counter-intuitive taking into account the nominal decrease in transport parameters. Finally, we will explore different structuring strategies of thick electrodes such as layering and laser perforation. First results indicate that a laser treatment of the electrode layers will improve the rate capability of the battery.

Our detailed 3D studies allow important insights on cell operation and are able to predict improved electrode structures and electrolyte formulations. The activities are performed within the BMBF project HighEnergy which investigates the opportunities and processing techniques for Li-ion batteries with high areal loading of active material.

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# Theory-based Investigation of SEI Formation

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The solid electrolyte interphase (SEI) is a thin film which separates the electrolyte from an electrode, e.g. the negative electrode in lithium-ion batteries. It is composed of electrolyte reduction products which are rapidly generated as long as the electrolyte is in contact with a negatively polarized and pristine electrode. This occurs during the first charge of the battery where SEI is quickly formed [1]. The SEI blocks electrons as well as electrolyte molecules and therefore stops the rapid electrolyte reduction. However, slow, long-term SEI formation reveals that electrolyte reduction is not completely supressed by this passivating layer. Therefore, at least one SEI precursor can migrate across the SEI at a small rate. Now, the throughput of this transport processes limits the rate of long-term SEI formation. Our model [2] uses this assumption to describe the evolution of a porous SEI as sketched in Figure 1. Our approach is similar to previous SEI model studies [3,4]. However, we trace the evolution of SEI volume fraction along the axis perpendicular to the electrode surface as shown in Fig. 2. This results in novel predictions, e.g., morphological properties such as the dual-layer structure.

The transport of SEI precursors, i.e., electrons, electrolyte molecules or neutral lithium interstitials [5], through either the SEI or its pores can be adjusted in our model. Theoretically, each of these processes can facilitate SEI growth on its own. We investigate SEI formation for each these transport mechanisms individually. In this way, we predict how the corresponding films can be distinguished. They do not only differ in the potential dependence of their formation rate but also in the dual layer structure. Additionally, some mechanisms tend form SEI with homogeneous film thickness whereas others form SEI with strongly fluctuating thickness. These results allow experimentalists to do draw conclusions with respect to the actual rate-limiting transport process, if they observe one of these features in a suitable experiment.
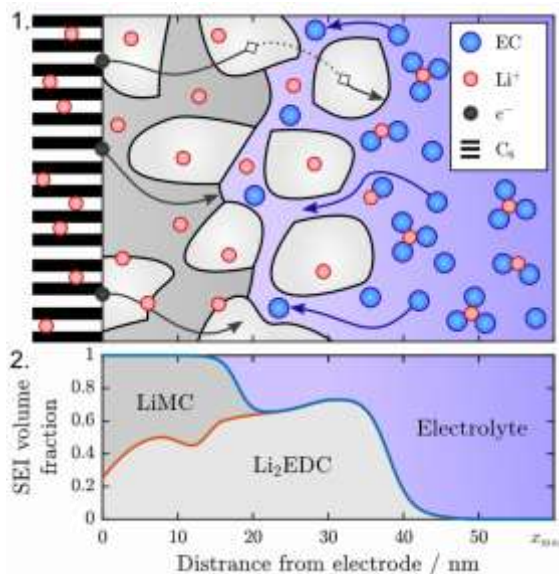
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# Electrochemical pressure impedance spectroscopy (EPIS): A promising tool for model parameterization and validation

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Electrochemical impedance spectroscopy (EIS) is a widely-used diagnostic technique to characterize electrochemical processes. It is based on the dynamic analysis of two electrical observables, that is, current and voltage. Electrochemical cells with gaseous reactants or products (e.g., fuel cells, metal/air cells, electrolyzers) offer an additional observable, that is, the gas pressure. The dynamic coupling of current and/or voltage with gas pressure gives rise to a number of additional impedance definitions, for which we have introduced the term electrochemical pressure impedance spectroscopy (EPIS) [1,2]. EPIS shows a particular sensitivity towards transport processes of gas-phase or dissolved species, in particular, diffusion coefficients and transport pathway lengths. It is as such complementary to standard EIS, which is mainly sensitive towards electrochemical processes. This sensitivity can be exploited for model parameterization and validation.

A general analysis of EPIS is presented, which shows the necessity of model-based interpretation of the complex EPIS shapes in the Nyquist plot (cf. Figure). We then present EPIS simulations for two different electrochemical cells: (1) a sodium/oxygen battery cell and (2) a hydrogen/air fuel cell. We use 1D or 2D electrochemical and transport models to simulate current excitation/pressure detection or pressure excitation/voltage detection. The results are compared to first EPIS experimental data available in literature [2,3].
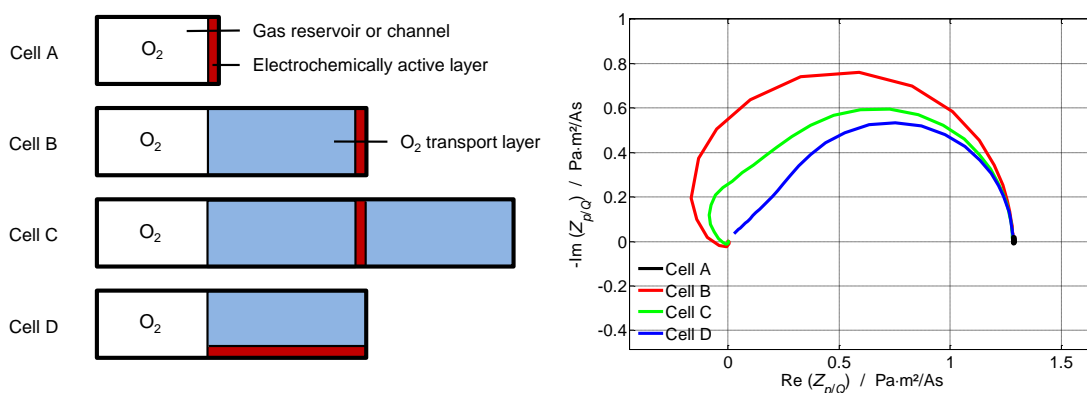


Figure: Typical transport situations in metal/air battery or fuel cell cathodes and their corresponding EPIS response in the Nyquist plot.

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# Measurement method for locally resolved current density measurements in redox flow cells and stacks

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Renewable energy sources such as solar power and wind turbines require large-scale energy storage systems to balance fluctuations in energy generation. Vanadium redox flow batteries are one of the most promising energy storage technologies for stationary applications. On the way to commercialization there is the challenge to transfer the results from laboratory cell to stack size. Inhomogeneous conditions in every single half-cell cause a nonuniform flow of electrolyte. This results in local overpotential and in degradation of the electrolyte, by which process flammable gases may occur.

In our study, a segmented electrode on a printed circuit board (PCB) was developed to illustrate the current density distribution and hence to draw conclusions from the flow behavior in a 40 cm² cell. This technique is used for fuel cell research since 1998 [1]. To avoid any smear of the signals and to increase the measurement quality the printed circuit board is directly installed as bipolar plate in the cell.
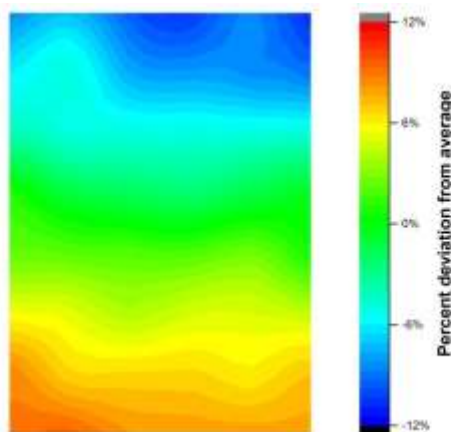


*Figure 2: Current distribution of a 40 cm² laboratory single cell, using heat treated (400 °C/ 1 h) GFA 5 graphite felt (SGL Carbon) and Fumasep FAP-450 membrane (fumatech®). Test conditions were discharging at SOC 80 with 100 mA cm⁻² and 5 mL min⁻¹. The electrolyte inlet is at the bottom of the chart, outlet at the top.*

When measuring in the mass transfer limited region Figure 1 shows an expected gradient of current density. At inlet, the currents reach a maximum density and show a continuously depletion to the outlet. Few studies to local current density measurements in redox flow batteries have been published so far [2], [3]. In this study, a segmented measurement method will be presented which may be used in stack setup, too. To prevent any corrosion of the PCB, it is protected by a coating. This chemical stable but electrical conductive coating is used for segmented electrode like a conventional but segmented bipolar plate. By this new layout, the measurement technique can be used for locally resolved measurements for single cells or stacks.

This measurement method affords to improve flow geometry of a redox flow battery. Furthermore, the printed circuit board helps to investigate the influence of different material properties such as compression of the porous graphite felt or battery properties such as flow rate.

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# Investigation of mass transport through Nafion® 115 in the vanadium redox flow battery

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Abstract text: A model explaining the water transport mechanism through Nafion® 115 is developed to examine the deviation of the amount of each electrolyte for the all vanadium redox flow battery (VFB) in the long term cycles. We develop transient model to explain capacity loss during operation and water transfer through the membrane considering effect of species transport, electro-osmotic drag, and convection. At first, we examine self-discharge phenomena across the membrane to understand the distribution of vanadium ions at each electrode. When the state of charge is 0, the amount of transfer of $V^{4+}$ from positive electrode to negative electrode is larger than that of $V^{3+}$ from negative electrode to positive electrode due to different diffusion coefficient. These ions transfer result in the higher concentration at anode side, so that more water accumulated at anode side. During charge-discharge process, however, larger amount of water is transferred from negative side to positive side. This is result from the net transfer of vanadium is from negative to positive electrode. Moreover, the amount of water at anode side increase and that at cathode side decrease at charge, and vice versa at discharge process. This is because of water transfer by electro-osmotic drag which is dominant factor for water transfer during charge-discharge process. Therefore, the amount of water accumulated at each side is depending on the sign of the current. It also shows that if the current density is increased, the difference of electrolyte amount at reservoirs is growing bigger. The model includes the convection effect which is resulted from the difference of hydraulic pressure. Lastly, we suggest semi-empirical equation to predict the changes of water volume at each reservoir according to operating condition. The findings of this study can contribute to long term stability of the electrolyte.

# Modeling of porous media effects on transport processes in sodium sulfur batteries

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Sodium sulfur batteries (NaS) have been identified as good candidates for power storage and load leveling for renewable energy sources such as wind and solar due to their low cost and relatively high power density. NaS batteries typically operate above 300°C and are comprised of liquid electrode materials suspended in porous media with an inert gas being present to fill the leftover void due to liquids being incompressible. The sodium anode and the sulfur/sodium-polysulfide cathode are separated by a solid electrolyte made of beta-alumina or NASICON material. Due to the presence of porous media, liquid and gas phases, capillary pressure and the resulting capillary action become important. Because of the exponential dependence of capillary pressure on wetting phase saturation, sharp concentration gradients are likely to occur between the inert gas and the electrode material. Such gradients may result in areas of high electrical potential variation, which in turn may lead to locally increased reaction rates. High reaction rates in the cathode can cause overconsumption of sodium during discharge, preventing sodium from penetrating the entire depth of the cathode. During charge, high reaction rates cause sulfur to accumulate on the electrolyte surface at a rate faster than the sodium-polysulfide can displace it producing an insulating effect. These phenomena can cause a compounding effect of higher potential variations, which can lead to decreased efficiency and may eventually lead to failures. To investigate these phenomena, a porous media flow model is developed and implemented into a three-dimensional, time dependent, multiphysics model for sodium sulfur batteries. Transport equations for charge, mass and heat transport are discretized using the finite volume method and then solved simultaneously in a time marching fashion. Mass transport is coupled with charge transport via Faraday's law. Darcy's law is used to model capillary action within the porous media between the wetting phase (liquid) and non-wetting phase (inert gas). The porous media model is coupled with the continuity equation and with a separate diffusion equation which is solved only within the liquid phase. Predicted cell performance is compared to experimental data and previous models available in the literature. Once the model is verified and validated against this data, the distributions of concentration, overpotential and reaction rate within the cell are studied throughout the range of the charge/discharge cycle for multiple current densities. Alternative electrode designs are suggested and studied to improve cell performance and reduce the risk of failure.

# Two-dimensional multiphysics simulation of Li-air button cells for electrolyte choice and electrode design

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Lithium-air cells are considered as a promising alternative to the currently popular Li-ion cells due to their much higher theoretical capacity [1]. Consequently, there have been intensive efforts to identify appropriate electrodes, electrolytes, and additives to enhance Li-air cell durability and performance [2]. However, in order to have a deeper insight in the complex interaction between various cell components, an investigation of a full cell prototype is required. In this study, with the help of a two-dimensional multiphysics model, we have investigated the effect of the choice of electrolyte (species transport) and electrode geometry (electrode design) on the performance of a lithium-air button cell. Fig. 1a shows the schematics of the axisymmetric computational domain. A comparative analysis of five different electrolyte classes was carried out, including water, ionic liquid, carbonate, ether, and sulfoxide. The study focuses on the 2D distribution of local current density and concentrations of electro-chemically active species ($O_2$ and $Li^+$) in the cell. Using two different cathode configurations, namely, flooded electrode and gas diffusion electrode (GDE) [3] at different cathode thicknesses, the effect of cell geometry and volume fraction of electrolyte on cell performance was explored. Furthermore, a detailed discussion on local current density distribution (cf. Fig. 1b) and electrode volume utilization is presented towards understanding the design induced performance limitations in a Li-air button cell prototype.



(a)                    (b)
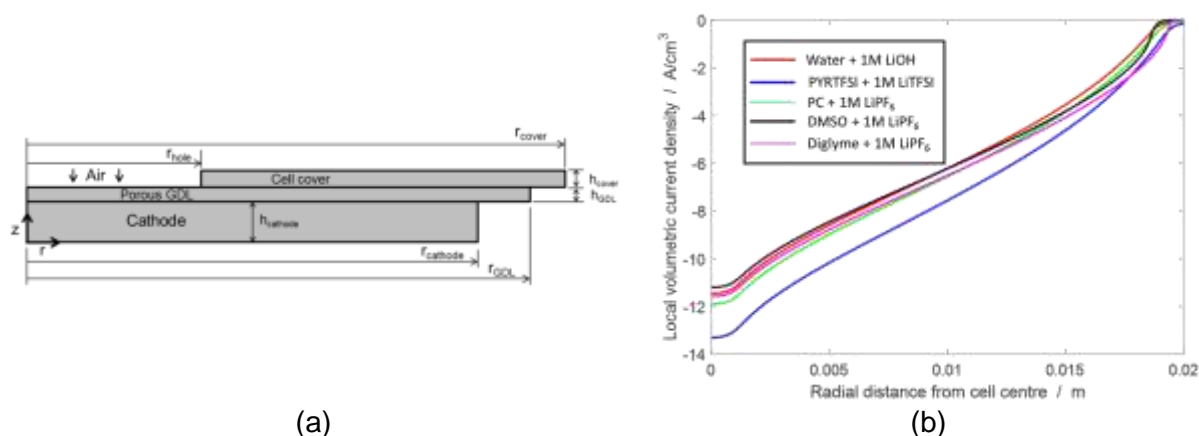
Figure 11: (a) Schematics of the 2D computational domain, (b) Radial distribution of local current density at the cathode-separator interface ($z = 0$) for 5 different electrolyte classes.

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# On the charging behavior of a multi-radii Newman-type battery model

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The aim of the work is the comparison between two reduced models of lithium-ion-battery cathode. The two models are of Newman-type. The first model is the extended pseudo two-dimensional (P2D) model which includes a homogenized electrolyte phase, a homogenized phase for the transport of electrons and microscopical spherical particles of active material with different radii [1]. The second model is a three-dimensional model with a homogenized electrolyte phase and carbon black phase and microscopic particles of active material.

In this talk, we present a finite element implementation of the P2D model including an a posteriori error estimation that separates the errors due to the space and time discretizations and the error due to the use of a finite number of particles. In fact, in the homogenized model an infinite number of particles is distributed along the electrode, while in the numerical realization only a finite number is implemented. We show numerical results of the many particle behavior of the model. In particular, the different behavior of the small and large particles depending on the open circuit voltage (OCV) curve. The effective parameters for the transport processes are obtained by computations based on reconstructions of real microstructures obtained by tomographical techniques such as focused ion beam (FIB) and scanning electron microscope (SEM). For these 3D computations, we use the extended finite element method that allows to define the microstructure by a level set function [2].
In addition, we show the first improvements on the 3D partially homogenized model and discuss some numerical challenges in the simulations of the considered electrochemical processes.

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# A Fully Coupled Electro-Chemo-Mechanical Model for Ion Transport in Solid Electrolytes at Large Strains

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Solid state batteries are gaining increasing attention due to their enhanced safety properties and their potential for high energy densities when using a lithium metal anode combined with a solid electrolyte separator that prevents dendrite growth. The solid electrolytes can be single ion conductors or those consisting of solid solvents with both mobile anions and cations. Especially for the description of the latter case, mechanics cannot be neglected or treated in a simplified manner as is usually done for liquid electrolytes, see e.g. [1], since an influence of stress gradients on ion transport is expected.

In this contribution we present a fully coupled electro-chemo-mechanical modelling framework for ion transport at large strains in solid electrolytes consisting of a solvent with two or more ionic species. Drawing on ideas presented by Bucci et al. [2], we formulate a transport theory in terms of electric field, mechanical deformation and anion and cation concentrations and follow the thermodynamically rigorous approach used e.g. by Dreyer et al. [3] to derive suitable constitutive relations for the fluxes of the different ionic constituents of the electrolyte based on the gradients of the respective electrochemical potentials.

The resulting model is capable of a fully coupled electro-chemo-mechanical description of ion transport including the formation of electrical double layers. Based on the dependence of the mechanical part of the free energy on the ion concentrations, the model also consistently predicts the coupling between species transport and stress gradients and gradients of material properties as observed e.g. in the context of lithium diffusion in active particles [4] or the swelling mechanism in polymeric gels [5].

Finally, we discuss the consistent introduction of a local electroneutrality condition and show representative numerical examples for a binary solid electrolyte consisting of a solid solvent with mobile anion and cations with results that highlight the features of our model.

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# Numerical simulation and optimization of lithium-ion batteries on the microscale

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Due to its high delivered energy density and rate capability, lithium-ion batteries are representing an attractive secondary energy storage system not only for portable electronic devices, but also for electrically powered vehicles. In order to further enhance its attractiveness for the mentioned applications the increase of the delivered energy density and its high-rate capability are representing key challenges in further development of lithium ion batteries. It is well known that the performance of the cathode active material is mainly influenced by its poor intrinsic electrical conductivity, ranging from $10^{-11}$ S m$^{-1}$ for $LiFePO_4$ to about $10^{-3}$ S m$^{-1}$ for $LiCoO_2$ [1]–[4]. Therefore usually it is inevitable to introduce electro-conductive additives like carbon black [5] into the cathode electrode in order to form a conductive network. As these additives are electrochemically inert, its fraction belongs to the passive material part of the battery, which in general lowers the battery's energy density. A possible approach to lower the necessary amount of electro-conductive additives is to numerically estimate an optimized spatial distribution within the electrode microstructure.

Therefore a spatially resolved three-dimensional micro-scale model of a lithium ion battery half-cell, focusing on the positive electrode, was developed following a bottom-up approach. Our model is made up of two non-overlapping subdomains, a solid cathode consisting of smooth spherical particles following a monomodal particle size distribution and a liquid electrolyte subdomain filling the pore volume in between the electrode particles, respectively. The cathode is assumed to consist of $LiMn_2O_4$ as active material and the separator is modelled by effective transport properties. In order to make the numerical results obtained from the microscale simulations representative for macroscopic cells the computational domain is designed as a unit cell which can be periodically extended in x- and y-direction.

In this talk our focus will be on a proposal of a numerical optimization approach for the local conductivity distribution within a given electrode microstructure.

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# A novel concept for the discretisation of the coupled Nernst-Planck-Poisson-Navier-Stokes system

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We propose a novel approach for the discretisation of the system which arises from coupling a modified Nernst-Planck-Poisson equation, taking into account finite ion size and solvation effects, with the Navier-Stokes equations. Such a model describes electro-osmotic flows through nanopores of fuel cell membranes and other situations where the Coulomb force arising from charge carrier polarization interacts with the momentum balance of the flow.

The new approach employs recently developed pressure-robust mixed finite element methods [1] that might be beneficial in the handling of the Coulomb force. These methods allow for a simple and local post-processing of the discrete velocity resulting in a divergence-free discrete velocity field which enters the advective part [2] of the Nernst-Planck equations. These are discretised by an exponentially fitted finite volume method based on a Voronoi tessellation of the domain [3]. The main advantage of the combination of the these two methods is the preservation of qualitative physical properties such as maximum principles, nonnegativity,  boundedness of concentrations and thermodynamic consistency.

We present first simulation results based on this new coupling approach and discuss the influence of a number of model parameters (ion sizes, pore geometry, wall charges) on the calculated results.

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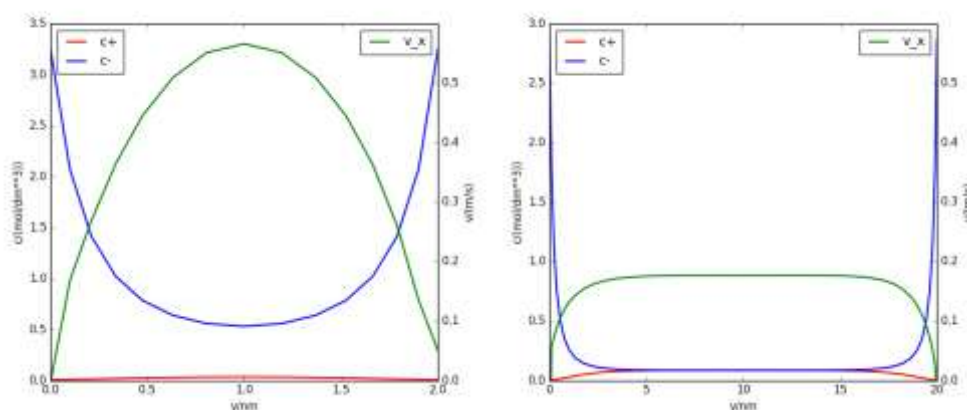
Fig 1:  Ion concentration and velocity profiles for an electroosmotic flow of a binary electrode through a nanopore with charged walls obtained by numerical simulation using the novel coupling concept. Left: pore width 2nm, right: pore width 20nm.

# Understanding the performance bottleneck in Li-S batteries: a model-informed approach

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Lithium-sulphur (Li-S) batteries could provide the next step-change in battery technology with a promising practical energy density of 500-600 Wh/kg. However, further improvement in the energy density and cycle-life of Li-S cells is arguably held back by a lack of understanding of their complex charge/discharge mechanisms. Acquiring this knowledge requires experimental characterizations in tandem with mathematical modelling.

In this presentation, we demonstrate the key factors determining the cycle-life and rate-capability of Li-S batteries through experimentally validated Li-S models. A zero-dimensional model accounting for degradation due to precipitation as well as polysulfide shuttle was developed to interpret the complex behaviour observed in cycling experiments and to distinguish between reversible and irreversible degradation. This model provides a tool for knowledge based choices between improving performance and sacrificing power or energy, such as through the introduction of recovery cycles. In addition, a one-dimensional model was developed to capture the limited rate-capability of Li-S cells caused by slow ionic transport. The model suggests polysulfide species remain in the separator due to mass transport limitations towards the end of discharge, but the resulting 'lost' capacity can be recovered through relaxation, which was then validated experimentally. Finally, we discuss the modelling of precipitation-induced electrode surface coverage, which we show to affect the discharge capacity and the charge characteristics of Li-S cells.

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# Measurements of Stress and Strain in Electrode Materials of Lithium-Ion Batteries

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Lithium insertion and extraction into/from electrodes of lithium-ion batteries leads to volume changes and mechanical stresses. The stresses are strongly coupled to the electrochemical processes and can cause mechanical damage. Knowledge of these stresses is not only important for assessing the reliability of an electrode material but also may be used in to infer the physical processes that govern electrode operation. Unfortunately, the measurement of stresses and strains is challenging inside a working battery. We have developed a setup for *in situ* light microscopy that can be used to measure local strains. In our setup we image electrodes at the resolution limit of light and use digital image correlation to measure local strains. In the talk, this technique will be illustrated by results showing the degradation of secondary particles of high nickel NMC. Besides *in situ* light microscopy also substrate curvature measurements can be used to directly measure mechanical forces inside electrodes. Our home-built substrate curvature setup can work with conventional electrodes and allows us to track mechanical processes in electrodes in real time. In this talk this laser based technique will be introduced and stress data from different electrode materials will be presented. The resolution of this technique is demonstrated using the zero-strain material $Li_4Ti_5O_{12}$ (LTO). Results on the stresses evolution of silicon and germanium show very high stresses and plastic deformation materials during electrode operation. Using silicon, it will be demonstrated that mechanical stress can serve as a physical probe that helps in the investigation of fundamental electrochemical mechanisms.

# Battery electrode imaging in 3D: Field of View or Resolution ?

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There are different ways to create a 3D image of the battery electrodes.

MicroCT uses the absorption of X-rays to create a 3D reconstruction. The Field of View is large enough to be representative with regard to the grain sizes (1). However, the submicron porosity in the electrodes is typically not well captured by microCT because of its limited resolution.

The FIBSEM technique which uses a Galium ion beam for sectioning and an electron beam for imaging has high enough resolution to resolve all porosity. However, the Field of View is typically of the order of 10 micrometer; which is not big enough to create a representative model of the pore space.

In this study we have used a plasmabeam for sectioning and an electron beam for imaging. The plasmabeam typically removes a layer of 100 nm followed by imaging by the electron beam. The material removal rate with the plasmabeam is magnitudes higher than with the Ga focused ion beam, allowing to expand the field of view to hundreds of micrometers.

A 3D reconstruction of the anode (Field of View 200micrometer) and the cathode (Field of View 100 micrometer) make it possible to calculate parameters such as the tortuosity on a representative volume.

Segmentation of the pore space is not straightforward due to minimal grey level differences between the different phases. Also, it is not uncommon to see details from layer N+1 through the pores in layer N. This so-called pore-back effect must be taken into account otherwise the permeability will be greatly underestimated.

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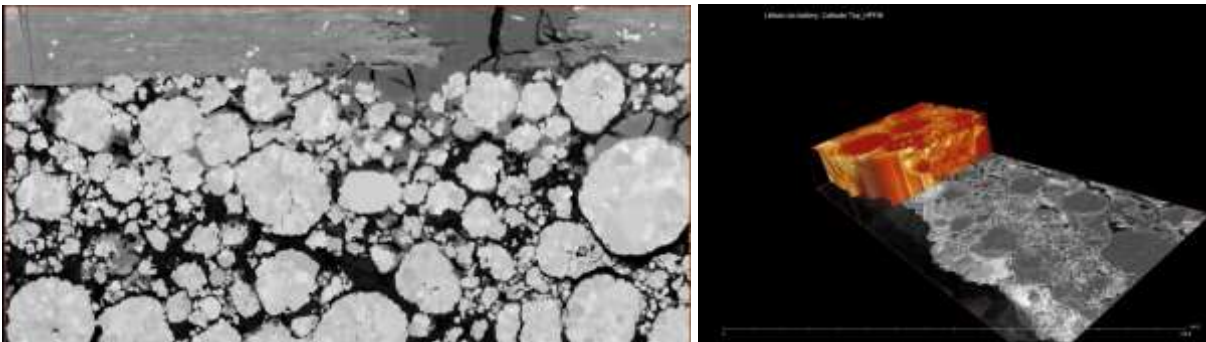


100 micrometer Field of View section through the 3D volume of the active cathode material with 3D reconstruction of the pore space.

# Mathematical Model of Binder Distribution During Drying of Lithium-Ion Battery Electrodes

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Electrodes are manufactured by coating a current collector with a slurry mixture, comprised of active material particles, conductive carbon nano-particles, polymer binder and solvent. This mixture is then dried (i.e. the solvent evaporated) by exposure to heat, and sometimes a reduction in pressure. The drying is a crucial step in manufacturing as it can affect the component distribution within the electrode. Phenomena such as binder migration during drying can have negative effects, in the form of poor cell performance or mechanical failure such as electrode peeling and cracking [1, 2]. Despite the importance of the drying process on the microstructure of the product, studies on electrode drying are scarce. As far as the authors are aware, theoretical models detailing the physical mechanisms governing the evolution of the component distributions during drying are as yet unestablished.

We will present a model based on first principles describing the evolution of the binder concentration in the electrode during the drying step of manufacture. Solutions of the model predict that low drying rates lead to a favourable homogenous binder profiles across the electrode film (Fig. 1, left panel), whereas high drying rates tend to unfavourably accumulate the binder near the evaporation (top) surface (Fig. 1, right panel). These results show strong qualitative agreement with the experimental data in [1], thereby providing a cogent explanation for why poor electrodes can result from fast drying conditions in practical applications. We will conclude by sketching ideas on how the model could be used to optimize the drying process and by discussing possible extensions of the model.
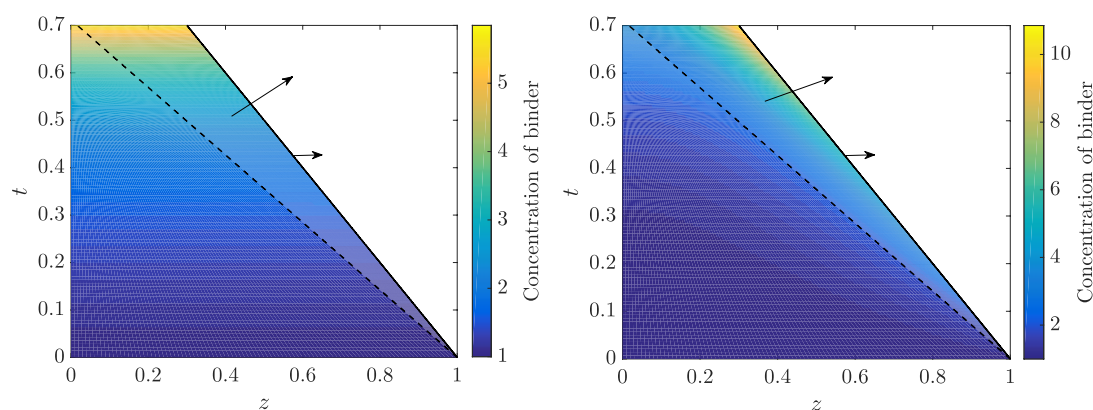


Figure 1: Concentration of binder in the electrode at low (left) and high (right) drying rates, where $z = 0$ represents the bottom and $z = H(t)$ (black solid line) the receding evaporation electrode surface. The black-dashed line represents the interface between a consolidated solid-like layer (crust) and a dilute liquid-like layer (colloid) occurring within the electrode as drying evolves.

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# Combined Impedance Study (EIS) and microstructure analysis (FIB/SEM) of intercalation electrodes: Determination of charge transfer parameters

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Lithium-ion batteries allow for a broad range of power to energy ratio, i.e., originating from their flexibility in terms of (positive) electrode material, blend ratio, and microstructure design. Electrode models, which consider the required functionality in an appropriate way, are mandatory for optimization. Among them, electrochemical models are based on fundamental equations describing migration, diffusion and intercalation kinetics.

A crucial and challenging part of the model development is its' parameterization. Material parameters, especially for (positive) intercalation electrodes, are hardly available from literature and/or the variance of the available values is (too) large, as discussed in [1].

The present work investigates the charge transfer process taking place at the interface between a (positive) electrode material and the liquid electrolyte. The model parameters (i) area specific charge transfer resistance (ii) exchange current density $j_0$ and (iii) rate exchange coefficient k are determined using a combination of focused ion beam milling (FIB), electrochemical impedance spectroscopy (EIS) and time domain measurements (TDM). The microstructure parameters tortuosity, porosity and active surface area are determined from a 3-dimensional reconstruction of the electrode and the measured impedance spectra are fitted with an appropriate transmission line model (TLM). These methods have already been applied by our group for the investigation of battery electrodes [2, 3] but a combination of both methods has not been performed so far. By correlating the microstructure parameters (obtained by FIB) with the loss processes (obtained by EIS) the required material parameters for modelling the charge transfer process became accessible.
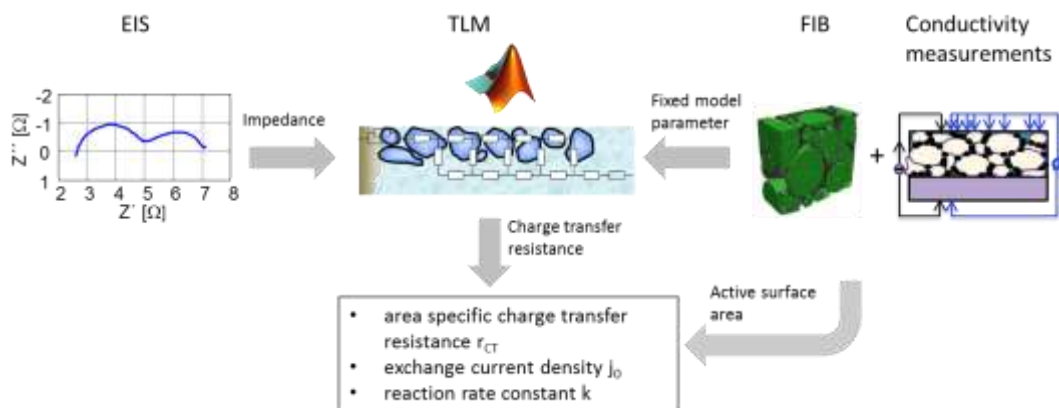


*Figure 12: Approach of this study: Impedance of the cathode is measured by EIS and evaluated by the TLM; Microstructure parameters are obtained by FIB-tomography and conductivity is measured and applied to the model. Finally the area specific charge transfer resistance $r_{CT}$, exchange current density $j_0$ and reaction rate constant k can be calculated.*

For validating the reliability of the presented approach, six cathodes of the ($Ni_xMn_yCo_{1-x-y}$) solid solution system with varying microstructure are examined and compared yielding very low variance compared to values from literature.

**References**
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[2]   M. Ender, J. Joos, T. Carraro and E. Ivers-Tiffée, *J. Electrochem. Soc.* **159**, A972-A980 (2012)
[3]   J. Illig, M. Ender, A. Weber, E. Ivers-Tiffée, *J. of Power Sources* **282**, 335-347 (2015)

# Transient Lithium Ion Battery Behavior Simulations Through Electrochemical Modelling

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The future of electric vehicles is mostly related to the battery improvement. The simulations are helpful to improve the knowledge of electrochemical phenomena, optimize the design and predict the behavior during dynamic cycling. Indeed, the mathematical models are crucial for the state-of-charge and state-of-health indicators used in any Battery Management System.

In the present study, one of the most common porous electrode based electrochemical model [1-4] is set in a dimensionless form allowing to decrease the number of parameters. Then, the numerical exploration allows to identify the impact of each dimensionless parameter responsible for each different transport limitation. The discussion is then focused on how these different transport limitations rule the polarization and relaxation during the impulsion-rest sequence simulations (Fig.1).

The results are compared to the measures on LG 18650 NMC cells, as reported in Fig.2. The simulations are run with the Comsol® language and the post-processing with MatLab®. This manuscript is part of a PhD partnership project between Renault, the French Atomic Commission (CEA) and the LEPMI laboratory of Grenoble.
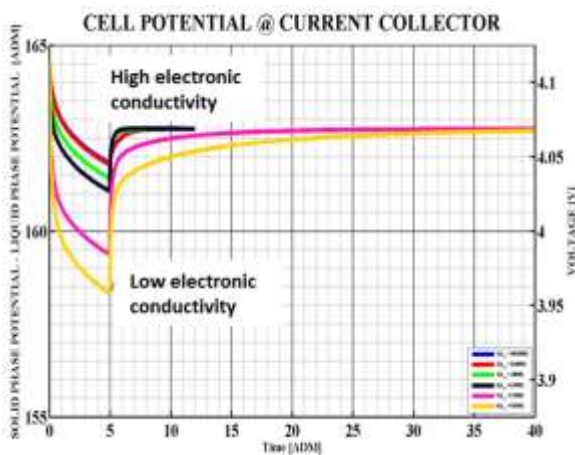


Fig.1 – Dynamic impulsion behavior governed under electron transport limitation.
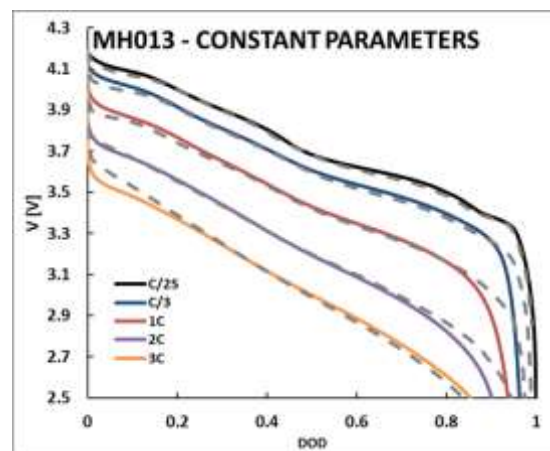
Fig.2 – LG 18650 C-rate cartography compared to simulations.

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# Parameters Controlling the Fast-Charging Limitations for Lithium Ion Batteries and their Temperature Dependence

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Safe operation of lithium ion batteries is achieved by limiting the working potential range of the battery cells. At high currents, internal resistances increase the cell polarization and the cut-off potentials are reached before the full-cell capacity is transferred. Especially at high charging rates, i.e., deintercalation from the cathode host material and intercalation into a commonly used graphite based anode, the cell polarization can become substantial and hinder faster cell charging.

We will illustrate that the cell polarization at higher C-Rates (> 1 C) depends mainly on the electrolyte transport parameters, namely the binary diffusion coefficient, the transference number of the lithium ion, the thermodynamic factor, and the electrolyte conductivity as well as the geometric constraints of the electrode, i.e., tortuosity, thickness, and, porosity.

Thus, for precise simulations of a lithium ion battery with predictive capabilities, it is necessary to know both electrolyte transport and electrode geometrical parameters, which have been under investigation in our group based on new experimental methods[1,2] as well as by employing known techniques. We will present an overview of our results on electrolyte transport parameters values for common EC (ethylene carbonate) based electrolytes in a temperature range from 20°C to 50°C in combination with the relevant geometrical parameters of porous anodes and cathodes at different compressions and compositions.



Figure 13. Exemplary relative temperature dependence of binary diffusion coefficient, transference number and thermodynamic factor of 0.1 M, 1.0 M and 2.0 M $LiClO_4$ in EC:DEC (1:1, w:w) in the temperature range from 20°C to 50°C.

As literature values for currently used electrolytes and electrodes are scarce,[3] we hope our results will help to better understand the sources of cell polarizations. By means of numerical simulations, employing measured rather than approximated parameters, we hope to provide better insights into current lithium ion battery technology, which might help to design improved cells in the future.

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3. L. O. Valøen and J. N. Reimers, *J. Electrochem. Soc.*, **152**, A882 (2005).

# Modeling capacity fade due to SEI formation in Li-ion cells validated by neutron diffraction data

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A one-dimensional physicochemical aging model is developed to simulate capacity fade due to solid-electrolyte interphase (SEI) formation in Li-ion cells. The model considering porous electrode and concentrated solution theory is based on the work of Fuller, Doyle and Newman [1, 2, 3]. Besides the main intercalation/deintercalation reaction, two side reactions are implemented in the anode: The first side reaction describes the existing SEI layer's growth. The second one models SEI layer cracking because of expansion and contraction of the particles during cycling which results in a new SEI layer formation [4]. Both side reactions are implemented by cathodic Tafel reaction kinetics that consume Li-ions. As Li-ions are lost in the film formation reaction, the anode gets less lithiiated in the cell's charged state. With increasing cycle number, both capacity fade and film growth decelerate as the overpotentials of the cathodic side reactions increase. This fact slows down the capacity loss during aging. The model allows estimating both battery life and performance and is able to simulate aging profiles including calendar aging as well as cycle aging with various charge and discharge profiles.

The model is fitted to electrochemical measurement data, in particular to the experimental capacity loss during aging and the voltage profiles of the uncycled and cycled cell. The long term cycling experiment of 18650-type NMC/C cells for 1000 cycles at 23 °C results in a capacity fade of 21 %. Besides this capacity loss, the model predicts a shift in the anode's stoichiometry, which is validated by in situ neutron diffraction data. Neutron diffraction of the uncycled and cycled cell, in their charged state respectively, shows a reduction in the $LiC_6$ weight fraction as well as an increase in the $LiC_{12}$ weight fraction during aging. Hence, a loss of cyclable Li-ions corresponding to a capacity loss of 23 % can be extracted. In spite of this capacity loss, both the anode and cathode materials are scrutinized to be structural stable and no evidence of active material loss is observed in the evaluation of these neutron diffractograms. As shown in the measurement and in the model, SEI formation is considered to be the main aging mechanism. The simulated shift in the anode's stoichiometry is in good agreement with the loss of Li-ions in the anode obtained from the neutron diffraction data.
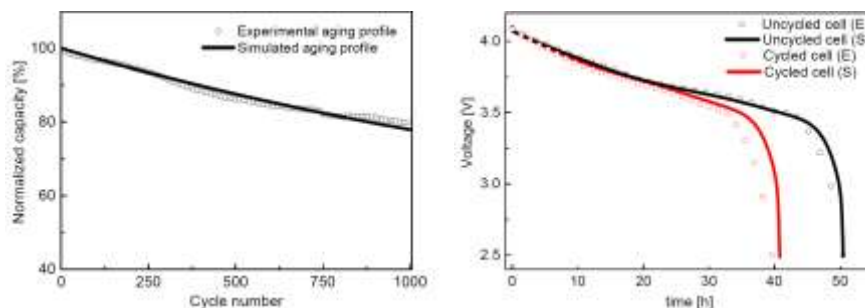
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# Inverse Modelling Approach to Determine Material Properties of Electrolytes: Effects of Faradaic Convection

**A. K. Sethurajan[1], J. M. Foster[2], S. A. Krachkovskiy[3], I. C. Halalay[4], G. Richardson[5], G. R. Goward[3], and B. Protas[*,6]**

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This contribution describes how the concept of *inverse modelling*, developed for electrochemical systems in [1], may be used to systematically assess the validity of different models for the transport of charged species in electrolytes. In combination with experimental measurements of concentration profiles *c(t,x)*, this approach allows us to infer optimal concentration-dependent material properties (diffusivity *D* and transference number $t^+$) for which a given model best fits the data. We consider different models describing the transport of Li ions in an electrochemical cell under galvanostatic conditions derived from the Planck-Nernst equation, cf. Eq (1). The measurements were obtained using $^{19}$F NMR imaging in a *LiPF$_6$* electrolyte solution in *EC/DMC* with *Li* concentration varying in the range 800-1200 mol/m$^3$. In agreement with the principles of Bayesian inference, the uncertainty of reconstruction of the material properties (resulting from measurement errors) is quantified with a Monte Carlo method, so that the obtained reconstructions of *D* and $t^+$ have the form of probability distributions. As is evident from Figure 1a, the standard Planck-Nernst model, obtained by setting *u=0* in Eq. (1a), does not yield physically consistent results, since the optimally reconstructed transference numbers are in fact negative. On the other hand, as shown in Figure 1b, consistent reconstructions are obtained with a recently proposed model involving Faradaic convection [2], for which *u>0* in Eq. (1a). We add that the latter case is also characterized by a significantly reduced reconstruction uncertainty. We will also comment on reconstruction approaches based on models involving ion pairing.

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} + \frac{(1-t^+)I}{FA}\right] \quad \text{in } (0,L)\times(0,T], \qquad (1a)$$

$$\left.\frac{\partial c}{\partial x}\right|_{x=0,L} = -\frac{I}{FAD}(1-t^+) + u \quad \text{in } (0,T], \qquad (1b)$$

$$c|_{t=0} = c_{init} \quad \text{in } (0,L), \qquad (1c)$$
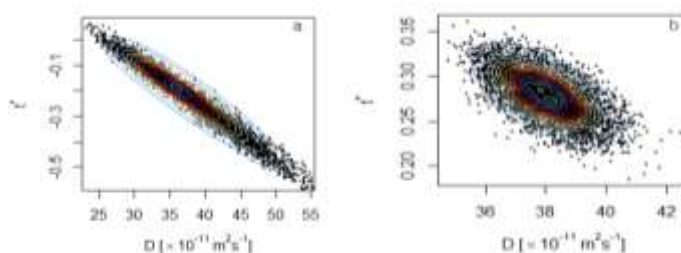


Figure 1. Posterior probability distribution of concentration-independent diffusion coefficient *D* and transference number $t^+$ obtained using a) $u = 0\ ms^{-1}$ b) $u = 3 \times 10^{-8}\ ms^{-1}$ in Eq. (1a). Innermost isolines represent the most probable values of *D* and $t^+$.

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# Passive hybridisation of battery cell and photovoltaic dell: modelling and experimental validation

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Battery systems are increasingly being used for storing fluctuating photovoltaic (PV) electric power, increasing self-sufficiency and self-consumption rates. Both PV and battery costs continuously decrease, significantly increasing market penetration (> 25.000 systems installed in Germany in the past three years) and opening pathways for new system concepts.

We are investigating an alternative topology for a coupled PV battery system by passively coupling PV and battery on the direct current (DC) level (cf. Figure). The approach is based on matching the solar cell's and battery cell's respective current/voltage behavior. The discharge characteristics of a battery cell can allow to run the solar cells close to its maximum power point (MPP) independently of the external power consumption. At the same time, upon battery full charge, voltage increase will drive the solar cell towards zero current and therefore self-prevent overdischarge.

Based on a modeling and simulation study [1], we have established an experimental setup for combining single PV cells with a lithium-ion NCA/LTO pouch cell. Different cell configurations were tested under real conditions during summer 2016. A battery cycler is used to simulate either constant power consumption or dynamic power profiles representing a scaled single-family house. The feasibility of the system could be shown.
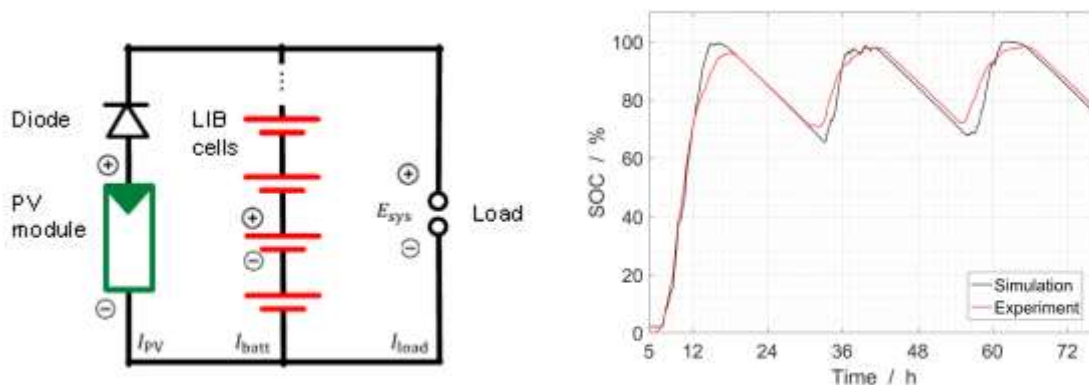


Left: Approach for passive hybridisation of PV cell and battery cell. Right: Simulated and experimental SOC over three summer days with a constant load.

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# A Computational Model for Thermal Management of Battery Storage Systems

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Fossil fuel based power generation causes air pollution and climate change. The consequences of these two factors are of at most importance for future generations. Thus, renewable energy sources can play a significant role by reducing the dependence on fossil fuels. However, if the energy storage problem is not solved renewable sources will not be useful. Sodium sulfur battery (NaS) is one of the practical solutions to store wind and solar energy. A NaS battery is comprised of two liquid electrodes and one solid electrolyte which operate between $300 - 350 \, ℃$. The molten sodium is in anode electrode, the molten sulfur and sodium-polysulfide are in cathode electrode, and solid electrolyte which is made out of beta-alumina or Nasicon material is between anode and cathode.

The purpose of this study is to develop a computational model for a NaS battery block which includes multiple cells and to predict the temperature inside the block during the operation cycles. The temperature distributions are calculated using a newly developed three-dimensional thermal model which takes cell temperatures as input from a lumped electrochemistry model. The properties required for solving governing equations are calculated and updated as a function of time and temperature based on the composition of each control volume. The lumped model is validated against experimental results from the literature. The 3D thermal model is used to perform a parametric study on key stack properties. The newly developed algorithm is robust and can be used for stack design analysis and improvement. An example validation case is shown in Figure 1 for a laboratory scale single NAS battery cell.



(a)                                             (b)
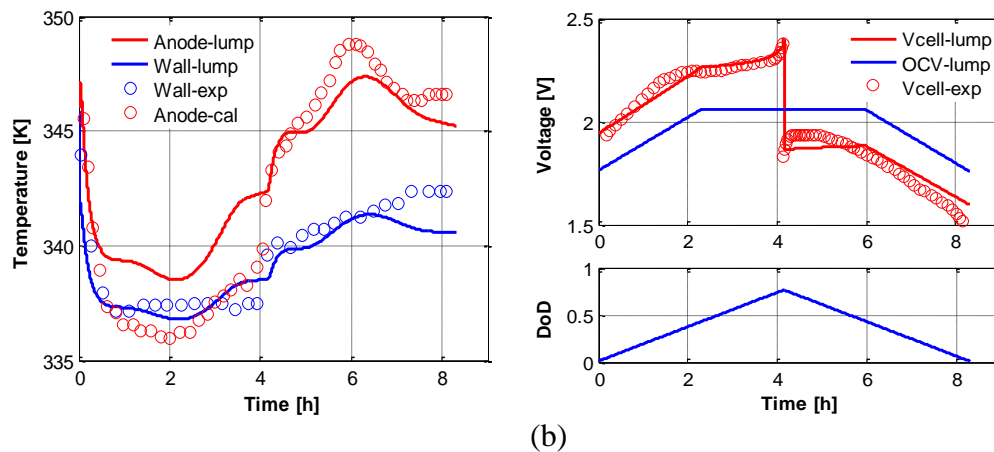
**Figure 1 -** (a) Temperature (b) Voltage & Depth of discharge for $i = 130/130 \, mA/cm^2$. (Experiments by Kawamoto and Kusakabe , Journal of ECS , 1989),

# Thermal management of Automotive Li-ion cells based on simulation-assisted geometry optimisation

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Increasing challenges for current Automotive Li-ion batteries, like fast charging capability, recuperation or charging at low temperatures, imply an increased complexity of the thermal management. The optimal design requires profound knowledge of the thermal processes within the batteries, since the electrochemical reactions, as well as the material parameters are highly temperature dependent, which influence the reliability, safety, performance and lifetime. Therefore, simulations of Li-ion cells need highly detailed thermal models. The inner geometrical structure of Li-ion cells has a high potential for improvement regarding optimal heat transfer paths and the connection to temperature control concepts. These influences on the thermal behaviour of large Li-ion cells can be calculated based on a detailed parametric implementation within an automated numerical simulation environment. For each component, especially the active materials within the cells, temperature-dependent and anisotropic material parameters are experimentally determined and implemented.
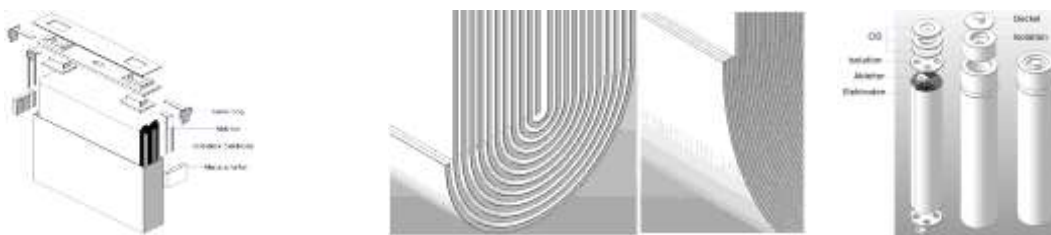


In this contribution a development tool is presented, which adaptively generates, meshes and simulates models of Li-ion cell designs, like cylindrical cells, prismatic hardcase cells or pouchbag cells. Each cell component can be modelled independently. For instance the influence of the design of the current collectors, the size and position of the jelly roll or the interface between the stack and the cell housing can be examined. The temperature of each inner cell component can be calculated. Single cells can be arranged to battery modules and connected to a variety of temperature control applications. At the cell surfaces a thermal resistance can be applied to simulate the thermal behaviour and interaction of each cell with the battery module and the temperature control applications, respectively. Such highly resolved thermal modelling is numerically complex but the modular and scalable simulation environment can be used to develop faster submodels with less geometrical resolution but comparable thermal behaviour, which can be coupled with detailed electrical or electrochemical models. Therefore, different thermal management strategies can be systematically investigated.

# Simulation of the coupled electro-thermal transport processes in generic anode structures of Li-ion cells

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The electrochemical behaviour and lifetime of Li-ion battery cells are strongly depending on thermal aspects like heat generation, thermal material properties and temperature control concepts. In this context, numerical simulation of the multi-physical coupled transport processes is an important tool to analyse and predict the behaviour of Li-ion cells. A frequently used modelling simplification of the electrode particles is the assumption of ideal spherical shaped particles with isotropic transport properties. Especially in case of graphite based anodes, this is a significant deviation from the actual characteristics of most types of graphite.

In this work the influence of non-spherical particle shape and anisotropic transport properties of the anode particles on the coupled electro-thermal performance of Li-ion cells is evaluated. Therefore, a three-dimensional generic particle model (GPM) was developed, which couples the electrochemical charge transfer at the solid-electrolyte interface with the lithium transport as well as the charge balance in solid and electrolyte phase. These processes of the galvanic electrode unit cell are again coupled with the primary heat generation and temperature distribution.

Using the GPM, the behaviour of different generic particle geometries (e.g. ellipsoid shape or flake like shape) with anisotropic transport properties are investigated and compared to the reference case of spherical isotropic particles. Based on parametric studies of particle size, shape and distribution as well as material properties, significant influences both on the local electro-thermal behaviour (i.a. the Li-intercalation and current distribution) and the overall performance of Li-ion cells are identified. Furthermore, the basic influence of different variations of the inter-particulate interaction on the model behaviour was investigated.

# Modelling and simulation of the thermal abuse of Lithium-ion batteries

## C. Ziebert*[1], M. Melcher, M. Rohde[1], H.J. Seifert[1]

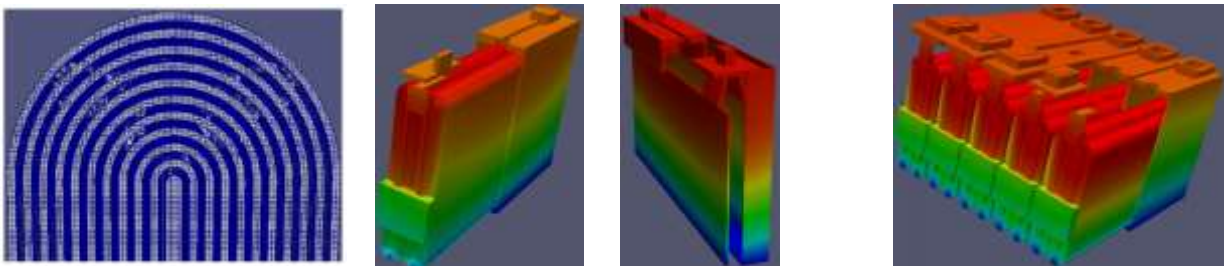[1] Karlsruhe Institute of Technology, Karlsruhe, Germany

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Lithium-ion batteries (LIB) have found a wide range of applications in the last three decades, like notebooks, cell phones, powertools or hybrid or fully electric vehicles. The thermal runaway of a single cell in a larger battery pack is the worst case scenario which must be avoided under all circumstances. Several exothermic reactions can occur as the inner cell temperature is increasing during thermal abuse. If the heat generation is larger than the dissipated heat to the surroundings, this leads to heat accumulation in the cell and acceleration of the chemical reactions, which can end up in a thermal runaway if the point of no return has been overcome. In this work the coupled electrochemical-thermal model for a Lithium-ion battery (LIB) based on porous electrode theory has been extended with contributions coming from exothermic side reactions based on an Arrhenius law to model abuse mechanisms, which could lead to a thermal runaway. These extensions have been modelled with a constant fuel model and for specified current profiles and exterior temperature profiles to simulate cell cycling under adiabatic conditions or an oven test respectively. The model has been implemented into COMSOL Multiphysics® (version 5.2) using the Battery and Fuel Cell Module coupled to the Heat Transfer in Solids Module. For a cylindrical 18650 cell with a $LiCoO_2$ cathode the spatial overall mean cell temperature during the time evolution of a thermal runaway has been computed [1]. Moreover the different stages of the thermal runaway have been classified (s. Fig. 1). Finally the simulation results will be compared with experimental measurements that have been performed in an ARC.
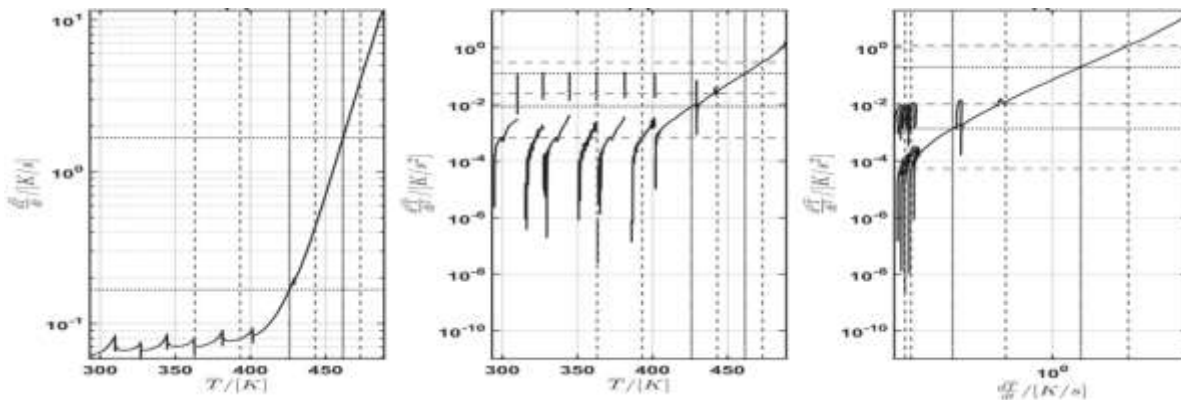


Fig.1 Two-dimensional projections of the phase-space during an oven test thermal runaway:
(a) $\overline{T} - d\overline{T}/dt$ -trajectory, (b) $\overline{T} - d^2\overline{T}/dt^2$-trajectory, (c) $d\overline{T}/dt - d^2\overline{T}/dt^2$-trajectory.

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# Experimental Material Characterization of Lithium-ion battery cells

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Lithium-ion batteries have been widely applied in hybrid and electric vehicles. In order to understand and improve the performance of the battery during cycling, it´s important to study the mechanical behaviour of the battery cells. To enhance the understanding of mechanical response of an entire battery cell, it´s helpful to investigate the mechanical properties of each material used in battery cells separately.

Various mechanical tests were performed on each representative single layer: a copper current collector, a negative electrode layer, a polyethylene separator, a positive electrode layer and an aluminium current collector. Appropriate test methods, including tensile test, compression test and dynamic mechanical analysis, were chosen for each layer by taking account of its material structure and property. The purpose of these tests is to figure out the stress and strain characteristics of the individual component existed in battery cells. Additionally, the thickness changes of the electrodes during charging and discharging were measured since the swelling effect has a significant influence on the mechanical behaviour of the battery cells and may cause high forces if the installation space is limited. In order to understand this effect comprehensively, electrode samples were taken out from battery cells with different State of Health. State-of-Charge-dependent and pre-load-dependent thickness changes of the negative and the positive electrode were measured respectively. Based on the experimental data, a detailed computational material model for each layer will be developed for simulation purpose in the near future.

The present poster demonstrates the experimental results and also shows suggestions for deriving computational models to represent the mechanical behaviour of the materials in battery cells.

# Lifetime Analysis of Lithium-Ion Batteries by OCV-curve Measurements and Impedance Spectroscopy

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Lithium-ion batteries deteriorate in energy and power density with time and area of application. Energy density is linked to the capacity, whereas power density is linked to the internal resistance of a battery. Reasons for capacity loss are: (i) a high overvoltage limiting the usable capacity, (ii) loss of active lithium changing the balance of anode and cathode, or (iii) loss of active mass within one or both electrodes; (ii) and (iii) affect the open circuit potential (OCV). Obviously, identification and quantification of all contributions to capacity loss is important over the entire lifetime of a battery. This task is resolvable by the application of our OCV model full cell [1] based on [2]. The OCV model full cell has to be parameterized at BoL (begin of life), EoL (end of life), or at an individual aging status, and calculates the different contributions to capacity loss depending on the individual loading profile.

The change of cell resistance is determined by impedance spectroscopy (EIS). The individual contributions (i) ohmic resistance R0, (ii) contact resistance between electrode/current collector RCC and (iii) charge transfer resistance between electrode/electrolyte RCT can be quantified, when using the distribution of relaxation times method (DRT) combined with a physically meaningful equivalent-circuit model. [3][4][5]

The capability of this combined approach is demonstrated by characterizing begin-of-life (BoL) and end-of-life (EoL) high-energy pouch cells (KOKAM 560 mAh). The correlation between test profile (temperature, charge/discharge rate and depth of discharge) and predominant aging mechanism for cell capacity and internal cell resistance is quantified and discussed in detail.

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# Lifetime prediction for lithium ion batteries: an impedance based approach

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Lifetime prediction for lithium-ion batteries is an important issue to ensure reliable integration into systems application. Currently, the State of Health (SOH) is used to estimate the actual status of a battery. This value is defined by a global parameter like the inner resistance or the capacity, which is then compared with its value at the Begin of Life (BOL) of the battery. However, depending on the aging parameters applied, the course of the inner resistance with time does not always show a systematic behavior. The contributions to the inner resistance are manifold and show completely different aging behavior. Hence, analyzing the development of the inner resistance with time does not allow a correct prediction of the SOH. In this work, a new approach is presented which identifies the individual contributions to the inner resistance first and ties each to a specific physical loss process. Each process shows a systematic aging behavior.

By the application of Electrochemical Impedance Spectroscopy (EIS) in the high and medium frequency range and a corresponding analysis of the Distribution of Relaxation Times (DRT), the individual contributions  are identified and separated by their different time constants [1,2]: i.e., the ohmic resistance $R_0$, the charge transfer of the cathode $P_{CT,K}$ and the SEI-process of the anode $P_{SEI,A}$. In a next step, their contributions to the inner resistance are quantified using an equivalent circuit model, as shown in figure 1.
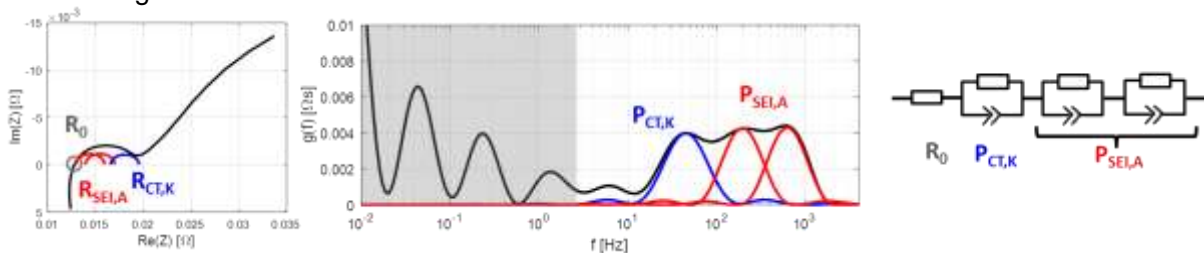


Figure 14: Nyquist plot (left), DRT (middle) and ECM (right)

First results demonstrate the applicability of this approach for a 18650 high power lithium-ion cell, which has been aged by cycling with a discharge current of 4C and a charge current of 1C at 25 °C. The impedance of the battery has been measured in defined intervals and the course of the individual resistance contributions with time for this specific aging type has been analysed. Physically motivated mathematical descriptions have been derived for each of them. In this way, all contributions can be predicted separately (figure 2) and by summation, the SOH can be forecasted too.
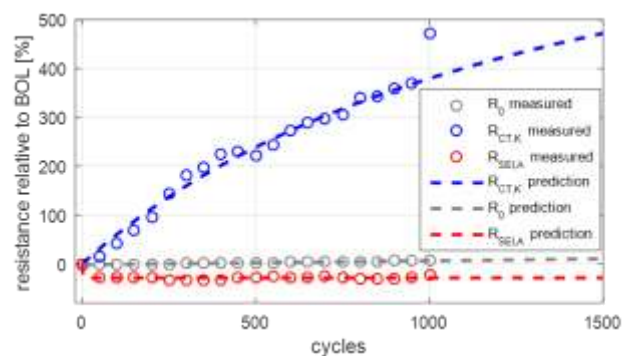


*Figure 15: Measured resistances during aging (circles) and prediction (dashed lines)*

[1] H. Schichlein, A. C. Müller, M. Voigts, A. Krügel, E. Ivers-Tiffée: *Deconvolution of electrochemical impedance spectra for the identification of electrode reaction mechanisms in solid oxide fuel cells.* Journal of Applied Electrochemistry, 32/8 (2002), pp. 875-882

[2] J. Illig, M. Ender, T. Chrobak, J. P. Schmidt, D. Klotz and E. Ivers-Tiffée: *Separation of Charge Transfer and Contact Resistance in LiFePO4-Cathodes by Impedance Modeling.* Journal of The Electrochemical Society, 159/7 (2012), pp. A952-A960

# Cyclic aging studies of 18650 lithium nickel manganese cobalt oxide-based cells: influence of temperature, current rate and depth-of-discharge

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A thorough understanding of aging processes that lead to battery degradation is vital to their acceptance in storage and automotive applications. In this work an extensive study on 78 similar cylindrical 18650 $LiNMCO_2$/graphite cells is undertaken in order to understand the influence of temperature, rate of charge-discharge and depth-of-discharge on degradation during cyclic aging. Cells were aged at 0 °C, 20 °C and 45 °C at 1C and 2C charge-discharge rates for different depth of discharges. The capacity and power fade of the cells were studied by electrochemical characterization techniques such as current pulse tests and electrochemical impedance spectroscopy (EIS) at well-defined charge throughputs.

Overall, the actual cell capacity first shows a slow linear decrease but later the capacity fade is more rapid. The occurrence of this transition depends strongly on the operating parameters. The EIS data were analysed during cycle life with an impedance model whose elements correspond to different processes. The change in the model parameters was quantified for analysis. The degradation in the battery performance is observed to be notably different depending on the operating condition. While high charge rate is found to be highly detrimental to the cell compared to high discharge rate, the dependence on depth of discharge is not straightforward. Expectedly low depths of discharge led to higher cycle life, but cells cycled at higher depths of discharge are surprisingly found to last longer than those cycled at medium depths of discharge. The effect of temperature on cycle life is seen to be worst at 0 °C and the least at 45 °C. Post mortem analysis of some cells is also conducted which reveals the physical origins of the different phenomena of degradation seen in cyclic aging. They are correlated with the analysis from impedance model fitting results.
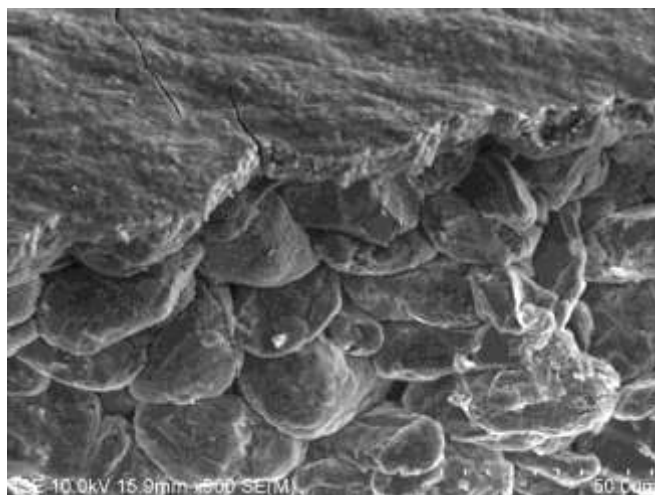
Figure: Post-mortem analysis with scanning electron microscopy of an aged graphite anode in the rapid capacity fade region with a clear layer on top, which does not occur in the linear slow aging region.

# Thermal and cycling behavior of an LTO/NCA lithium-ion pouch cell

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Aging and rate capability of lithium-ion batteries are key issues for stationary storage devices for industrial and private usage [1,2]. LTO/NCA cells are a promising technology to cope with this problem, as they are supposed to provide a long lifetime.

In this work, commercial 16 Ah LTO/NCA pouch cells which are designed for stationary energy storage have been extensively characterized thermally and electrically. Surface temperature and electrical properties (capacity, internal resistance, electrochemical impedance) were measured at different environmental temperatures (5 … 50 °C) and different C-rates (0.1 … 4 C). The cell behavior shows a strong temperature dependence. The cell was exposed to 10,000 cycles at a 4C-rate (CC charge, CC discharge, 100 % DOD, no rest times) in order to investigate the long-term cycling stability. After each 1000 cycles capacity and internal resistance was measured, as well as EIS spectra. As main result, the cells exhibit an extraordinary cycling stability (capacity loss after 10,000 cycles < 5 % for CC discharge and < 2.5 % for CCCV discharge) even under these harsh conditions.

Aging mechanisms are discussed based on equivalent-circuit evaluation of the experimental data. The experimental data furthermore serve as input for a numerical lithium-ion battery model [3] which can describe the asymmetry between discharge and charge branches [4] as well as the temperature behavior.
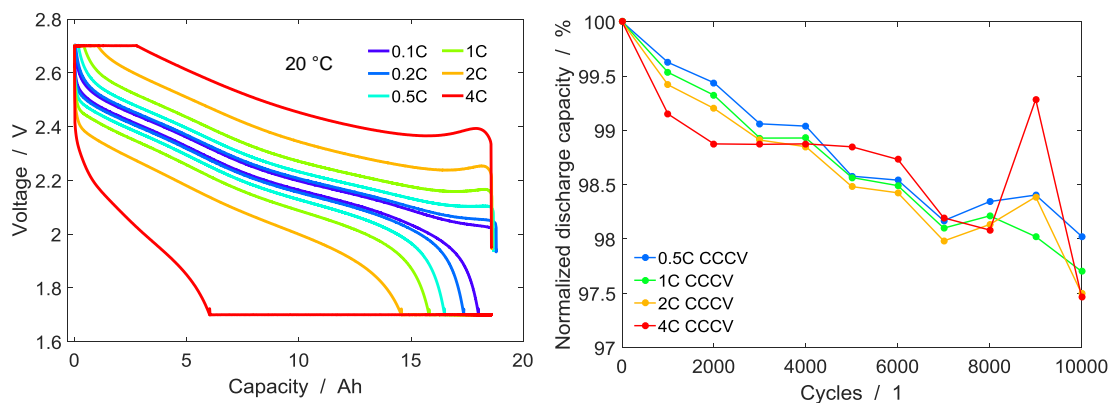


Left: Electrical characterization. Right: Discharge capacity as function of 4C cycle numbers.

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# Multi-Scale Thermo-Electrochemical Modelling of Ageing Mechanisms in an LFP/graphite Lithium-Ion Cell

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Ageing of lithium-ion batteries has become of major interest with the emerging markets of electromobility and stationary energy storages. Knowledge driven numerical simulations play an important role in predicting and understanding ageing phenomena in lithium-ion batteries. Most numerical models of lithium-ion batteries focus on one specific phenomena like temperature distribution or one specific ageing process. However, the different mechanisms are highly complex and difficult to categorize and to study independently from each other. Therefore, a detailed physicochemical description of the battery is required, considering the interactions and accounting for the macroscopic effects of ageing.

We present a multi-scale modelling approach coupling a 1D thermal cell-level (macro-scale) model, a 1D electrode-pair level (micro-scale) model, and a 1D particle-level (nano-scale) model in order to describe all relevant multiphysics processes [1]. We assume solid electrolyte interphase (SEI) formation as dominant ageing mechanism, which is known to be the main contributor to calendaric ageing within the recommended operating range of lithium-ion batteries [2]. The model is parametrised to commercial lithium iron phosphate cells, a promising cell chemistry which is increasingly in commercial use, especially for large-scale applications. The model predicts battery ageing as function of temperature, SOC and storage time. Detailed time-resolved charge and discharge cycles as well as long-time simulations for lifetime prediction are presented. The simulation of detailed electrochemical side reactions with the help of the coupling between DENIS and Cantera software is one of the main advantages of the model. The model is able to capture the nonlinear feedback between performance, ageing, and temperature.
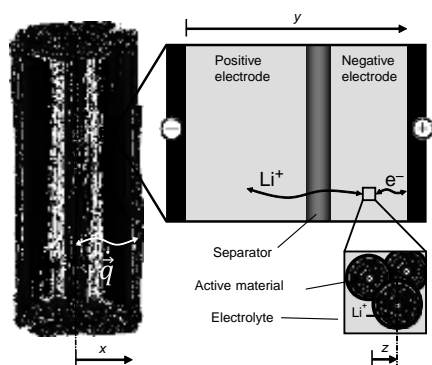


Figure 1 - Scheme of the model
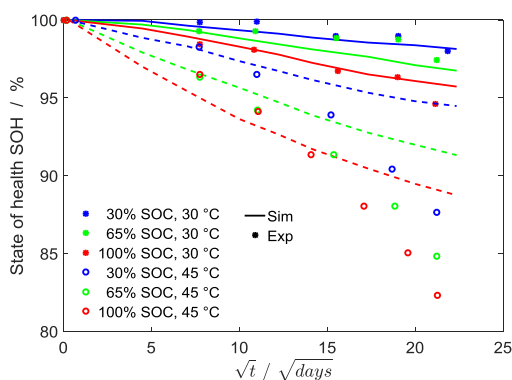


Figure 2 - Calendaric ageing of LFP/graphite cell

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# Determination of aging parameters based on experimental investigation of the calendar degradation of Li-ion cells

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As idle periods in automotive applications of Li-ion cells are usually considerably longer than operating periods, a thorough investigation of the calendar degradation is an important complement to cycle life studies. Conducting such an examination, conditions in terms of cell temperature and state of charge (SoC) are the main parameters that are to be controlled. In order to improve calendar life behaviour, the quantification of their influence is one of the key aspects for the development of sophisticated charging strategies during idle periods that take into account the daily usage profile.

In this contribution a comprehensive analysis of calendar ageing under different storage conditions will be presented. The experimental data is obtained using a set-up that enables a precise temperature control via the cell tabs and the planar surfaces of the investigated pouch cells. They are exposed to homogeneous thermal boundary conditions with both constant and varying temperature. The application of plates on the planar surfaces for a defined temperature also ensures a proper mechanical pressure on the electrode stack, that equals automotive conditions in the cell assembling to achieve comparable ageing results and improves the reproducibility.

The degradation of the cells is quantified by means of the reversible and irreversible capacity fade, the self-discharge during storage, the overall discharge resistance as well as the rise in electrochemical impedance which are determined in periodic characterisations. The correlation of the evaluated data with the storage parameters enables the determination of model parameters that describe the aging behaviour.

In a subsequent approach these coherencies serve coupled electrochemical-thermal cell models for numerical investigations.

# Simulation-based degradation assessment of lithium-ion batteries in a hybrid electric vehicle

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The insufficient lifetime of lithium-ion batteries is one of the major cost driver for mobile applications. The battery pack in vehicles is one of the most expensive single components that practically must be excluded from premature replacement (i.e., before the life span of the other components end). Battery degradation is a complex physicochemical process that strongly depends on operating condition and environment.

We present a simulation-based analysis of lithium-ion battery degradation during operation with a standard PHEV test cycle. We use detailed multiphysics (extended Newman-type) cell models that allow the assessment of local electrochemical potential, species and temperature distributions as driving forces for degradation, including solid electrolyte interphase (SEI) formation [1]. Fig. 1 shows an exemplary test cycle and the predicted resulting spatially-averaged SEI formation rate. We apply a time-upscaling approach to extrapolate the degradation analysis over long time scales, keeping physical accuracy while allowing end-of-life assessment [2].

Results are presented for lithium-ion battery cells with graphite/LFP chemistry. The behavior of these cells in terms of degradation propensity, performance, state of charge and other internal states is predicted during long-term cycling. State of health (SOH) is quantified as capacity fade and internal resistance increase as function of operation time.
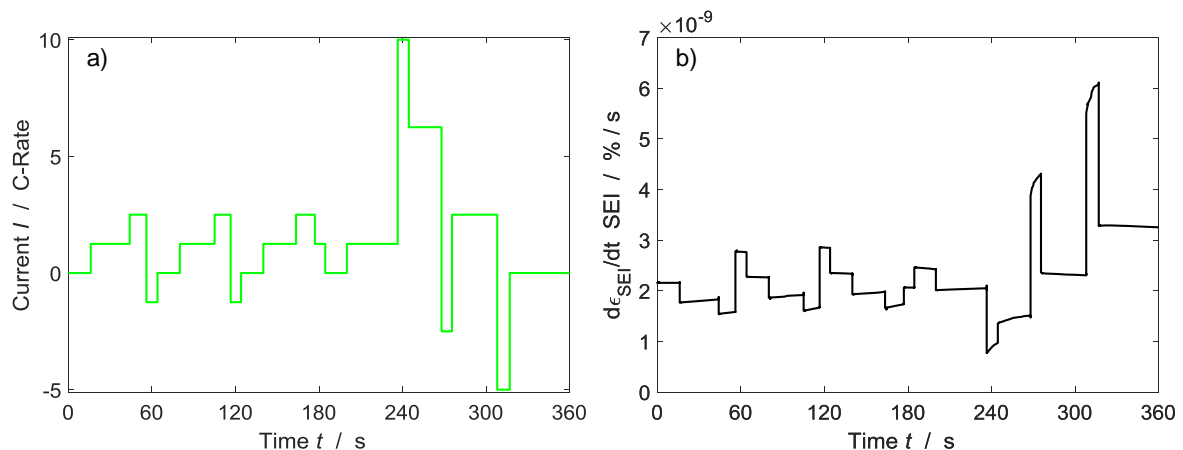


*Figure 16: (a) Standard test cycle ISO 12405 (I > 0 discharge / I < 0 charge) and (b) the related spatially averaged SEI formation rate (in vol.-% SEI per second).*

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# Detection of critical operation modes in lithium-ion cells by a physically based, online applicable model based on half-cell potentials

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The widespread application of lithium-ion cells in critical applications such as electric mobility greatly depends on operational safety, i.e. if severe operation modes or aging mechanisms can be detected reliably and counteracted by the battery management system. Lithium deposition is such a mechanism that entails pronounced capacity loss and impedance increase. One solution to detect lithium deposition in operando is to apply suitable models to predict its occurrence in a wide parameter range [1,2]. Those models, mostly based on porous electrode theory, are computationally expensive and require extensive parametrization, thus limiting their potential in real-time applications. Equivalent circuit approaches (ECM) present a trade-off between costly electrochemical and simple behavioural models. However, in most cases ECM either lack physical meaningfulness or are restricted to the description of the full cell behaviour. In this study, we present an approach to predict lithium deposition by a physically motivated ECM taking into account the evolution of half-cell potentials during charging. The model structure accounts for the distribution of current density and lithium concentration in both electrodes thus allowing to predict over-charge and under-discharge of the active particle layers close the electrode/electrolyte interface. The parametrization of the model structure is carried out by a combination of impedance spectroscopy and time domain methods (e.g. pulse fitting) which are both inexpensive and well investigated [3]. The obtained model is validated through a reengineering approach where commercial cell material is examined in reconstructed three electrode cells [4]. As will be shown, the model is well capable of predicting overcharge situations depending on the experimental conditions (C-rate, temperature, state of charge). The model is easily transferable to the commercial cell scale and presents a sound basis for investigation of critical operation modes from electrode to cell level.

a)
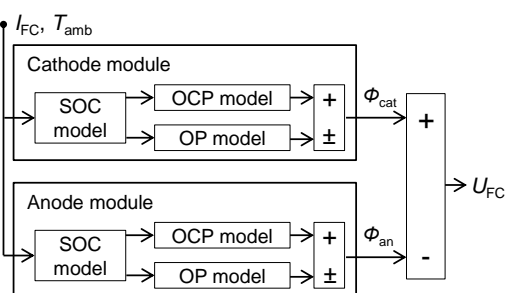
b)
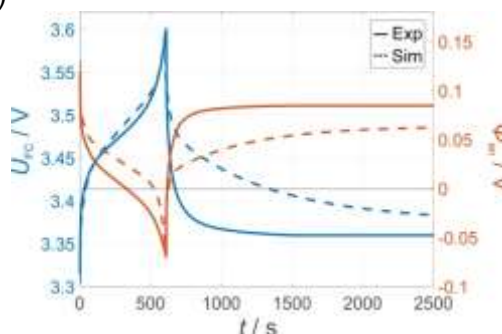


*Figure 17: a) Schematic model structure (SOC: state of charge, OCP: open circuit potential, OP: overpotential) b) Simulation example: Lithium deposition is indicated by negative anode potentials $\Phi_{an}$.*

[1] P. Arora, M. Doyle, and Ralph E White; Mathematical modeling of the lithium deposition overcharge reaction in lithium-ion batteries using carbon-based negative electrodes; J. Electrochem. Soc. **146**, 3543-3553, (1999)
[2] S. Hein and A. Latz; Influence of local lithium metal deposition in 3D microstructures on local and global behavior of lithium-ion batteries; Electrochimica Acta **201**, 354–361, (2016)
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# Modeling electrode structures of lithium-ion batteries: Influence of particle-size distribution on the performance

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The performance of lithium-ion batteries (LIB) is strongly influenced by the composition and fabrication of the electrode structures. On the one hand, the used material and its microstructure plays an important role. On the other hand, the mechanical densification processes, such as calendering or sintering, impact on the quality of the battery. Due to the low electrical conductivity of the active material (AM) inside a LIB, carbon black (CB) powder is being added to overcome this drawback.

In the work of (1), the author analyzed the influence of the relation between volumes of AM and CB on the percolation probability and the amount of AM being connected to percolated pathways, for this is one crucial aspect for the performance of LIBs. For simplicity reasons, the AM- and CB-Particles had been approximated by binary-sized spheres and the radius ratios had been fixed to the value of $r_{AM}/r_{CB} = 10/1$, whereas only the volume fractions had been varied between $\phi_{AM}/\phi_{CB} = 0.1/0.9 \dots 0.85/0.15$.

In the following, the above mentioned study is being extended by polydisperse spheres according to the particle size distribution of AM and CB for a $LiFePO_4$ (FPO) electrode found by (2). For this purpose, randomly distributed assemblies of polydisperse, densely packed and overlap-free spheres are generated using the random close packing algorithm (RCP) (3). Further, intercalation-induced swelling of the AM is being simulated and both the formation of percolated pathways of CB and the connectivity of AM to the latter is being analyzed. Finally, a comparison to the findings of (1) is given.

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# Die Numerische Simulation eines Mikroskalenmodells für Li-Ionen-Batterien

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Es wird das thermodynamisch konsistente Mikroskalenmodell nach [4] zur Modelllierung des Lithium- und Ladungs-Transports bei der Entladung einer Li-Ionen-Batterie betrachtet. Dabei werden jedoch die thermischen Effekte, durch die Annahme einer konstanten Temperatur, vernachlässigt. In [3] wird auf experimentelle Hinweise verwiesen, die darauf hin deuten, dass die Diffusion der Li-Ionen in dem Aktiv-Material der Kathode (etwa $LiCoO_2$) bei der Interkalation komplexer abläuft als mit dem Fickschen Gesetz beschrieben werden kann. In Artikeln wie [6] wird zur Modellierung des Diffusionsprozesses ein Zwei-Phasen-Diffusionsmodell verwendet, welches auf ein Stefan-Problem in den aktiven Partikeln führt.

Das elliptisch-parabolische System an partiellen Differentialgleichungen mit einer stark nichtlinearen (exponentiellen) Kopplung am Elektrode-Elektrolyt-Übergang, welches den Transport im Mikroskalenmodell beschreibt, kann um ein Zwei-Phasen-Diffusionsmodell für die Aktiv-Partikel erweitert werden. Die erweiterten Gleichungen werden dann zur numerischen Lösung in die Enthalpie-Formulierung überführt. In [2] wurde ein solcher linearer Finite-Element-Ansatz nach der Rothe-Methode zur Lösung der Transport-Gleichungen entwickelt. Neben der Diskretisierung des Zeitschritts mit dem Theta-Euler-Verfahren wird auch ein semi-implizites Verfahren nach [5] betrachtet. Dabei wird das vollständige System in ein elliptisches und ein parabolisches Teilproblem aufgeteilt und nacheinander gelöst.

Der wesentliche Punkt des Ansatzes ist die fehlende Regularität der Enthalpie-Funktion durch eine Regularisierung auszugleichen, um das nichtlienare Gleichungssystem weiterhin mit dem Newton-Verfahren lösen zu können.

Durch die Überführung in die Enthalpie-Formulierung ergibt sich der Vorteil, dass der Wechsel in Ein-Phasen- und Zwei-Phasen-Diffusionsmodell ohne Weiteres erkannt wird. Als weiteren Vorteil bietet die Darstellung in Enthalpie-Formulierung eine vollständige Unabhängigkeit von der gewählten Geometrie sowie der Raum-Dimension.

Das Verfahren wurde mit der freien Finite-Elemente-Bibliothek deal.II [1] implementiert und anhand mehrerer Testfälle für ein Ein-Phasen-Diffusionsmodell validiert.

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# Modelling chemical kinetics at electrified interfaces

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The study of structures and processes at the interface between two conducting phases are without a doubt the pivotal objects of electrochemistry. At this boundary between two chemically different conductors an arrangement of free charge carriers occurs and the interface gets electrified. Thus, local electric fields and potential differences emerge. This process is of general nature. It is substantial in many different electrochemical systems. Worth mentioning here in particular are solid-air interfaces in metal-air conversion batteries or solid-solid interfaces in all-solid-state batteries. A detailed theoretical description of the interface reactions is decisive for deriving predictive models, which allow to obtain a comprehensive understanding and to improve those electrochemical systems.

Recently, we developed a generic theory for charge and electron transfer reactions at electrified interfaces, which is able to describe adsorption, respectively a charge accumulation at the electrode-electrolyte interface [1]. Addressing solid-liquid interfaces, we discuss our generic theory in context of both intercalation and conversion batteries. As for the intercalation system, a well established transport theory for lithium ion batteries is used for a LMO half cell [2]. The interplay of the interface kinetics, thus the transport of lithium ions from electrolyte to electrode with the electrochemical double layer at the domain boundary is investigated [1,3]. As an example for conversion reactions, a lithium sulfur cell is simulated based on a continuum model, which was recently developed in our group [3]. This continuum model describes both reaction and transport of solid and dissolved species in a single S/C composite particle as well as on cell level. In lithium sulfur cells the overall concentration of charged species increases during discharge, which leads to higher viscosity and cell resistance. It can thus be concluded that surface effects like adsorption are more prominent in the case of lithium sulfur batteries and therefore a detailed theoretical description of interface reactions is even more important.

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# Phase-field modeling for lithium iron phosphate cathode material with the coupling between diffusion and mechanics

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Electrochemical energy storage is needed for many mobile technical systems, such as communication and electromobility. Furthermore, stationary energy storage becomes more important as the amount of highly fluctuating wind and solar generation of electrical energy increases. Reliability up to very large numbers of charge-discharge-cycles is needed. Lithium ion batteries are considered promising candidate systems meeting these needs.

Mechanical properties and electrochemical processes influence performance and degradation of lithium ion batteries. In this talk, we consider the interaction of mechanics and diffusion in individual electrode particles. In most storage materials, phase transitions occur during regular operation and, thus, cannot be avoided. Phase segregation causes the tremendous stresses due to the strain mismatch [HK12]. The respective phases of a storage material possess different lattice constants giving rise to a strain mismatch of up to a few hundred percent which, in turn, causes mechanical stresses and, thus, leads to damage of the electrode particles [WCC10, CISG11]. For non-linear Cahn-Hilliard type models describing diffusion, a thermodynamic framework for the coupling with mechanics has been provided in [G96]. Lithium iron phosphate, like many other electrode materials of lithium ion batteries shows phase changes during lithium insertion or extraction. Here we investigate the modeling of phase changes using the traditional Cahn-Hilliard theory coupled to small and finite deformation theories by means of simulations of electrode particles of lithium iron phosphate. Different finite deformation theories in terms of elasticity based on elastic Green strain and elasticity based on logarithmic elastic strain are compared. The finite and small deformation theories are also compared.

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# DEM micromechanical modelling of electrode structures with regard to stress evolution during lithium intercalation

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Structural stability and mechanical integrity of lithium-ion electrode materials during electrochemical cycling are highly correlated with the performance of the battery. The intercalation-deintercalation of lithium ions in the host structure is accompanied by substantial dimensional and volume changes which lead to deformations and stress generation in the active cathode and anode materials.

Lithium-ion electrodes consist of porous composite materials (active material, conductive additives and binder) coated on a substrate. Bearing in mind their particulate nature,this work proposes a discrete element method (DEM) simulation approach to characterize the mechanical behavior of such structures. A key aspect of DEM simulations is the suitable selection of a contact model, which describes the forces acting on the particles and therefore defines the mechanical behavior of the bulk material.To this purpose, a Hertzian-bond contact model is developed to capture the elasto-plastic behavior of the electrodebycomputing bonds between particles under certain conditions and combining both particle and binder stiffness.

In this study, different anodes made of MesoCarbonMicroBeads (MCMB) graphite as active material were produced and experimentally characterized with regard to active material particle size, electrode porosity and electrode thickness.Nanoindentation experiments and corresponding simulations were carried out with the aim of calibrating and validating the model. This technique, coupled with DEM simulations, contributes to get a deeper look into the mechanical properties of the electrodes.

The validated computer-generated structures were subsequently used to simulate the intercalation process by conducting volume changes in active material particles. As a result, the macroscopic stress arisen from individual stresses within the particles was calculated and associated with the lithiated state of the electrodes. Figure 1 shows the stress evolution during the intercalation process for a certain MCMB anode structure.

Furthermore, additional structures were numerically generatedvarying certain properties such as porosity or binder content. These simulations help assess the influence of microstructural parameters on stress generation which may be useful to optimize electrode microstructure with the aim of mitigating stress-related damage mechanisms.
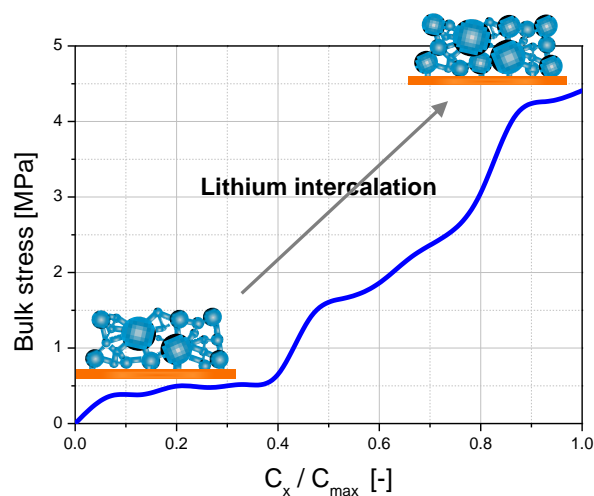


Figure 1: Stress evolution during the intercalation process of an MCMB anode. $C_x$: lithium concentration ($mol/m^3$); $C_{max}$: maximum lithium concentration ($mol/m^3$)

# Stochastic model for LiFePO4-electrodes

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A promising electrode material for lithium ion batteries is LiFePO4 (LFP). A phase transition from a lithium poor to a lithium rich phase occurs in the LFP electrode during the charging/discharging process of a LFP electrode.

Investigations on LFP electrodes show that the phase transition is a many-particle effect, i.e. the LFP particles in the electrode make the phase transition according to the rule "one after the other" [1,2]. The incorporation of the many-particle effect in an electrode model is mandatory because the effect dominates the behaviour of a LFP electrode.

We have developed a thermodynamically consistent model of a many-particle LFP electrode [3] including (i) the many particle effect, (ii) the particle size distribution of the LFP particles, (iii) the surface area where the lithium intercalation takes place, (iv) the kinetics of the electron transfer reaction and adsorption. The model describes the dynamics by only two parameter τ and ν, where τ controls the intercalation rate and ν takes into account the strength of micro fluctuations within the electrode. Simulations show all features of the voltage-capacity diagram of the LFP electrode against a metallic lithium counter electrode. The many-particle model is general enough so that it can be adopted to other materials with similar behaviour.

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# Multi-Reaction Intercalation Model of NMC electrode with Empirical Mixing of Reaction Equations

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A multi-reaction intercalation model is presented. Usually the intercalation of lithium is described as one electro-chemical reaction, described by the Butler-Volmer equation (1)[1]

$$j_{BV} = i_0(SoC)\left(\exp\left(\frac{\alpha F}{RT}\eta\right) - \exp\left(\frac{-(1-\alpha)F}{RT}\eta\right)\right) \quad (1)$$

where the open-circuit voltage ($U_{OCV}$) curve is needed to determine the over-potential η. However, the Lithium intercalation process for NMC electrodes involves the reduction and oxidation couples $Ni^{4+}/Ni^{3+}$ and $Ni^{3+}/Ni^{2+}$, and in the presented work these two intercalation stages are both treated separately.

$$E = E_0 + \frac{RT}{F}\ln\left(\frac{1-x}{x}\right) + \omega(1-2x) \quad (2)$$

The equlibrium voltages of each reaction, derived from a regular solution model, are given by equation (2), which describes the standard Nernstian behaviour, supported by an Enthropy term[2]. That way the model can be parametrized without the need of an open-circuit voltage curve.

The two reactions are coupled with empirical expressions that handle their interdependencies and are embedded into a single particle model. Figure 1 shows some preliminary results of the mixed model. Here the model parameters were fitted to measurement data from NMC half-cells that where charged and discharged at a C-Rate of 0.33 C.

The presented work aims at a deeper understanding of the intercalation electrodes and to form a connection between the theory of intercalation reactions, leading to equation (2), and the real non-ideal open-circuit voltages. That way a model is built up, that is able to help optimization and simulation purposes, based on a small number of parameters.

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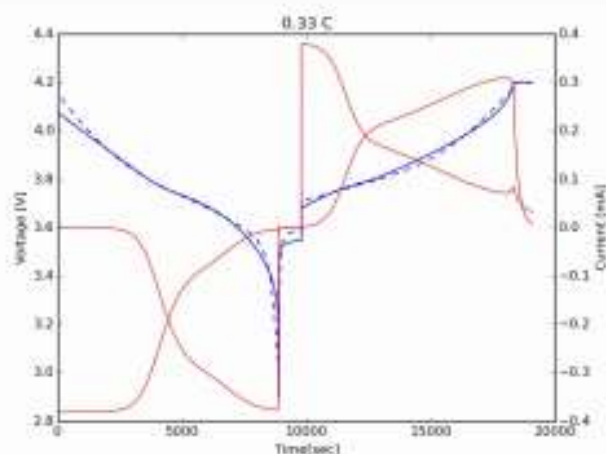
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Figure 1:Red lines are the reaction currents. Blue line is the voltage and dashed blue line is the measuremetn voltage.

# Model order reduction of lithium-ion cell models based on orthogonal collocation

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In the field of battery modeling, the complexity of the model corresponds to the specific design problem. Physics-based models give access to physical and geometrical parameters at the electrode level, while providing accurate information about cell internal processes. Highly resolved models, such as Newman's model [1,2,3], need a considerable amount of computational time to solve the set of partial differential equations. With regard to these considerations, much effort is put into reducing the order of physics based models while maintaining their unique ability to describe mass and charge transfer reactions [4]. Typical reduced order models, such as single particle models, approximate the system of partial differential equations with ordinary differential equations. In addition, these kinds of models often neglect solid concentration gradients within the electrode by simplifying both anode and cathode with one representative particle. This results in a considerable accuracy loss compared to full electrode models at high current rates. With their ability to fully resolve solid and liquid phases in the electrode, models based on orthogonal collocation [5,6] are a promising method to reduce the order of physics-based models.

In our work, we present an orthogonal collocation model based on typical Jacobi polynomials. Therefore, the choice and order of these polynomials and their impact on model accuracy and model performance is discussed. Simulation results are benchmarked with respect to Newman's model which is parametrized for a nickel-cobalt-manganese lithium-ion cell at different discharge currents. All model equations are solved by means of the commercial finite element software COMSOL Multiphysics 5.2a. The computational effort to solve the different models is determined by using a MATLAB - COMSOL interface.

## 2. Acknowledgement

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# Improving the performance of Li-S cells, a model-informed approach

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Lithium-sulfur (Li-S) could provide the next step-change in battery technology with a promising practical energy density of 500-600 Wh/kg, increased safety and possible low cost. However, a lack of understanding of the complex electrochemical, transport, and phase-change phenomena in Li-S cells is arguably holding back improvements in their performance[1] and thus its successful commercialisation. Acquiring this knowledge requires experimental characterisation in tandem with mechanistic modelling.

To address the latter, we developed a zero dimensional model that captures the essential features of Li-S performance during charge and discharge. The model accounts for two electrochemical reactions via the Nernst formulation, power limitations through Butler–Volmer kinetics, and precipitation/dissolution of low order polysulfides, including nucleation.[2] The model is an improvement on the existing zero dimensional models, while requiring considerably fewer input parameters and computational resources than one dimensional models. Model results help identify the dominant effects in a real cell.[3] The flat shape of the low voltage plateau typical of the lithium–sulfur cell discharge is caused by precipitation. During charge, it is predicted that the dissolution can act as a bottleneck, resulting in reduced charge capacity and an earlier onset of the high plateau reaction, and indicated by the merging of the two voltage plateaus.

Here we use this model as a base to understand the interplay between shuttle, shuttle-related degradation and precipitation, and the impact on the total capacity available from a cell throughout its lifetime. To this end, model predictions of cell performance under cycling are compared to experimental data gathered for various operational conditions. The model helps interpret the complex behaviour observed during cycling and quantify two types of degradation: reversible and irreversible. The model interprets the observed SOC drift during cycling as mainly caused by accumulated precipitation (reversible loss), while showing that some features can only be obtained if active material is gradually lost irreversibly. The prediction of a reversible loss associated with precipitation is verified experimentally by the successful use of 'recovery' cycles.

This model can thus be used to make informed choices regarding improving performance while sacrificing either power or energy, such as through the introduction of recovery cycles.

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# First steps towards a continuum model of Mg-S batteries

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Modern Lithium-ion batteries hold more than twice as much energy by weight and are ten times cheaper than the first commercial versions sold by Sony. But today they are near its limits. The use of lithium metal for 'beyond Li-Ion' batteries, such as lithium-sulfur, promises higher energy density and lower costs. However, dendrite formation and battery safety still is an issue. In recent years magnesium batteries are discussed as attractive next-generation energy storage system. Magnesium can be directly used as anode material due to its dendrite-free deposition and thus increases the safety as well as energy density of such a cell. Two electrons are stored per Mg atom which compensates the typically rather low cell voltage during discharge. Recently, magnesium-sulfur cells were proposed which provide a high theoretical capacity of 3832 mAh/cm$^3$ and 2230 mAh/g with an energy density of over 3200 Wh/l [1]. Such an energy density is beyond that of lithium-sulfur batteries and is therefore very promising for automotive and stationary applications. Furthermore, magnesium and sulfur are both naturally abundant, low in price and non-toxic.

However, magnesium-sulfur batteries are in a very early stage of research. The reactions at both the positive and negative electrode are not yet fully understood. At the sulfur electrode a mechanism analogous to lithium-sulfur batteries was proposed. Zhao-Karger et al. were able to demonstrate a lifetime of more than 50 cycles [2]. In their cell concept they use a newly developed electrolyte in combination with a micro-porous sulfur-carbon composite electrode. However, analogous to lithium-sulfur batteries magnesium-sulfur batteries show high overpotentials during charging, low cycling stability, and a strong capacity fading.

To the best of our knowledge there are no continuum models of Magnesium-sulfur batteries in the literature. Therefore, we present the first step towards a mechanistic model of magnesium-sulfur cells. We use a 1+1D model (particle + cell domain) to take into account the structural properties of the sulfur-carbon composite electrode. The sulfur kinetics are included via a reduced reaction mechanism which was able to reproduce the key experimental results for Li-S batteries [3]. The particle model is coupled to a cell model describing the macroscopic transport of dissolved species. In both models the species transport is described by the Nernst-Planck equation where transport occurs via diffusion and migration. The model intrinsically takes into account the polysulfide shuttle which allows us to include side reactions at the negative electrode. The model is calibrated with experimental data measured in the group of Maximilian Fichtner at the Helmholtz-Institute in Ulm and is able to qualitatively describe the experimental findings.

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# 3D Modelling and Simulation of Rechargeable Zinc-Air Cells

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Metal-air batteries offer high energy densities and use abundant materials, which makes them attractive candidates for next-generation energy storage. Zinc-air batteries in particular are cheap to produce, non-toxic, and environmentally friendly. Potential applications lie in the fields of electro-mobility, portable electronics, and stationary grid storage. Up to now, only primary cells have been commercialized and further research is required to surpass lithium ion batteries on the rechargeable battery market.

In this contribution, we present three-dimensional modelling and simulation of rechargeable zinc-air batteries. Metal-air batteries are typically modelled along a single dimension connecting anode and cathode [1]. We develop a fully three-dimensional model of zinc-air batteries based on our one-dimensional model of primary zinc-air button cells [2]. Our model is capable of predicting full charge and discharge cycles. Local volume averaging is employed to describe nano-sized phase boundaries between gaseous, liquid, and solid phases and macro-sized battery cells in a single simulation [3]. Diffusion, migration and convection of all species are the relevant transport mechanisms; the electrolyte is locally electroneutral and incompressible [4]. We model thereby the reactions of zinc dissolution, zinc oxide precipitation and oxygen and carbon dioxide dissolution. Our numerical implementation is done in the software BEST [5]. It deploys a finite volume method with a non-equidistant Cartesian grid. We model an alkaline potassium hydroxide solution as electrolyte, which contains $K^+$, $OH^-$, $Zn(OH)_4^{2-}$, $CO_3^{2-}$ and dissolved $O_2$. We focus on optimizing performance and cycle-life of the cells with a detailed study of distinct geometries and porosities of the electrodes. Our model is thereby validated by comparisons with recent and ongoing experiments with specially designed zinc anodes providing an exactly known geometry.

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# Modelling Zinc-Air Batteries with Ionic Liquids

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The large theoretical energy density of metal-air batteries has recently stimulated a lot of research on these high-potential batteries [1],[2]. The extensive research revealed that enormous challenges lie ahead before the metal-air technology can outperform lithium ion batteries by a factor of two or three in terms of cost and energy density [3]. The key component is the electrolyte connecting the electrodes because it must be stable over a wide electrochemical window, allow reversible metal deposition, and be tolerant to air.

Ionic liquids are promising candidates for stable battery electrolytes [4]. Their advantages comprise a large electrochemical window (up to 6V), chemical and thermal stability, non-flammability (as safety asset) and low vapor pressure [5]. In particular, ionic liquids minimize dendrite growth during electrodeposition and have high ionic conductivity [5]. Zinc-air batteries with ionic liquids are potentially stable towards moisture as well as carbon dioxide and can support a reversible oxygen electrochemistry.

In this talk we present a thermodynamically consistent transport theory of zinc-air batteries based on room temperature ionic liquids. Our focus lies on the systematic derivation of a set of fully coupled transport equations for the ions, charge and heat based on the development of modeling methodologies for lithium-ion batteries [6]. Viscosity and particle nature of the medium are incorporated into the theory. Emphasis is laid on a reasonable definition for incompressibility in the context of a multi-component species. The transport theory is used to simulate the ionic liquid EmimTfo in the vicinity of an electrified interphase. We observe the two characteristic effects of crowding and overscreening. During the latter, a quasi-crystalline double layer emerges.

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