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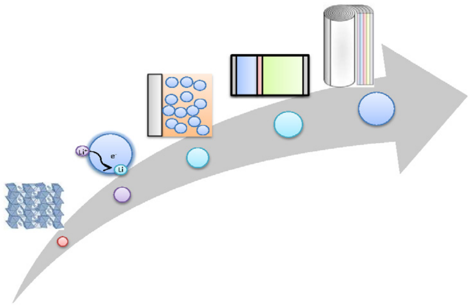

Book of Abstracts

ModVal 2022

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HIU HELMHOLTZ INSTITUTE ULM
Electrochemical Energy Storage

18th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies

March 14-16, 2022
Schloss Hohenkammer, Germany

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Conference Schedule

Day 1 (March 14, 2022)

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16:45	End	

Tejs Vegge (March 15)

Tejs Vegge heads the Section for Autonomous Materials Discovery at the Technical University of Denmark, working on the development of autonomous methodologies for accelerating materials discovery and innovation processes.
Prof. Vegge is an elected member of the Academy of Technical Sciences (ATV) and the Danish government's commission on green transportation and has pub-lished more than 180 papers in the field of computational design of advanced battery materials and next-generation clean energy storage solutions. He serves as a coordinator of the Battery Interface Genome—Materials Acceleration Platform (BIG-MAP) project and as a member of the executive board of BATTERY 2030+.

Marc Secanell (March 15)

Marc Secanell is a Professor in the Department of Mechanical Engineering at the University of Alberta, Canada, and the director of the Energy Systems Design Laboratory. He received his Ph.D. and M.Sc. in Mechanical Engineering from the University of Victoria, Canada, in 2008 and 2004, respectively. He holds a B.Eng. degree (2002) from the Universitat Politècnica de Catalunya (BarcelonaTech). In 2008, he was an Assistant Research Officer at the National Research Council of Canada, Institute for Fuel Cell Innovation in Vancouver, Canada and in 2015-16 he was a visiting research scholar in the Energy Conversion Division at the Lawrence Berkeley National Laboratory, US. His research interests are in the areas of: a) analysis and computational design of energy systems, such as polymer electrolyte fuel cells, polymer electrolyzers, flywheels and cooling towers; b) fabrication and characterization of polymer electrolyte fuel cells and electrolyzers; c) finite element analysis; and, d) multidisciplinary design optimization. His current research projects include the development of the open-source Fuel Cell Simulation Toolbox (OpenFCST), an open-source framework to analyze fuel cells, the development of mathematical models and optimization strategies for cooling towers, methane pyrolysis reactors and high-speed composite flywheels, and the fabrication and characterization of low loading polymer electrolyte fuel cells and electrolyzers. He has authored over 50 journal articles, 30 conference proceedings and two book chapters receiving over 3,000 citations (h-index: 34 in Google Scholar). He has been an invited speaker at prestigious conferences such as the Electrochemical Society Meeting and the Gordon Research Conference in Fuel Cells. He has received several awards including University of Alberta, Faculty of Engineering Teaching Award (2020), Excellence in Engineering Research Award (2018), the Association of Professional Engineers and Geoscientists of Alberta (APEGA) Early Accomplishment Award (2013) and a Hydrogen and Fuel Cells Canada Scholarship (2007). He is the co-chair of the 2022 GRC Fuel Cell conference.

David Howey (March 15)

David Howey is Professor of Engineering Science at the University of Oxford, UK. He leads a group researching on modelling and control of energy storage systems, with a particular focus on Li-ion bat-teries for electric vehicles and grid/off-grid storage. He received the MEng degree in Electrical and In-formation Sciences from the University of Cambridge in 2002 and his PhD from Imperial College London in 2010. Since 2010 he has co-authored 80+ peer-reviewed journal and conference articles, and 5 patents. He is an editorial board member of IEEE Transactions on Industrial Informatics and the new OUP journal Oxford Open Energy, and is co-founder of the Oxford Battery Modelling Symposium. He is the recipient of recent funding from EPSRC, InnovateUK, UKRI, Faraday Institution, Continental AG and Siemens, and he co-leads control and estimation tasks in the Faraday Institution Multiscale Modelling project. Howey is also academic lead for the £40m Energy Superhub Oxford that is building a transmission connected 50 MWh hybrid battery. He previously led the Faraday Institution "UK EV and Battery Production Potential" project (with McKinsey), and was academic lead in InnovateUK projects on battery re-use (EP/P510737/1) and solar home systems in Africa (EP/R035822/1), and a $1.2m Korean project on microgrids, plus Co-I in EPSRC projects TRENDS, FUTURE vehicles, STABLE-NET and RHYTHM. Professor Howey is co-founder of Brill Power Ltd., a company spun-out of his lab in 2016 focused on advanced battery management system topologies. They have raised significant early stage funding and adopted several patents from his group. Howey also won a Samsung GRO Award on modelling leading to two R&D contracts and a multi-year collaboration, with results patented by Samsung Electronics.

Momo Safari (March 16)

Momo Safari is a professor at faculty of engineering technology of Hasselt University (Belgium) and leads the group of Electrochemical Engineering (EE) at the Institute for the Materials Research (IMO) and EnergyVille. He earned his PhD degree in Electrochemical Engineering from Picardie Jules Verne (France) in 2011, working with Dr. Charles Delacourt and Prof. Jean-Marie Tarascon. Momo was a postdoctoral Fellow in the groups of Prof. Linda Nazar and Prof. Michael Fowler at University of Wa-terloo (Canada) before joining the Hasselt University in 2015. Momo is interested in the fundamental investigation of electrochemical systems to shed light on and quantify the charge transfer reactions and charge transport phenomena in the electrodes and electrolytes, as well as the aging phenomena.

Andrea Baricci (March 16)

Andrea Baricci is associate professor since 2021 at Politecnico di Milano in the MRT Fuel Cell & Battery laboratory where he carries out his research activities on hydrogen polymer fuel cells including both experimental and modeling work at single cell level. Andrea Baricci's reasearch interest is focused on characterization of both reversible and irreversible degradation of the cathode catalyst layer under real-world operation and the development of related accelerated stress tests. This activity was carried out in the framework of European Projects (SECOND ACT and ID-FAST) as well as national italian projects, industrial projects and international collaborations.

Abstract Tejs Vegge

POLiS Post Lithium Storage Cluster of Excellence

ML-accelerated simulations of solid-liquid interfaces in batteries and fuel cells

Tejs Vegge
Technical University of Denmark, Department of Energy Conversion and Storage,
2800 Kgs. Lyngby, Denmark (teve@dtu.dk)

Understanding and controlling the complex and dynamic processes at solid-liquid interfaces in electro-chemical devices like batteries, fuel cells, and electrolyzers holds the key to developing more efficient and durable technologies for the green transition. Fundamental and performance-limiting interfacial processes like the oxygen evolution/reduction reactions (OER/ORR) in electrocatalysis [1] and the formation of the Solid-Electrolyte Interphase (SEI) in battery cells span numerous time and length scales [2]. Despite decades of research, the fundamental understanding of structure-property relations remains elusive. Computational modeling at the scale of density functional theory (DFT) and ab initio molecular dynamics (AIMD) generally provides sufficient accuracy to describe the making and breaking of chemical bonds at these interfaces [3]. Still, the calculational cost is often prohibitively high to reach sufficiently long time- and length-scales to ensure proper statistical sampling [4]. Machine learning (ML) potentials offer a potential solution to this challenge. Still, the training of ML-based potentials capable of handling liquid (organic or aqueous) electrolytes remains a fundamental challenge since the potential must capture both intra- and intermolecular interactions in the electrolyte and during chemical reactions at the interface (Figure 1) [5]. Here, we present new approaches for machine/deep learning models to predict the spatio-temporal evolution of electrochemical interphases in batteries and electrocatalytic systems such as the platinum-water interface (figure 2) [6]. We also discuss the development of methods for uncertainty quantification training and evaluating neural network ensemble models [7] and AI-based optimal experimental design [8] using models trained on multi-sourced and multi-fidelity data from multiscale computer simulations operando characterization, high-throughput synthesis, and laboratory testing. Finally, we will give our perspectives on a path towards better and smarter batteries by combining AI with multisensory and self-healing approaches [9].

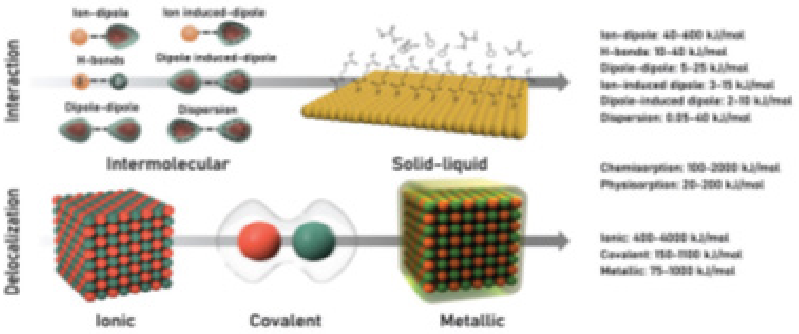

Figure 1: Variations in inter- and intra-molecular forces [5].

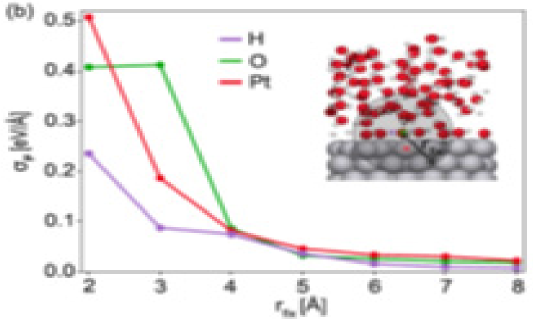

Figure 2: Locality of H2O/Pt(111) [6].

Keywords: solid-electrolyte interfaces, ML potentials, uncertainty quantification, closed-loop discovery

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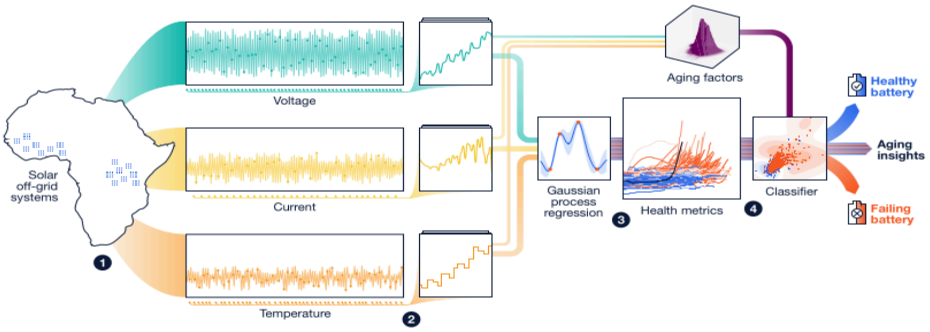
Abstract David Howey

Data-driven battery health diagnosis in real-world applications

David Howey
University of Oxford, Department of Engineering Science

Accurate diagnosis of battery health and prediction of future failure from live operational data greatly improves user experience and reduces costs. This allows industry to unlock value by detecting faults and planning maintenance, extending operational range, and understanding asset depreciation. But lack of controlled cycling, noise from low-cost sensors, and sparsity of validation data mean that existing lab-based techniques applied to this problem may struggle to give good results [1]. Battery health is generally quantified either through capacity estimates or resistance estimates; existing approaches for health estimation [2] try to fit the values of these health metrics from measured current, voltage and temperature data, usually using equivalent circuit models. However, it is often assumed that the model parameters vary as a random walk, whereas in reality they vary as a function of operating conditions and are correlated. Circuit parameters such as internal resistance vary with temperature, state of charge, applied current and over time as a cell degrades. These variations need to be understood to extract accurate and calibrated health metrics from data.

This presentation will first motivate the general topic of battery health diagnostics and prognostics, and then discuss our recently developed approaches to tackle this problem using probabilistic machine learning, primarily looking at data from off-grid solar battery systems in sub-Saharan Africa [3]. To improve the accuracy of model fits and the smoothness of health estimates, we use an approach that combines a simple circuit model for battery dynamics with Gaussian processes [4] for modelling the dependence of model parameters on conditions.
A computationally efficient recursive approach [5] al-lows simultaneous estimation of states and functional parameters from lab or field measurements. These techniques are also be applicable in other applications, from automotive starter batteries, to electric vehicles and grid energy storage. This highlights the opportunity to use cloud based `big data' techniques to understand battery health, extend lifetime and improve performance in real-world applications.



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Abstract Marc Secanell

Transient, multi-scale, multi-phase analysis of polymer electrolyte fuel cells and electrolyzers

M. Secanell, A. Kosakian, M. Moore, J. Zhou, S. Jung, M. Sabharwal,
F. Wiesner, W. Fei, M. Mandal
University of Alberta, Mechanical Engineering Department, AB, Canada

Polymer electrolyte fuel cell and electrolyzer operation at high current density requires a delicate balance between gas and liquid transport. This fine balance is accomplished by the careful selection and design of fuel cell components. Porous transport layers (PTLs) should be able to transport both gaseous and liquid products and reactants, maximize charge transport, and maintain an appropriate water and thermal management. Similarly, the catalyst layer (CL) design should be able to achieve a high catalyst utilization by maintaining an appropriate network of gas, liquid, ion, and electron transporting phases. A departure from this careful balance results in large mass transport losses and, in extreme cases, cell instabilities, e.g., spurious current/voltage oscillations with time and/or a steady decline in cell voltage during a current hold leading to eventual cell failure. At the low capillary number observed in fuel cells and electrolyzers, saturation is controlled by capillary pressure and the pore-size distribution of the material; however, the majority of membrane electrode assembly fuel cell and electrolyzer models in the literature, with a few exceptions such as Eikerling [1], Weber et al. [2] and Zhou et al. [3], do not use the pore-size distribution as an input parameter even though it is intimately connected to saturation, dry and partially-saturated diffusivity, permeability, and liquid-vapour interfacial area. Furthermore, none of the models above are transient even though two-phase flow behaviour in fuel cells has been shown to lead to temporal oscillations, and, as a result, non-steady operation. The lack of pore-size distribution information in the past might have been justified by limited characterization data, but recent advances in tomography imaging and stochastic reconstruction have enabled quick visualization of the structure of PTLs and CLs, information that can be used to estimate pore-size distribution and related transport properties at the micro-scale, and then transfer the information to macro-scale models.

In this presentation, the micro-scale simulation tools developed in the open-source software OpenFCST to estimate pore size distribution and transport properties from tomographic and stochastic reconstruction images will be discussed. A cluster-based full morphology algorithm will be presented to study water intrusion. Finite element solvers will also be presented to study transport and electrochem-ical reactions in CLs with varying pore-size distribution [4,5]. Our results show that the pore-size distribution can clearly affect transport parameters and the liquid pressure at which the onset of mass transport is manifested. Then, a transient, macro-scale (volume-averaged), multi-phase membrane electrode assembly model, based on the pore-size distribution framework by Zhou et al. [3], will be presented that can integrate micro-scale findings into the macro-scale model. This advanced model will be shown to be able to predict fast and slow linear sweep voltammograms of fuel cell operation at low and high current density, impedance spectroscopy of fuel cells at low and moderate current density, and to predict large fluctuations in cell voltage/current density at high saturation. Numerical results will be compared to experimental data obtained using a single channel fuel cell. A similar framework will be proposed for electrolysis applications.

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Abstract Momo Safari

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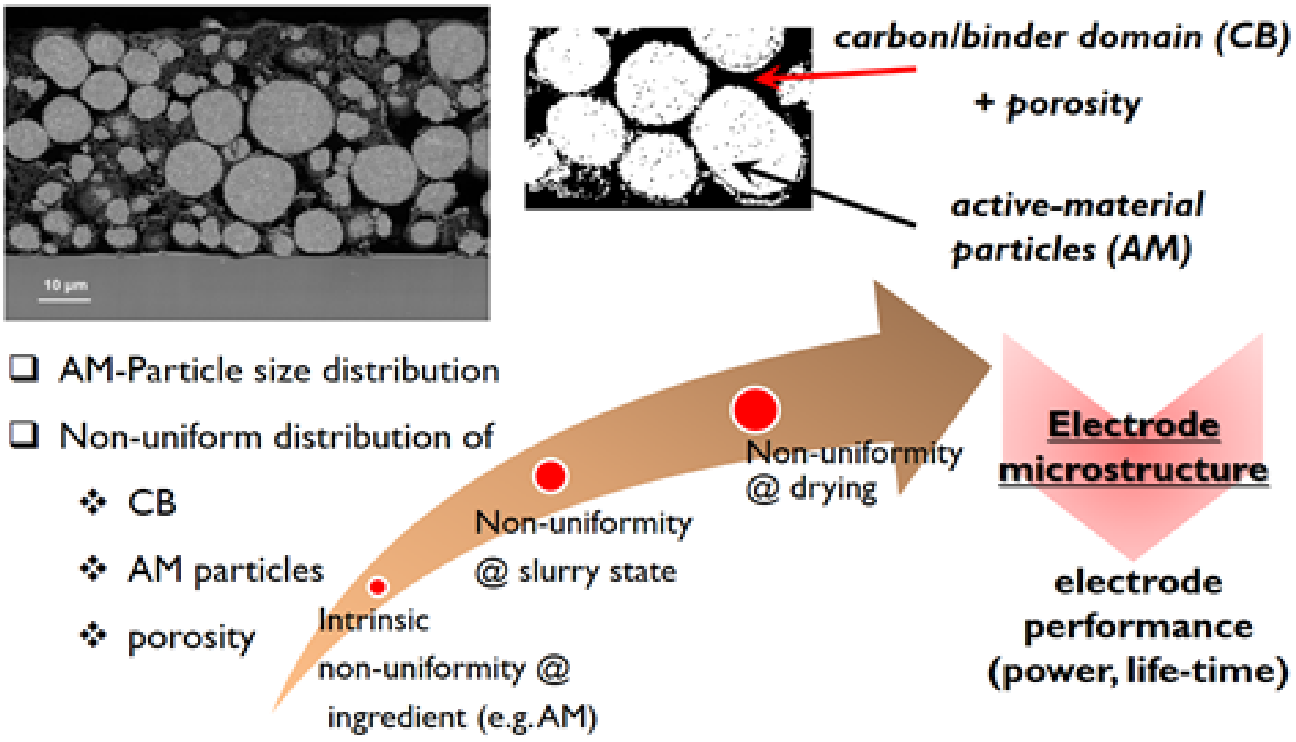
Formulation, design, and characterization of NMC porous electrodes: a model-assisted approach

M. Safari
1Institute for Materials Research (IMO-imomec), UHasselt, Martelarenlaan 42, B-3500 Hasselt, Belgium, 2Energyville, Thor Park 8320, B-3600 Genk, Belgium, 3IMEC division IMOMEC, B-3590 Diepenbeek, Belgium

The existing literature provides important insights into the local microstructure of the porous electrodes of lithium-ion batteries. The majority of studies employ the advanced characterization techniques such as FIB-SEM, X-ray tomography and/or full simulation of electrode microstructure [1-4]. Less attention is being paid, however, to develop (simple) formalisms to shed light on the possible correlations among the microstructural indexes (e.g. porosity, tortuosity, heterogeneity), adjustable design parameters such as slurry formulation, and the cell performance. Development of such correlations will be the main focus of this presentation. In this regard, the experimental data from a large pool of NMC electrodes will be discussed with the aid of modeling.



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Abstract Andrea Baricci

Modelling voltage loss in polymer electrolyte membrane fuel cells after catalyst layer degradation

A. Baricci[1]*, A.Grimaldi[1], E.Colombo[1], A. Bisello[1], D. Casadei[1], T. Jahnke[2], A. Casalegno[1]
[1] Politecnico di Milano, Dipartimento di Energia, MRT Fuel Cell & Battery Laboratory, Milano, Italy
[2] Deutsches Zentrum für Luft- und Raumfahrt
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Hydrogen produced from renewable resources is becoming a crucial asset to tackle the impact of climate change in those hard-to-abate sectors in which no competitive and scalable technology is currently available for decarbonization. These sectors, which are responsible for nearly one-third of global carbon emission include heavy-duty transport, i.e. road trucks, maritime and rail. Proton exchange membrane fuel cell (PEMFC) is a commercially available technology in the automotive sector that was already demonstrated as efficient, scalable, reliable and climate neutral solution, but requires further improvement for heavy duty applications, specifically regarding durability requirements.

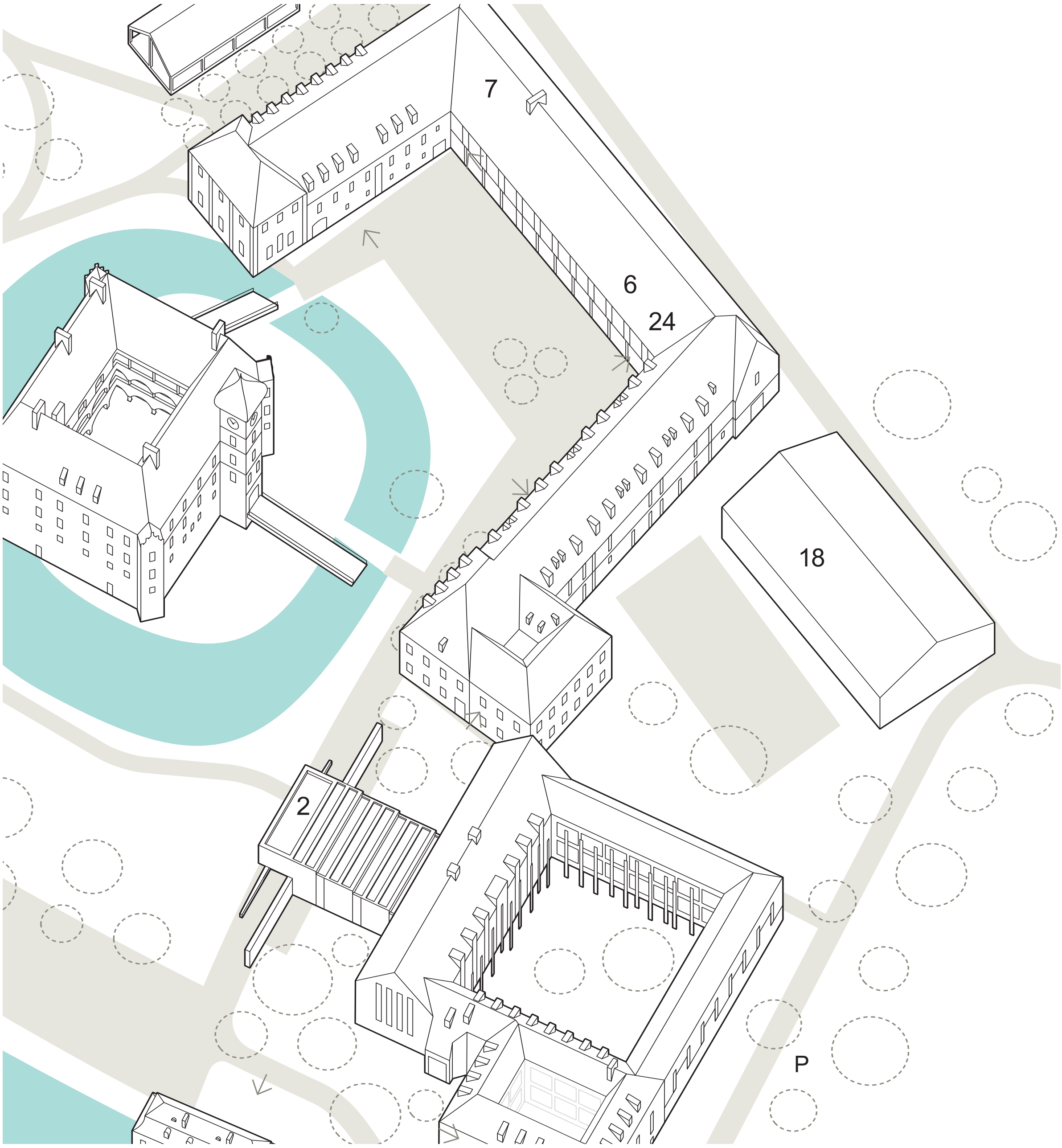
Durability of PEMFC is a wide topic and a subject of a wide scientific literature reporting identification of degradation mechanisms and stressors and interplay between them, but also a significant complexity leading in few cases to apparently contradicting results. Aiming to disentangle the complexity of this phenomenon, modelling is expected to play a relevant role. In this work a distinction is made between models that simulate degradation mechanisms and models that aim to predict the voltage loss that results as a consequence, focusing mostly on the latter ones. Single cell experimental data collected in the European Project ID-FAST are used as a starting point for the modelling analysis aiming to understand the voltage loss that results from real world operation and newly developed accelerates stress tests. A monodimensional model is developed and validated over a large set of experimental data from zero-gradient cell hardware, including polarization curves, limiting current tests and electrochemical impedance spectroscopy. This parametrization is later adopted in multidimensional and transient models to simulate degradation under mitigated air start-up and dynamic driving cycles. Impact of cathode catalyst layer degradation on fuel cell performance is simulated based on the experimental evidence to analyse the impact of catalyst surface loss. Specific emphasis is dedicated to the evaluation of mitigated air start-up, which analysis is supported by means of a 2D transient model that captures the time evolution of electrode potential and the impact of carbon and platinum degradation. Another relevant case that is analysed considers the voltage loss that results from the application of dynamic driving cycles, which are simulated by means of a 1D+1D transient model and a complete system model.

Experimental data on single cell were collected under ID-FAST project
(Grant Agreement No 779565, Joint Undertaking, EU Horizon 2020).

Keywords: PEMFC, degradation, accelerated stress test, air start-up, driving cycle.

Plan of Site

Schloss Hohenkammer



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7	Gutshof-Saal	Fuel cell & Redox Flow Battery sessions
18	Eventhalle	Battery sessions
24	Gutshof-Foyer	Coffee breaks & poster session

Day 1 - March 14, 2022

14:30 I Arrival

17:00 I Registration @ Hotel

19:00 I Conference Dinner @ Gutshof-Restaurant

Day 2 - March 15, 2022

08:00 I Welcome

08:15 I **Keynote: Tejs Vegge**
ML-accelerated simulations of solid-liquid interfaces in batteries and fuel cells
Eventhalle

09:00 I Coffee Break @ Gutshof-Foyer

I Data-Driven Battery Modeling
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Chair: Birger Horstmann

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13:30 I Simulation of a Chemo-Mechanical Model for SEI Growth on Battery Anode Particles
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13:30 I Analytical Multiphase Flow Modeling of Parallel Plate Electrolyzers
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Jörn Brauns

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Data-driven battery health diagnosis in real-world applications
Eventhalle

15:00 I **Keynote: Marc Secanell**
Transient, multi-scale, multi-phase analysis of polymer electrolyte fuel cells and electrolyzers
Gutshof-Saal

I Battery Degradation
Chair: Birger Horstmann

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16:05 I Mathematical Modelling of Anion exchange membrane based water electrolysis **Ronit Panda**

16:30 I Poster Session

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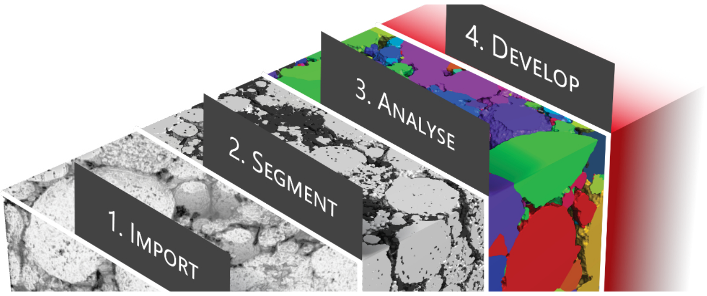

Day 3 - March 16, 2022

08:15 | **Keynote: Momo Safari**
Formulation, design, and characterization of NMC porous lectrodes: a model-assisted approach
Eventhalle

08:15 | **Keynote: Andrea Baricci**
Modelling voltage loss in polymer electrolyte membrane fuel cells after catalyst layer degradation
Gutshof-Saal

09:00 | Coffee Break @ Gutshof-Foyer

Battery Fundamentals
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Prof. Hans-Georg Steinrück

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Zeyang Geng

10:10 | Modelling the Transport of Secondary Carriers in a Solid Lithium-Ion Conductor
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10:30 | A system identification approach to estimate lithium-ion battery entropy coefficients
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13:30 | 3D microstructure characterization of polymer-based battery electrodes by statistical image analysis based on synchrotron tomography
Marten Ademmer

13:50 | Microstructure-resolved modelling of solid-state batteries: The importance of anisotropy and secondary phases in the composite cathode
Moritz Clausnitzer

14:10 | A Computational Approach for 3D Resolved Electro-Chemo-Mechanical Analysis of ASSB Including Contact Effects
Christoph Schmidt

Redox Flow Batteries
Chair: Roswitha Zeis
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12:50 | 3D printed electrodes for redox flow batteries
Dr. Jonas Hereijgers

13:10 | Modelling and Simulation for the Search for New Active Materials for Redox Flow Batteries - Results of the International Project SONAR
Prof. Jens Noack

13:30 | Non-solvent Induced Phase Separation: A Versatile Synthetic Method for High Performance Redox Flow Battery Electrodes
Prof. Antoni Forner-Cuenca

13:50 | In situ and in operando detection of redox reactions during vanadium transport in ion exchange membranes
Torben Lemmermann

14:10 | Pore-scale resolved 3D simulation of aqueous organic flow batteries
Amadeus Wolf

Day 3 - March 16, 2022

14:30 I Coffee Break @ Gutshof-Foyer

I Lithium Intercalation
Chair: David Howey

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Eventhalle

14:45 I Current Constriction at the Li|Li7La3Zr2O12 Interface
Janis Kevin Eckhardt

15:05 I Linear stability analysis of a graphite multi-layer phase field model
Antoine Cordoba

15:25 I Compensatory measures to overcome performance limitations of recycled Li-ion battery materials
Marco Lagnoni

15:45 I A guideline to the time-adaptive reduced order modelling of lithium-ion cells
Eduardo Jané

16:05 I Development and Verification of a Method to efficiently solve Discontinuous Thermal Transport Models
Oliver Queisser

I PEMFC Microstructure & Degradation
Chair: Andrea Baricci

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Gutshof-Saal

14:45 I Macroscopic simulation of 1000 PEMFC ageing cycles
Dr. Guillaume Serre

15:05 I Modeling of platinum oxides formation and reduction: a performance model for O2 reduction reaction
Florent Vandenberghe

15:25 I High-fidelity pore-level simulation of the flow in the channel and GDL of a micro-PEFC
Seyyed Khatoonabadi

15:45 I Predicting optimal catalyst layer microstructures in low Pt loading PEMFCs
Corey Randall

16:05 I Automating Image Analysis for Electrochemical Materials Characterization with Deep Learning
André Colliard Granero

16:30 I Concluding Remarks and Announcement of ModVal19 @ Eventhalle
16:45 I End

DLR

Batteries

Battery Fundamentals

B1.1 | A Geometry-corrected Pore Network Model for the Electrolyte Filling of Batteries **Benjamin Kellers**

B1.2 | Why do we observe a momentum flow in eNMR measurements? **Franziska Kilchert**

B1.3 | Analysis of Nonlinear Features in the Machine Learning-based Modeling of Lithium-Ion Batteries **Joachim Schaeffer**

B1.4 | Simulative Analysis of Efficiently Computed Chemical-Mechanical Coupled Contact Problems for Battery Active Particles **Raphael Schoof**

B1.5 | Solvation Behaviour in Electrochemical Double Layers: Modelling Solvation Energy **Constantin Schwetlick**

B1.6 | Incorporating Transport Effects in Coatings and Grain Boundaries into a Monolithically Coupled Electro-chemistry-Mechanics Model for ASSB **Stephan Sinzig**

Battery Degradation

B2.1 | Degradation and State Estimation of Li-Ion Batteries in Satellite Applications **Linda Bolay**

B2.2 | Coupled modeling of the thermal, electrical and aging behavior of Li-ion battery cells **Lisa Cloos**

B2.3 | Modeling and Simulation of Transport, Interfaces and Mechanics inside the SEI **Lukas Köbbing**

B2.4 | Towards physically interpretable neural ODEs with an example for SEI formation **Srivatsan Ramasubramanian**

B2.5 | An Efficient Numerical Solver for SEI Degradation in Li-Ion Batteries **Falco Schneider**

B2.6 | Chemical Thermal Runaway Modelling of Lithium Ion Batteries for Prediction of Heat and Gas Generation **Niklas Weber**

Battery Cell Models

B3.1 | Prediction of Reversible Lithium Plating with a Pseudo-3D Lithium-Ion Battery Model **Dr. Serena Carelli**

B3.2 | Investigating sodium-iodine battery cathodes using EIS simulations **Felix Gerbig**

B3.3 | A Multi-Process Cathode Model for MnO2-based Aqueous Zinc-Ion Batteries **Niklas Herrmann**

B3.4 | Lithium-ion cell optimisation using a time-adaptive reduced order model **Ruth Medeiros**

B3.5 | Full parametrization of commercial 18650 battery cell for physics-based modelling **Bhawna Rana**

B3.6 | Reduction of battery module equivalent circuit models using a distribution of time constants analysis **Tom Rüther**

B3.7 | Parameterization of Lithium-Ion Batteries: Differences and Similarities between High Energy and High Power Cylindrical Cells **Christina Schmitt**

B3.8 | A new continuum model of Metal-Sulfurized Polyacrylonitrile (SPAN) batteries **Esther Kezia Simanjuntak**

B3.9 | Conceptual design of solid-state electrode for eVTOL urban air mobility **Dr. Somayeh Toghyani**

B3.10 | From Particle-Scale Information to Cell Performance **Johannes Wiedemann**

Battery Electrode Models

B4.1 | Simulation of Li-Plating in Si/Graphite Composite Electrodes **Lioba Boveleth**

B4.2 | The Effect of Mechanical Cycling on the Electronic Conductivity of Composite Electrodes **Thimo Brendel**

B4.3 | Influence of Carbon Binder Domain on the Performance of Lithium-Ion Batteries: Impact of Size and Fractal Dimension **Anshuman Chauhan**

B4.4 | Methods from machine learning for the structural analysis of Li-ion electrode particles **Orkun Furat**

B4.5 | Binder identification in granular and fibrous energy material scans **Dr. Ilona Glatt**

B4.6 |

B4.7 | Modelling of Laser Structured Electrodes **Dr. Franz Pichler**

B4.8 | Modelling Lithium Flow from Power-Law Creep in 2D **Albert Pool**

B4.9 | Effect of a Heterogeneous Distribution of the Conductive Additives and Binder Domain on the Impedances of Lithium-Ion Battery Electrodes **Mrudula Prasad**

B4.10 | Reconstruction of the carbon-binder domain in Li-ion battery cathodes and its influence on the electrochemical performance **Benedikt Prifling**

B4.11 | Particle based computation of mechanics in granular multiphase electrodes **Alexandra Wahn**

Fuel Cells, Electrolysis & Redox Flow

Fuel Cells

F.1	Control of hybrid PEM fuel cell system reducing degradation based on Reinforcement Learning	**Matthias Bahr**
F.2	Distribution of current density across the active area of the JRC ZERO∇CELL single cell PEM fuel cell testing hardware	**Dr. Tomasz Bednarek**
F.3	In-situ estimation of effective diffusion coefficients in PEMFC	**Rémi Bligny**
F.4	Evaluation of different system configurations for a heavy duty PEM fuel cell system model	**Joscha Böhm**
F.5	Fault detection and identification for Polymer Electrolyte Membrane Fuel Cell	**Prof. Yann Bultel**
F.6	Performance degradation of Proton Exchange Membrane Fuel Cells under Repeated Compression for the Maintenance	**Bogeun Choi**
F.7	Investigation of Water Cluster and Droplet Interactions in PEFC using Operando XTM	**Tim Dörenkamp**
F.8	Multiphase and Pore Scale Modeling on Catalyst Layer of High-temperature Polymer Electrolyte Membrane Fuel cell	**Kangjun Duan**
F.9	Machine Learning in Dynamic Fuel Cell Modeling	**Dieter Froning**
F.10	Impedance-Based, Multi-physical DC-Performance-Model for a PEMFC Stack	**Tobias Goosmann**
F.11	2-D + 1-D PEM fuel cell model for fuel cell system simulations	**Dr. Sönke Gößling**
F.12	Model-based investigation of PEMFC ageing under realistic automotive conditions	**Amedeo Grimaldi**
F.13	Simulating the Cathode Catalyst Layer of a PEM Fuel Cell using Lattice Boltzmann Modelling	**Konrad Gülicher**
F.14		
F.15	Monte Carlo simulation of electrical and thermal conductivity for highly filled compo-site in fuel cells	**André Kayser**
F.16	Application of Loewner framework for data-driven modeling of electrochemical energy technologies	**Bansidhar Patel**
F.17	The impacts of GDL contact angle on the water management of the PEMFC: 3D simulation and optimization using artificial neural networks	**Hossein Pourrahmani**
F.18	Unravelling the Water Distribution in the Cathode of a Polymer Electrolyte Fuel Cell	**Yufan Zhang**

Electrolysis

E.1	Water management in gas-fed CO2 reduction devices with bipolar membranes	**Matthieu Dessiex**
E.2	TFFA model for electrochemical CO2 reduction at silver gas diffusion electrodes	**Marco Löffelholz**
E.3	Elucidating the Effect of Electro-Osmotic Drag on H2 Crossover at High Current Densities in PEM Water Electrolysis	**Agate Martin**
E.4	A Scaling Analysis for Bubble Plumes in Gas Evolving Electrodes	**Aviral Rajora**
E.5	Simulation-aided Prototyping of Photo-electrochemical (PEC) Cell Design	**Carmen Tenholt**
E.6	Quantifying Water Transport Limitations in Bipolar Membrane Electrolysis in Dependence of Membrane Thickness	**Oskar Weiland**

Redox Flow Batteries

R.1	Kinetics of Oxygen Evolution Reaction in Soluble Lead Flow Batteries	**Miji Joy**
R.2	Detailed Model of a Vanadium Flow Battery Including Separator Crossover and Electrolyte Composition Changes	**Alexander Kubicka**
R.3	Reactive Transport in Porous Electrodes: From Pore-scale to Macroscale Descriptions	**Dr. Roman Schärer**
R.4	The mass transfer effects of pulsating flow in redox flow batteries	**Renée De Wolf**
R.5	Performance evaluation of vanadium redox flow battery: An effect of pre-treatment and porosity of carbon felt electrode	**Anand Kumar Tripathi**

Assessing a novel method for joint state-parameter estimation and optimal fast-charging

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Battery management systems typically employ equivalent circuit models (ECMs) due to their low computational cost and simplicity. However, the development of new methods is desirable to unlock the power of physics-based models and improve battery performance and longevity. We test the capabilities of a new mathematical approach to optimisation, based on recent developments in the field of measure-moment theory for polynomial models [1]. In contrast to a Kalman filter-type approach [2], this method does not require discretisation in time to estimate the evolution of the states and parameters. Instead, a linear matrix inequality (LMI) hierarchy is constructed in terms of moments.

We will begin by explaining the unique advantages of our approach and the types of (nonlinear) optimisation problem that can be addressed. We will then demonstrate the utility of the method by numerically solving (using [3]) a selection of battery management optimisation problems. For this, we will use the Thévenin model with a variable series resistance and synthetic data. Our first example is state-of-charge (SOC) estimation from current-voltage data [2]. Secondly, we tackle a joint state-parameter estimation, in which both of the model states (SOC and voltage across the RC pair) are estimated along with the variable series resistance from current-voltage data. The series resistance varies with SOC as well as time and is identifiable when the input current is non-zero. Our third application is a constrained, optimal fast-charging problem where the aim is to identify the optimal input current profile to achieve the shortest possible charging time subject to a given set of constraints [4]. In each case, we benchmark the approach in terms of computational speed and accuracy.

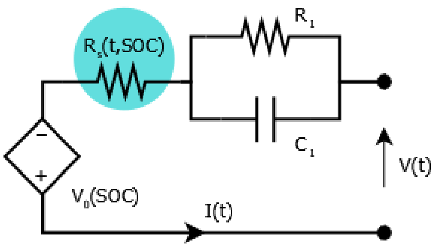

Figure 1: Equivalent circuit model.

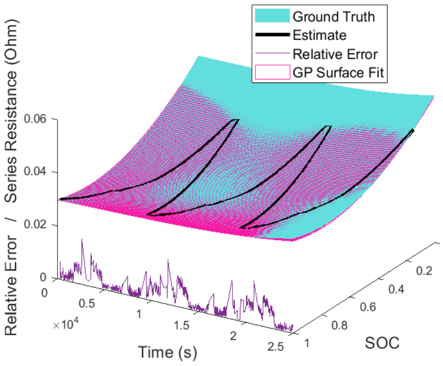

Figure 2: Time- and SOC-dependent series resistance.

Keywords: equivalent circuit models, estimation, optimisation, lithium ion batteries.

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Bayesian Quadrature for Fast Parameter Estimation of a Lithium-ion Battery Model

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Electrochemical models are useful for the design and control of devices—however, estimating their parameters is a challenging task. A parameter identifiability problem arises in certain conditions, e.g., when the graphite anode potential is on a plateau [1], and, to judge the reliability of the estimated parameters, we require reliable uncertainty quantification. Using a Bayesian approach provides such uncertainty quantification by inferring posterior distributions of each parameter. However, a Bayesian approach requires sampling, and existing sampling methods, such as Markov Chain Monte Carlo (MCMC), have poor sampling efficiency for capturing the posteriors, often requiring over 100,000 samples for convergence [1].

In this work, a Bayesian quadrature (BQ) approach was adopted to accelerate the parameter estimation of the lithium-ion battery model, a single particle model with electrolyte dynamics (SPMe) [2]. The SPMe spatial discretisation was implemented using spectral methods with Chebyshev orthogonal collocation [3] for speed. BQ is a model-based numerical integration technique, designed to minimise the number of samples [4, 5]. This method can infer the marginal likelihood integral by adopting a surrogate model for the intractable SPMe likelihood function—usually a Gaussian Process (GP) surrogate is used. As such, BQ can translate the posterior inference task into making a GP surrogate model more accurate in inferring the marginal likelihood by carefully choosing sample points. In each iteration, BQ picks the best candidate sample that contributes to the reduction in the entropy of the integrand-based on an acquisition function. This method is particularly effective for evaluating an expensive likelihood, such as a simulation-based likelihood that results in fitting electrochemical battery model parameters. Moreover, BQ delivers a reduced-order probabilistic model of the simulation, which is useful for downstream tasks such as control.

Our current research shows that BQ can infer the posteriors of SPMe parameters within 1,000 samples, approximately 50 times the speed of MCMC in a like-for-like comparison. This has significant implications for its further application, such as the higher dimensions of parameters and larger, or more complex, models.

***Keywords**:* Bayesian Inference, Bayesian Quadrature, parameter estimation, battery, lithium-ion

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Generation of digital twins for one- and two-layer battery electrodes containing differently sized active material particles

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Low rate performances and insufficient energy densities of batteries are a limiting factor for electromobility. This gives rise to the development of specific structuring concepts for electrode materials such as, *e.g.*, blend electrodes with different active material particles, which lead to an increase in the volumetric energy density. In this contribution, digital twin models are presented which support the experimental optimization of structuring concepts by a combination of stochastic 3D microstructure modeling with locally resolved transport simulations similar as in [1]. In particular a generalization of the stochastic 3D microstructure model presented in [2] allows us to generate digital twins of two-layer electrodes with differently sized active material particles in the two layers as well as digital twins of blend electrodes with an arbitrary mixing ratio of the contained types of active material particles. The parameters of the generalized stochastic 3D microstructure model are calibrated to 3D image data obtained by synchrotron tomography. This data-driven modeling approach enables us to statistically reproduce electrodes manufactured with different structuring concepts. By variation of model parameters, a large range of virtual, but realistic electrode microstructures can be generated which have not been manufactured so far. The virtual microstructures are used as an input for locally resolved electro-chemical simulations in order to determine the behavior of lithiation as well as the energy density of the virtual electrode structures. The presented modeling and simulation workflow opens the possibility to provide structuring recommendations for optimized structuring concepts used for electrode design.

Keywords: digital twins, electrochemical simulations, lithium-ion batteries, stochastic 3D microstructure modeling, 3D image data, structuring concepts

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2. Westhoff, D.; Manke, I.; Schmidt V. *Computational Materials Science* **2018**, *151*, 53-64. DOI: 10.1016/j.commatsci.2018.04.060

On Uncertainty Quantification in the Parametrization of Newman-Type Models of Lithium-Ion Batteries

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We consider the problem of parameterizing Newman-type models of Li-ion batteries focusing on quantifying the inherent uncertainty of this process and its dependence on the discharge rate. In order to rule out genuine experimental error and instead isolate the intrinsic uncertainty of model fitting, we concentrate on an idealized setting where “synthetic” measurements in the form of voltage curves are manufactured using the full, and most accurate, Newman model with parameter values considered “true”, whereas parameterization is performed using simplified versions of the model, namely, the single-particle model and its recently proposed corrected version. By framing the problem in this way, we are able to eliminate aspects which affect uncertainty, but are hard to quantify such as, e.g., experimental errors. The parameterization is performed by formulating an inverse problem which is solved using a state-of-the-art Bayesian approach in which the parameters to be inferred are represented in terms of suitable probability distributions; this allows us to assess the uncertainty of their reconstruction. The key finding is that while at slow discharge rates the voltage curves can be reconstructed quite accurately, this can be achieved with some parameters varying by 300% or more, thus providing evidence for very high uncertainty of the parameter inference process. As the discharge rate increases, the reconstruction uncertainty is reduced. However, the fits to the voltage curves become less accurate and the reconstructed parameter values begin to deviate from the “true” ones. The decrease in the accuracy of fits is concomitant with the simplified models losing validity; at C-rates of 2C and above the single-particle model does not accurately capture the physics of (dis)charge. This reveals a pitfall that one needs to be mindful of, namely, that an accurate fit does not necessarily mean that the fitted model accurately describes the physics [1].

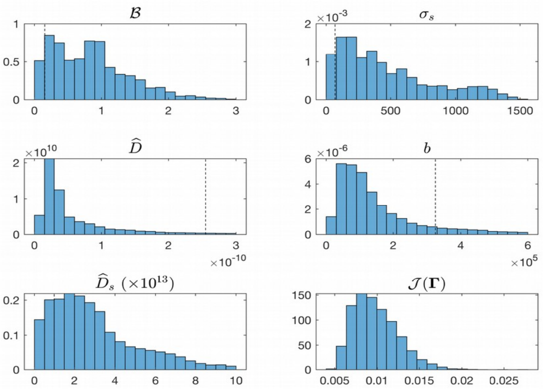

Figure 1. Probability density functions of the inferred material parameters: permeability (B), conductivity in the solid phase (σ_s), diffusivity in the electrolyte (D), particle surface area per unit volume (b), diffusivity in the solid phase (D_s), and of the error functional J obtained in the solution of the Bayesian inverse problem for the corrected Single-Particle (cSP) model with the charging rate 2C [1]. The spread of these distributions signals significant uncertainty of parametrization.

***Keywords**:* Newman model, inverse modelling, parametrization, uncertainty quantification

1. Morales Escalanta, J. et al., Journal of The Electrochemical Society, 2021 **168** 110519

Bayesian Optimization for Automated Parameterization of 1+1D Battery Cell Models

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Our goal is the automated parameterizing of battery cell models for model-based evaluation of experimental databases. The manual standard approach requires cell disassembly and individual measurements on the various cell components [1]. Measurement techniques include, e.g., galvanostatic intermittent titration technique (GITT) [2] or impedance spectroscopy [3]. They are complicated by their long run-time and considerably noise sensitivity.

Bayesian algorithms can directly incorporate the inherent uncertainties of model and measurement. The standard approach for parameterization is Markov-Chain Monte Carlo (MCMC) [4]. But with 1+1D battery cell models, their simulation time is too large for the tens of thousands of required samples.

In this contribution, we extend Bayesian Optimization (BOLFI) [5] with Expectation Propagation (EP) [6] to create a black-box optimizer suitable for modular 1+1D battery cell models. The algorithm can exploit a partitioning of the experimental data into features that is motivated by physico-chemcial understanding. However, the algorithm does not rely on approximative formulas and can be applied to a broad range of techniques. This approach reduces the number of required simulations for four parameters from 100,000 [4] to about 500. Furthermore, we can estimate parameter uncertainties and inter-dependencies. As an example, we process GITT full-cell measurements of lithium-ion batteries to non-destructively characterize the diffusivities of both electrodes at the same time.

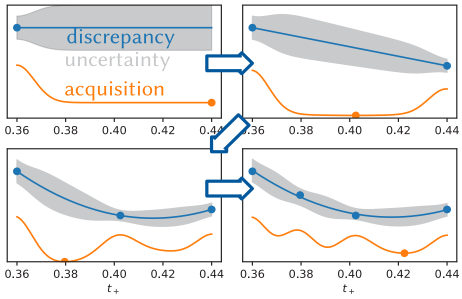

Figure 1: Scheme of Bayesian Optimization

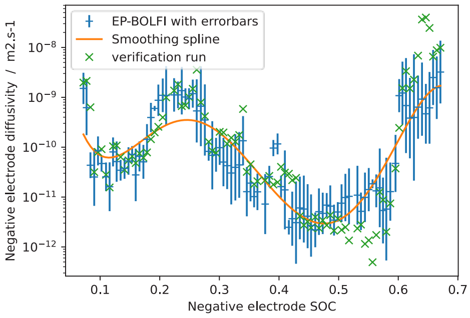

Figure 2: automated fitting of anode diffusivity to GITT

***Keywords**:* battery, uncertainty quantification, parameter sensitivity, model parameterization, mesoscale, Bayesian, in situ characterization, volume-averaged cell modelling, data-driven modelling.

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Functional Data-Driven Framework for Fast Predictions of Mechanistic Simulations Results

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The developments on multiscale computational modeling in material sciences surged in the last years, providing a deep insight of complex multi-parameter systems [1]. However, running the corresponding simulations is typically time and resources intensive, forcing researchers to make a compromise between the application of various parameter set and the time required to recover the full simulation process, especially for models parametrization [2]. In this work, we tackled this issue by proposing a functional data-driven framework for fast predictions of mechanistic simulations results, that combines Functional Principal Component Analysis and K-Nearest Neighbors algorithms [3]. This leads to an improved understanding of simulations, which is beneficial for computational resources management. The aforementioned framework was applied to lithium-ion battery electrode manufacturing in the context of coarse-grained molecular dynamics simulations for the modeling of in-silico slurries (Figrue 1A). The results show the potential to handle functional data analysis to any mechanistic model for fast predictions of results, highly reducing the computational cost (Figure 1B) [4].

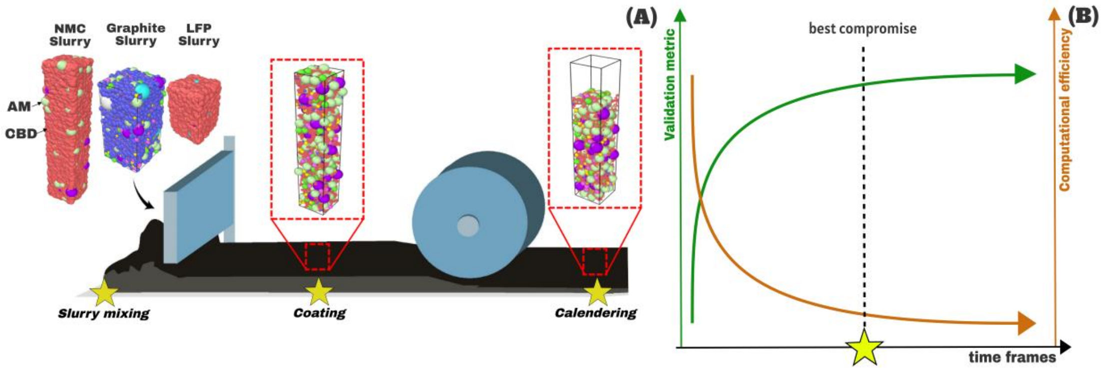

Figure 1: *(A)* : schematic of a lithium ion battery (LIB) electrode manufacturing process. *(B)* Overall compromise for computational cost decrease.

***Keywords**:* machine learning, functional data analysis, simulations, batteries.

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Cracking Predictions of Lithium-ion Battery Electrodes by X-ray Computed Tomography and Phase Field Modelling

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Fracture of lithium-ion battery electrodes is found to contribute to capacity fade and reduce the lifespan of a battery.[1] Traditional fracture models for batteries are restricted to consideration of a single, idealised particle;[2] here, advanced X-ray computed tomography (CT) imaging, an electro-chemo-mechanical model and a phase field fracture framework are combined to predict the void-driven fracture in the electrode particles of a realistic battery electrode microstructure (see Fig. 1.).

An electrode is shown to exhibit a highly heterogeneous electrochemical and fracture response that depends on the particle size and distance from the separator/current collector. The model enables prediction of elevated cracking due to enlarged cycling voltage windows, cracking as a function of electrode thickness, and increasing damage as the rate of discharge is increased. This framework provides a platform that facilitates a deeper understanding of electrode fracture and enables the design of next-generation electrodes with higher capacities and improved degradation characteristics.

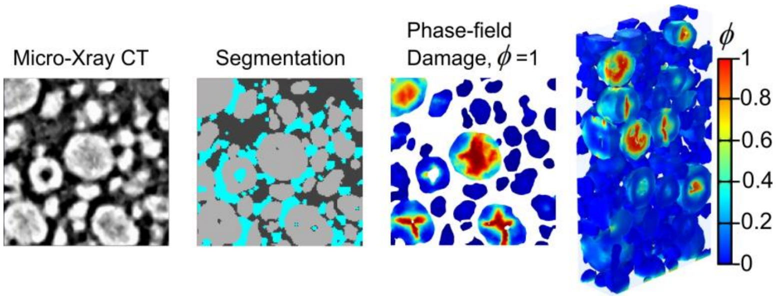

Figure 1: *An X-ray tomogram, segmented image and simulated cracking of a realistic electrode microstructure.*

***Keywords**:* electrode microstructure, image-based model, phase field.

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Experimentally validated simulation of strain-induced battery aging

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During cycling, volumetric changes of the active material induce stresses on the micro- and macro-scale, leading to cracks and delamination, and deformation of the inactive layers and the casing [1]. The altered microstructure is said to "age" and it suffers from capacity loss and damaging effects like lithium-plating [2]. The quantitative simulation of this battery aging on a microstructural level is now jointly pursued by Math2Market and the MaDE group of Prof. Vanessa Wood (ETH Zürich) in the framework of the EU-project "SOLVED!".

Our approach is to analyze NMC cathode and graphite anode microstructures via 3D in-vivo tomography and electrochemical characterization [3]. The experimental data is used to validate the degradation simulations in which local volumetric changes and damage, due to lithium intercalation on the microscale, are linked to the local Li-ion concentration in the active material and its mechanical deformation. In a dynamic process, the altered microstructure is considered for each charging and discharging step. In this way, the influence of structural changes on the electronic and ionic transport processes and on the macroscopic performance of the cell is digitally predicted and monitored.

The usage of reliable quantitative simulations allows for the timesaving and streamlined finding of new prototype materials with superior lifetime and performance. This unique workflow represents a new efficient, state-of-the-art approach to digital R&D material design for energy materials in e-mobility and energy storage.

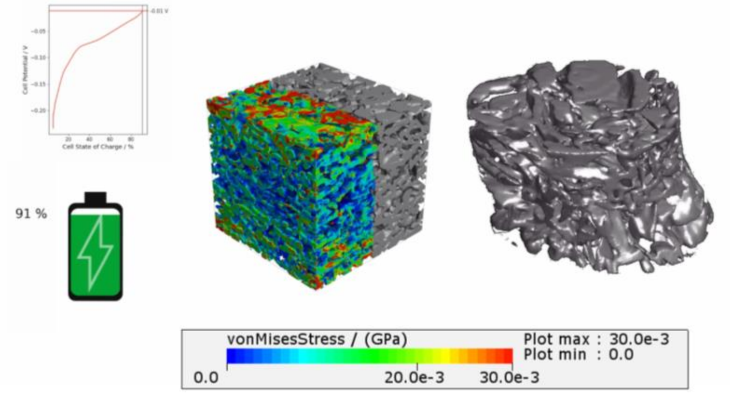

Figure 1: Expanded graphite anode due to Li-concentration changes during charging. Simulation results (left) vs experimental results (right)

***Keywords**:* battery, microstructure, mechanical aging, material design, aging.

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Simplified models for electrochemical degradation (SEI and Li plating)

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Understanding the degradation behaviour of batteries is a key step towards a better battery performance and longer battery life. However, coupling the Doyle-Fuller-Newman (DFN) model with degradation effects is computationally expensive as often degradation effects are not noticeable until after hundreds of cycles. This limitation motivates the need of simpler models which are usually posed in an ad hoc manner. This approach has led to inconsistencies with the full DFN model and to multiple formulations of the same model.

In this work we present a Single Particle Model with electrolyte and a side reaction (SPMe+SR) derived from the full DFN model using asymptotic techniques. The advantage of this well-established mathematical technique is that it is systematic and the assumptions on which is based can be validated *a priori*. This allows for the derivation of robust and physically consistent models. The side reaction included in the model is arbitrary and therefore the SPMe+SR can capture both SEI growth and lithium plating, in addition to scenarios which combine several reactions.

We have implemented the SPMe+SR in PyBaMM [1] and validated it against a DFN model for multiple scenarios, finding very high accuracy at a lower computational cost. The preliminary results are shown in Figure 1, and also show that SPMe+SR is about 8x faster. Moreover, SPMe+SR has a much lower-level complexity, which makes it suitable for battery design and control applications.

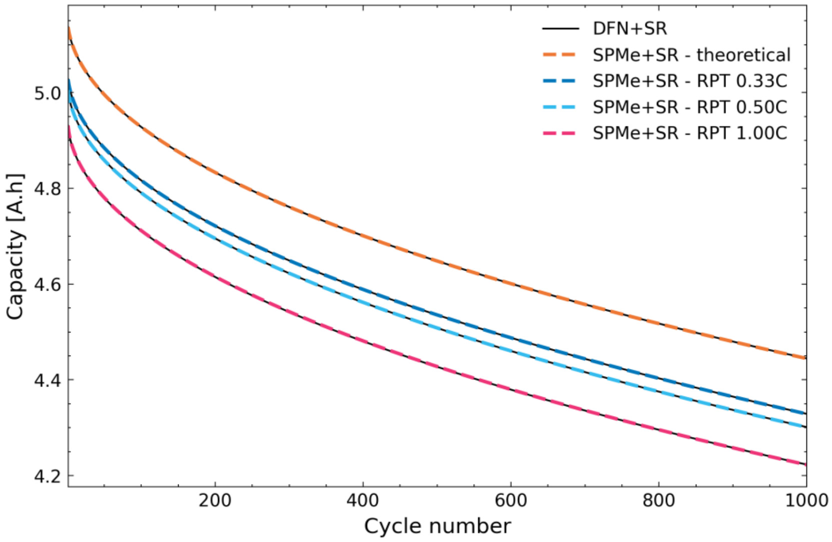

Figure 1: Comparison between the DFN model and the SPMe+SR for different conditions.

***Keywords**: battery modelling, physics-based models, model reduction, degradation, SEI growth, lithium plating*

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Simulation of a Chemo-Mechanical Model for SEI Growth on Battery Anode Particles

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Currently investigated anode materials such as graphite or silicon show the formation of a solid-electrolyte interphase (SEI). On the one hand, the SEI serves as a protection shield for the anode particles, on the other hand, the repeated fracture and healing of the SEI increases the capacity fade. With highly efficient numerical simulations, we want to predict the mechanics and the growth of the SEI on particles beyond the limited one-dimensional simulations.

For the modeling, we follow the recently developed thermodynamically consistent continuum model of an anode particle with a surrounded SEI layer as presented in [4]. This model considers the chemistry and mechanics of the particle and couples these to the deformation and growth of the SEI.

Accurate simulations of one-dimensional examples already require a large computational effort. Especially multi-dimensional geometries and long-term simulation of cycling the (dis-)charge over years are computationally expensive. To overcome these limitations, we implement the model with finite elements and apply our adaptive solution algorithm from [1,2,3]. Moreover, we employ advanced numerical techniques such as automatic differentiation and parallelization on distributed and shared memory to simplify and speedup the simulation process. Thus, with the efficient numerical implementation, we are able to study the effect of SEI growth and aging in nonuniform scenarios and critical parameter regimes within a reasonable time.

***Keywords**:* Lithium-ion battery, Mechanics, SEI, Numerical simulation, Finite element method

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Li-ion battery degradation: how to model it

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Predicting lithium-ion battery degradation is worth billions to the global automotive, aviation and energy storage industries, to improve performance and safety and reduce warranty liabilities. However, there are no reliable models and developers must resort to expensive and time consuming experiments, and only a few can afford to test under every realistic combination of operating conditions. In this paper, we report the first published attempt to directly couple more than two degradation mechanisms in the negative electrode, and map different pathways through the complicated path dependent and non-linear degradation space. Four degradation mechanisms are coupled in PyBaMM [1], an open source modelling environment uniquely developed to allow new physics to be implemented and explored quickly and easily. Crucially it is possible to see `inside' the model and observe the consequences of the different patterns of degradation, such as loss of lithium inventory and loss of active material. For the same cell we have already uncovered five different pathways that can result in end-of-life, depending on how the cell is used. Such information would enable a product designer to either extend life or predict life based upon the usage pattern. However, parameterization of the degradation models remains as a major challenge, and requires the attention of the international battery community.

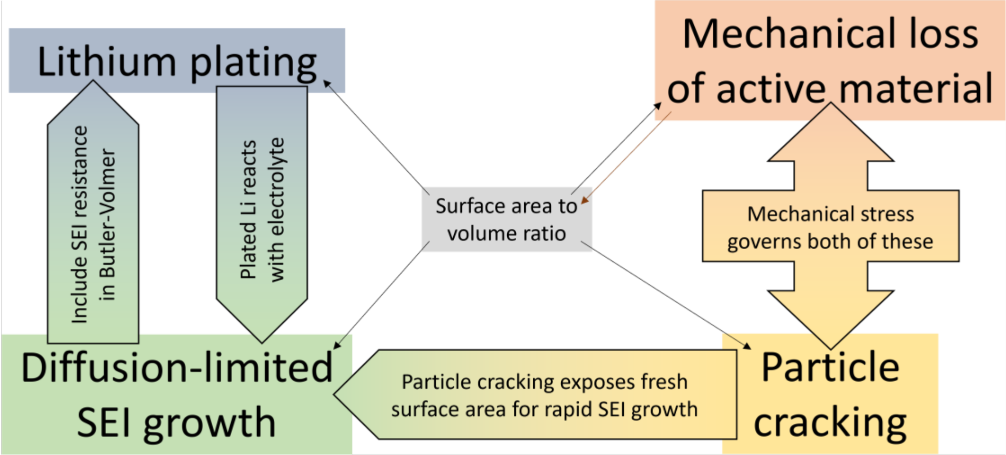

Figure 1: degradation mechanisms included in the model and how they interact

Keywords: Battery, pseudo-2D, degradation, SEI, lithium plating, particle cracking

[1] Sulzer V., Marquis S. G. et al. *J. Open Research Software* **2021**, *9* (1), 14. DOI: 10.5334/jors.309

Physics-based interpretation of LIB ageing through P2D model parameters identification

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The Doyle-Fuller-Newman (DFN) pseudo-two-dimensional model is a standard modelling environment, physics-based, able to reproduce all the major characteristics of lithium-ion battery operation and dynamics. In the previous edition of this symposium[1], we presented a novel methodology for its calibration, resulting from an extensive sensitivity analysis and employing a multi-measurement protocol, including electrochemical impedance spectroscopy, discharge and relaxation dynamics, at specific operating conditions able to maximise the identifiability of model parameters. The combination of three different techniques and two temperature levels enabled a reliable calibration of the model on a pristine sample, limiting its typical overfitting issues.

In order to demonstrate its application as an aging interpretation tool, the multi-measurement protocol is now applied for diagnosis on eight commercial samples undergoing an experimental cycling campaign at low temperatures (0°C, -10°C) at varying charging C-rates (0.5C, 1C), depth of charge (DoC, 30%, 50%) and maximum state of charge (SOC, 60%, 80%), expected to mainly trigger lithium plating-related degradation mechanisms. The diagnostic protocol is applied every 3 equivalent full cycles (EFC) and data are fed to a particle swarm optimization (PSO) algorithm that updates the model calibration, calculating the values of key physical parameters, hence translating the performance loss of the cell into the variation of parameters which have inherent physical meaning.

The interpretation identified a clear degradation of physical parameters related to both thermodynamic and kinetic properties of the negative electrode and a decrease in available lithium inventory, strongly related to temperature and average charge C-rate applied during cycling as the main stressors.

Considering the consistency of such results with the expected degradation mechanism, this first attempt achieved promising results, to be extended on close-to-real-world operations to distinguish among different mechanisms inducing similar and overlapping performance changes.

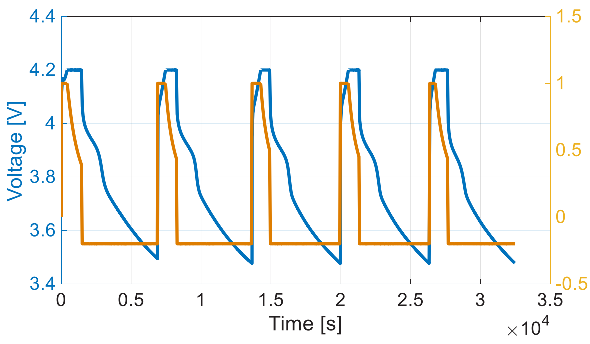

Figure 1: Example of ageing profile: load C-rate and corresponding cell voltage response.

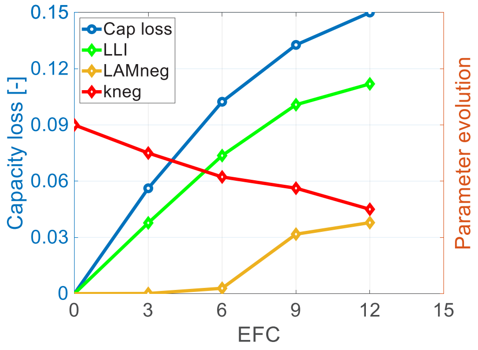

Figure 2: Example of physical parameters trends upon ageing, obtained through the calibration.

***Keywords**:* lithium-ion battery, ageing, calibration, P2D.

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Modeling and validation of thermally and intercalation-induced thickness change of a lithium-ion pouch cell during cycling

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One of the manifold aspects affecting cyclic aging of lithium-ion batteries are mechanical interactions, taking place inside the electrodes. Alternating phases of expansion and contraction can lead to stress, thus causing mechanical fatigue. As these interactions are of significant influence, they are increasingly gaining attention in modeling and simulation of lithium-ion batteries (*1*).

This work presents the implementation of mechanical interactions into a previously-developed model of a 350 mAh high-power lithium-ion pouch cell (*2*). Following a pseudo-3D modeling approach, the mechanical interactions are included on the electrode-pair level. Thermal strain is considered as well as intercalation-induced strain of the active materials. Moreover, this model takes into account non-ideal partial molar volumes that describe the volume change of the active materials as a function of lithium stoichiometry. So far, the model is capable of describing the unconstrained displacement of a lithium-ion pouch cell.

We furthermore show the experimental validation of the simulation results. With a fairly simple, yet precise experimental setup, we measure the unconstrained displacement of the pouch cell at various C-rates. Furthermore, to derive effective thermal properties, we characterize the thermal strain behavior by performing a thermal excitation experiment with 10C/1 Hz rapid cycling. Using these effective parameters as an input for the mechanical model, the simulations can well describe the observed thermal strain.

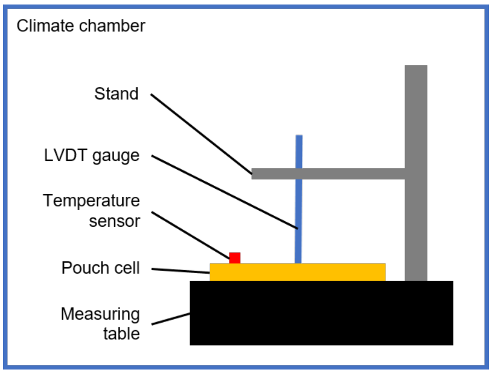

Figure 1: experimental setup

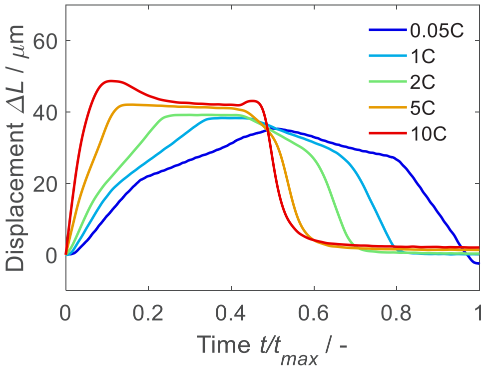

Figure 2: experimental displacement curves during CC CV charge / discharge at various C-rates

***Keywords**:* lithium-ion pouch cell, mechanical simulation, experimental validation, intercalation-induced strain, thermal strain, P3D.

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Concentration and Velocity Profiles in a Polymeric Lithium-ion Battery Electrolyte

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Predictive understanding of ion and mass transport in electrolytes is at the heart of electrochemistry. The goal is to accurately simulate the performance of an electrochemical cell, for which the concentration-dependent transport coefficients of a given electrolyte must be known[1]. These include the transference number, which is an important metric to energy and power density of batteries. Nevertheless, researchers still argue about transference number values, even in baseline electrolytes. This stems from the difficultly to experimentally measure the transference number in concentrated (non-ideal) electrolytic solutions; typically, assumption-based electrochemical relaxation and NMR techniques are used[2, 3].

We developed an alternative approach towards determining transport coefficients[4]. Specifically, we measured microscopic and macroscopic physical properties of electrolytes upon cell polarization in Li/electrolyte/Li cells, combined this with concentrated solution theory continuum modelling, and rationalized our findings with microscopic insight from molecular dynamics simulations. We utilized a well-studied benchmark model system electrolyte consisting of LiTFSI and PEO. Under constant voltage polarization, we directly measured the velocity associated with electrolyte and ions via heterodyne synchrotron X-ray photon correlation spectroscopy (XPCS), and the TFSI-concentration gradient via X-ray absorption microscopy. The significance of our results lies in the unification of microscopic and macroscopic predictions from simulation with experimental measurements as well as the self-consistent determination of a concentration-independent transference numbers of approximately 0.2.

***Keywords**: battery, electrolyte, transference number*

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Validity of solid-state Li$^+$ diffusion coefficient estimation by electrochemical approaches for lithium-ion batteries

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The solid-state diffusion coefficient of the electrode active material is one of the key parameters in lithium-ion battery modelling. Conventionally, this diffusion coefficient is estimated through the galvanostatic intermittent titration technique (GITT) [1]. In this work, the validity of GITT and a faster alternative technique, intermittent current interruption (ICI) [2], are investigated regarding their effectiveness through a black box testing approach [3]. A Doyle-Fuller-Newman model with parameters for a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ electrode is used as a fairly faithful representation as a real battery system, and the GITT and ICI experiments are simulated to extract the diffusion coefficient. With the parameters used in this work, the results show that both the GITT and ICI methods can identify the solid-state diffusion coefficient very well compared to the value used as input into the simulation model. The ICI method allows more frequent measurement, but the experiment time is 85 % less than what takes to perform a GITT test. Different fitting approaches and fitting length affected the estimation accuracy, however not significantly. Moreover, a thinner electrode, a higher C-rate and a greater electrolyte diffusion coefficient will lead to an estimation of a higher solid-state diffusion coefficient, generally closer to the target value.

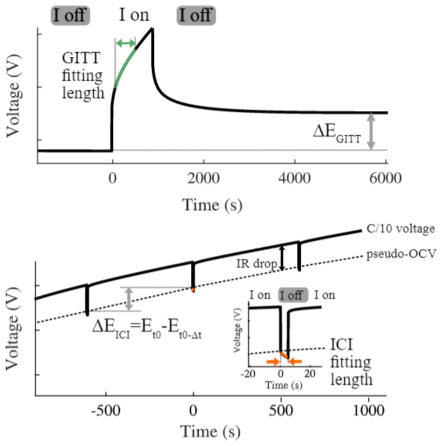

Figure 1: The voltage response during one current pulse, comparing the GITT (above) and ICI (below) approaches

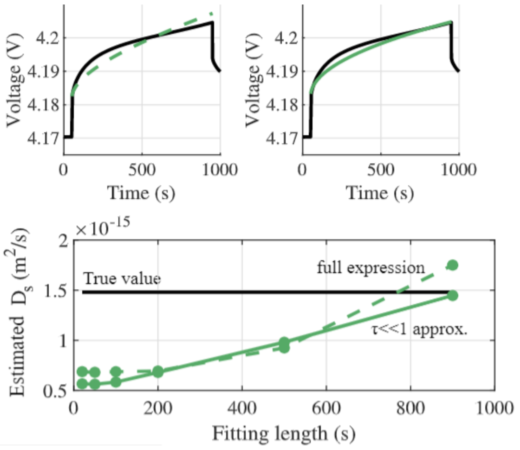

Figure 2: The voltage response of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ and its fitting to obtain its diffusion coefficient Ds in the GITT method.

***Keywords**:* Li-ion battery, modelling, galvanostatic intermittent titration technique, intermittent current interruption

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Modelling the Transport of Secondary Carriers in a Solid Lithium-Ion Conductor

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All-solid-state batteries based on solid inorganic ion conductors are widely studied. These tough electrolytes are generally not flammable and can make the battery safer and more durable. Solid electrolytes could potentially support metal electrodes and double the energy density of lithium-ion batteries. The near-unit transference number of an ideal single-ion conductor eliminates the diffusion polarization, implying a theoretical infinite limiting current [1]. Experiments have observed that dopants [2] and defects [3] can exist in solid electrolytes and impact ion transport considerably. Secondary charge carriers can possibly induce element segregation and cause solid electrolyte degradation and failure.

This research uses Newman's concentrated-solution theory to develop a chemo-mechanical transport model for elastic-solid ionic conductors containing two mobile ions [4]. We simulate the lithium-ion conducting $Li_5La_3Nb_2O_{12}$ (LLNO) garnet oxide. Experiments indicate that mobile protons can be freely substituted for lithium in LLNO to form $Li_{5(1-y)}H_{5y}La_3Nb_2O_{12}$ [5]. We investigate the dynamic and steady-state response of $Li_{5(1-y)}H_{5y}La_3Nb_2O_{12}$ subjected to a current. Ion transport is studied in both double layer and bulk regions. We show that the proton-substituted LLNO exhibits bulk lithium polarization. The diffusion limiting current is determined by the extent of proton substitution and cation/cation interactions. We quantify the limiting current and Sand's time and analyse the experimental data to show how a competitive proton transport can affect the performance of solid electrolytes [5,6].

Keywords*:* solid-state battery, continuum modelling.

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A system identification approach to estimate lithium-ion battery entropy coefficients

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Accurately predicting lithium-ion battery temperature is key for battery applications. For example, battery charging algorithms rely on mathematical models of the cell surface temperature to design the thermal management system and control strategy. There are several heat source terms that contribute to a cell's thermal dynamics, of which the reversible heat term is often neglected in such models due to the long experimental time associated with the potentiometric technique [1] to characterise it (20 hours to 35 hours per state-of-charge). Reversible heat can however contribute to around 70% of the total heat generated (with low currents) and is quantified by the associated *entropy coefficient*. The entropy coefficient is a thermodynamic quantity relating the open-circuit-potential (OCP) to temperature and varies over the cell's state-of-charge (SoC).

Robust techniques are required that can significantly reduce the experimental time and quantify the entropy coefficient over the full SoC window, leading to higher fidelity battery thermal models. In this work, system identification techniques are used to derive the entropy coefficient via the underlying *kernel function* between the cell OCP and temperature. The kernel function is a non-parametric estimate of the dynamics from which the entropy coefficient can be determined. Temperature signals are designed with multiple frequency components and applied to a cell via Peltier elements. The corresponding OCP response is then analysed, in the frequency domain, to estimate the kernel function (Figure 1). Unlike the potentiometric method, which drives the battery to steady-state and necessitates long experimental durations, the kernel function can be estimated under transients, facilitating faster characterisation. Figure 2 demonstrates comparable results of the entropy coefficient, over the full SoC interval, when estimated via the kernel function and the potentiometric approach. The approach, compared to the potentiometric method, however, brings around a five to six times reduction in experimental time per SoC and gives insight into the OCP and temperature dynamics. The signal design, kernel estimation and entropy coefficient estimation procedures are detailed in this work.

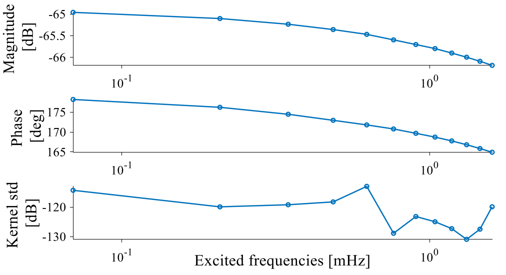

Figure 1: The OCP-Temperature kernel function estimate and its uncertainty when the battery is at 40% SoC

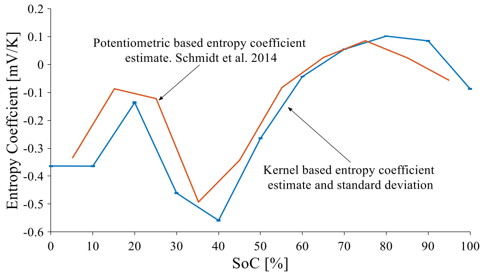

Figure 2: The entropy coefficient estimated via the kernel function and the potentiometric approach

Keywords: Entropy coefficient, reversible heat, potentiometric, System Identification

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Entropy measurements of Li and Na battery materials

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The open circuit voltage (OCV) and its variation with respect to temperature, as described by the partial molar entropy, are important parameters to describe and diagnose the state of a cell. These parameters also have an atomistic origin, being related to the interactions between the guest atoms in the electrode. We earlier developed a method to substantially reduce the time required to measure the partial molar entropy. We have also developed lattice gas methods to quantify and interpret the partial molar entropy [2,3].

In the present work, we demonstrate how the combination of rapid entropy profiling measurement with lattice gas models allows us to interpret key features with respect to the amount of Li or Na in the electrode material. In particular, we can separate out the OCV features into entropy and enthalpy components. We demonstrate how this approach can help to understand two very challenging systems: ***Figure 1***. the lithiation/delithiation hysteresis in graphite [2] and ***Figure 2.*** separating insertion of sodium into the interlayers versus the nanopores in hard carbons [3]. The method therefore helps to understand the anode material in virtually all commercial Li-ion cells, while also being applicable to next-generation battery materials as well.

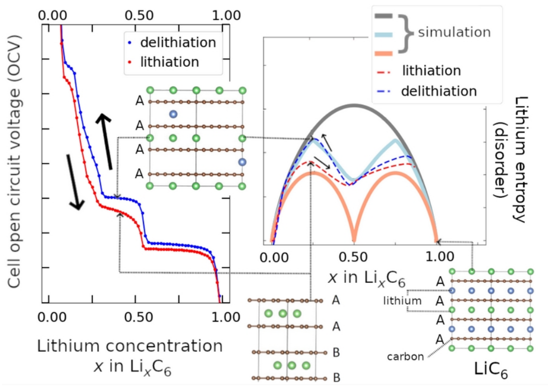

Figure 1: use of entropy profiling measurements and models to elucidate lithium disorder during lithiation/delithiation of graphite. Ref. [2]

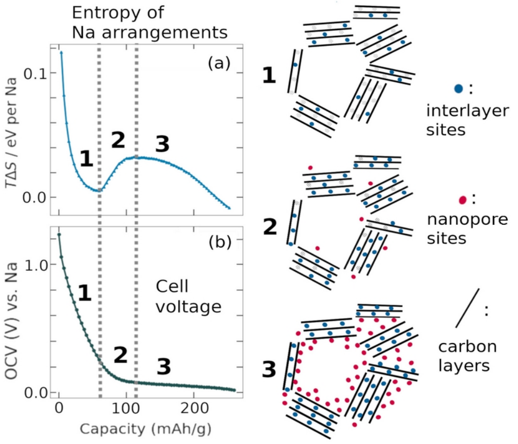

Figure 2: (a) the measured entropy of sodium insertion in hard carbon shows pronounced features, but the commonly measured cell voltage (b) is featureless. Fitting our model therefore allows interlayer and pore filling to be quantified. Ref. [3]

Keywords*:* battery, experiment, modelling, entropy, lattice gas.

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Nonlinear Frequency Response Analysis – a Modelling Assessment for Li-ion Batteries

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Nonlinear Frequency Response Analysis (NFRA) is an extension of the widespread Electrochemical Impedance Spectroscopy (EIS). It is a nonlinear method which allows the investigation of the nonlinear behaviour of Li-ion batteries via the exhibited higher harmonics Y_i as shown in Figure 1. From our previous studies, changes in the reaction kinetics show nonlinear phenomena that can be better detected via NFR signals in contrast to EIS [1]. In addition, the second harmonic shows unique sensitivities to the charge transfer symmetry [2], whereas the identifiability of the charge transfer symmetry remains ambiguous via existing methods such as C-rates and EIS [3]. These features make NFRA a potential tool for the characterisation of the inherent nonlinear behaviour of Li-ion batteries.

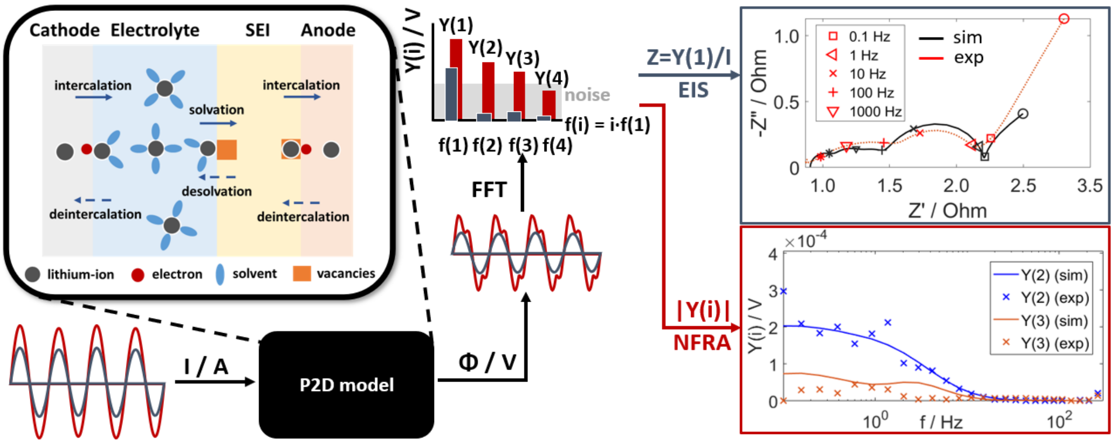

Figure 1 : Simulation of EIS & NFRA via P2D model with incorporated SEI.

In this contribution, we demonstrate the modelling approach of nonlinear behaviour in Li-ion batteries based on pseudo-two-dimensional (P2D) model as shown in Figure 1. The implemented P2D model incorporates a detailed depiction of the underlying processes at and between the two interfaces of the solid electrolyte interphase (SEI) at the anode, i.e., electrode/SEI and SEI/electrolyte interfaces, while an electrode/electrolyte interface is assumed at the cathode. Based on the P2D model, we propose a systematic characterisation of Li-ion batteries via NFRA in conjunction with the conventional C-rate and EIS measurements [3]. The characterisation was performed on lithium-ion batteries with NMC-811 cathode and Si-C_6 graphite anode respectively. By this, we show for the first time that the experimentally recorded nonlinear signals can be reproduced (Figure 1). Furthermore, it is shown that the de-/intercalation reactions at both anode and cathode are strongly nonlinear while the de-/solvation reaction behaves weakly nonlinear. From the ageing experiment, we further identify that degradation mostly impacts the rate of de-/intercalation reaction, which could be possibly due to loss of active materials. The major degradation in the de-/intercalation reactions not only causes a significant increase in the corresponding impedance but also the nonlinearities. In contrast to the de-/intercalation reaction, the de-/solvation reaction at the electrode/SEI interface is barely hindered as neither impedance nor the nonlinearities at the corresponding frequency range show any significant changes.

***Keywords**: Nonlinear Frequency Response Analysis, Li-ion batteries.*

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Modelling inhomogeneous degradation in lithium-ion batteries: the effect of thermal gradients

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Understanding degradation is critical to unlock the true potential of lithium-ion batteries. Poorly understood degradation leads to reduced energy/power density through over-engineering, and increased safety risks and failure rates. Thermal management is key to minimizing battery degradation. Yet, previous experimental results [1] have shown the effect of different thermal management strategies on degradation is still not fully understood.

In this work a 3D distributed electrical-thermal model including inhomogeneous degradation is used to explore the effects of thermal gradients on degradation for the first time. An equivalent circuit network (ECN) model (as shown in Fig. 1(a)) is used which can simulate thousands of cycles per day on a normal desktop computer. The model is capable of reproducing previously published experimental data [1] showing differences in the rate of degradation when surface cooling compared to tab cooling (results shown in Fig. 1(b)). The model shows that there is significant positive feedback which significantly accelerates battery degradation, if there are significant thermal gradients within the active region of the cell, and if the dominant degradation mechanism is a function of current in addition to temperature. Most cells suffer from internal thermal gradients during operation, and many degradation mechanisms are a function of current, suggesting these effects cannot and should not be ignored, and lumped models will have a high risk of significant underfitting. The findings should be of immediate interest to anyone attempting to model degradation in lithium-ion batteries, in addition to cell and battery pack designers.

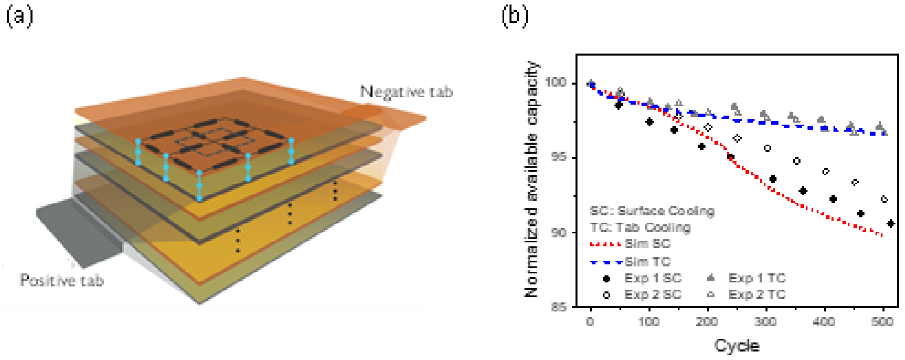

Figure 1: Schematic representation of the electro-thermal model for a pouch cell and cycling degradation results.

Keywords: Lithium-ion battery; Non-uniform degradation; Thermal management; Electro-thermal-degradation model

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Performing Fully-Coupled Electrochemical-Thermal Simulations of Cylindrical Cell Jelly Rolls in 3D

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Batteries have become indispensable components in modern energy systems, and model-based design tools are essential to improve both the cell itself and its integration into systems. A variety of simplified models including Single-Particle Models (SPMs) and pseudo-2D (P2D) continuum models have become standard tools in the battery community. These approaches help understand how the spatiotemporal evolution of quantities like concentration, temperature and electric potential affect the performance of the cell. However, these models rely on simplified volume-averaged approximations of the cell geometry, which can lead to the loss of important information about local conditions that might occur in the cell.

Simulations on a 3D mesh of the cell are necessary to fully resolve the local anomalies in the battery. 3D models have been proposed to address this need and have been successfully demonstrated for pouch cell geometries or electrode microstructures [1]. However, there is a dearth of studies using this approach to investigate cylindrical cell jelly rolls.

In this contribution, we present a fully coupled 3D electrochemical-thermal model of cylindrical Li-ion battery jelly rolls. The model uses a finite volume approach to solve the non-iso-thermal equations for mass, charge, and energy continuity on a discretized mesh of the jelly roll geometry. We explore the effects of tab design on 18650, 21700, and the novel 4680 cell formats. Using the 3D modelling approach, we can resolve some strong variations in the local conditions in the battery that can lead to inhomogeneous (de)lithiation of the electrodes and accelerated aging.

The simulations presented in this contribution are performed in the MATLAB Battery Simulation Toolbox (BatMo) developed in the EU project HYDRA. BatMo is an open-source framework for continuum modelling of electrochemical devices, which will be launched to the public in Spring 2022 to coincide with the ModVal conference.

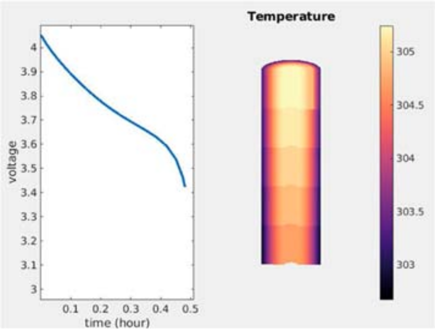

Figure 1. Screenshot from the BatMo framework showing the temperature distribution in an 18650 cell jelly roll.

Keywords: battery, continuum model, P4D, cylindrical cell, open-source

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3D microstructure characterization of polymer-based battery electrodes by statistical image analysis based on synchrotron tomography

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Technological advances, e.g., of consumer electronics and electric cars, continuously increase the requirements batteries have to fulfil. This led to the development of many different cell chemistries, optimized for specific applications. For next-generation batteries, one approach is to use organic polymers as active material in the electrodes. Those polymer-based batteries have potentially higher power densities and a smaller ecological footprint, compared to classical Li-ion batteries. Different classes of polymers have shown promising results, despite of some drawbacks, such as a limited lifetime or a high self-discharge [1].

It is well known that the microstructure of electrodes is a key factor for the performance of battery cells [2]. Thus, the 3D microstructure of two differently manufactured electrodes for polymer-based batteries is investigated by combining tomographic 3D imaging with statistical image analysis. In particular, synchrotron tomography is used to resolve the 3D microstructure consisting of redox-active polymer, binder-conducting additive phase and pores (Figure 1). This allows for the computation of morphological characteristics that are experimentally not accessible, see, e.g., [3]. In this talk, we focus on the local heterogeneity of volume fractions of the constituents, specific surface area of the polymer phase and the length of shortest transportation paths through both, polymer and binder-additive phase. The performed statistical analysis helps to get insights into the influence of the manufacturing process on the electrode microstructure and thus, on the performance of the cell.

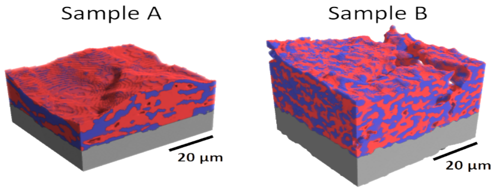

Figure 1: Sample cutouts representing the 3D microstructure of two differently manufactured electrodes consisting of a redox-active polymer as active material (blue), binder-conducting additive phase (red) and micropores (transparent).

Keywords: polymer-based battery electrode, microstructure characterization, 3D image data

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Microstructure-resolved modelling of solid-state batteries: The importance of anisotropy and secondary phases in the composite cathode

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Solid electrolytes are being considered to play an important role in future battery systems due to safety aspects and the possibility to use Li-metal anodes. A promising class of materials is the garnet-type $\mathrm{Li_7La_3Zr_2O_{12}}$ (LLZO) which shows a high stability towards Li-metal while providing a high ionic conductivity. However, the processing of composite cathodes is challenging and several aspects need to be considered in the optimization of the electrode microstructure. On the one hand, the electrode fabrication includes a high-temperature sintering step which can lead to the formation of secondary phases. These are often highly resistive which hinders the lithiation of the cathode active material and limits the cell performance. On the other hand, a preferential orientation of active material particles was observed in the sintered microstructure which affects both the mechanical and electrochemical properties of the electrodes [1].

In this contribution we investigate the influence of secondary phase formation and anisotropy of the cathode active material on the battery performance by continuum-modelling and simulation. By including an interface model in our simulation environment [2], we determine the limiting effect of secondary phases on the cell performance. Our results show a strong reduction of battery capacity due to secondary phases forming in the composite cathode during sintering. Secondary phases at the interface between cathode active material and electrolyte act as a blocking layer which can explain the relatively poor performance sometimes reported in experiments [3].
Furthermore, we investigate the effect of anisotropic chemical diffusion of Li in the active material. While the anisotropic properties of the active material play a minor role for homogeneous composite cathodes with moderate active material fractions, there is a stronger effect when considering inhomogeneous microstructures. Longer diffusion pathways resulting from an unfavourable particle orientation hinder the lithiation of the cathode active material and cause smaller capacities.

***Keywords**:* Continuum modelling, solid-state batteries, composite cathode, secondary phases, anisotropy.

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A Computational Approach for 3D Resolved Electro-Chemo-Mechanical Analysis of ASSB Including Contact Effects

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Conventional lithium-ion batteries will reach its technological limit soon [2], whereas all-solid-state lithium-ion batteries (ASSB) are currently expected to offer high energy and power densities. Hence, research activities investigating this promising technology for future energy supply have continuously increased. Computational methods enabling a thorough and deep understanding of the occurring phenomena are of increasing importance, especially as a comprehensive experimental investigation of these systems is not always feasible. Yet, due to the high complexity of the physical effects that are relevant in ASSB most of the existing simulation and modelling techniques base on various simplifying assumptions. Therefore, those methods do neither enable reliable predictions, nor profound analysis of the underlying phenomena.

Within this work, we introduce a novel computational approach to investigate the interdependence of the solid mechanics field and the electrochemical fields. It is derived from nonlinear continuum mechanics and does not rely on spatial homogenization. Consequently, we can consider large deformations and local physical phenomena. For thiophosphate-based ASSB, [3] showed indications for the delamination of active material and solid electrolyte due to volume changes of the active materials during cycling. To the best of the authors' knowledge, there are only very few publications addressing contact loss phenomena in ASSB by means of modelling and simulation available to date. In [6] the effect of delamination is introduced phenomenological in the context of a one-dimensional Newman model, whereas [4] introduces contact loss in a 3D-resolved simulation by a priori deactivating parts of the interface, but without further mechanical information or coupling. Against this background, we propose a Nitsche-based contact formulation for ASSB based on previous work in the field of thermo-mechanics [5]. Thereby, the three-dimensional microstructures as well as the complex mechanisms and interactions present in ASSB are considered. To maximize computational robustness and efficiency of the formulation, all governing equations of the electrochemical and solid mechanics fields are monolithically coupled. Furthermore, the advanced, physics-oriented block preconditioners and solution techniques for the resulting linear systems of equations, as presented in [1], are extended to be applicable to the outlined system. In combination with the full MPI parallelization of our implementation, this opens up the possibility for large-scale and high-performance computations while satisfying strict demands on accuracy.

***Keywords**:* all-solid-state battery, electrochemistry-mechanics coupling, mechanical contact and separation, numerical simulation.

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Current Constriction at the Li|$Li_7La_3Zr_2O_{12}$ Interface

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The realization of the lithium metal anode may represent a new milestone in the development of novel battery technologies with higher energy densities and lifetimes. The theoretical capacity on the anode side can be increased approximately by a factor of 10 when replacing graphite with lithium. The side reactions occurring due to the high reactivity of lithium metals, however, are challenging. To suppress the growth of dendrites on the one hand and to reduce the flammability of the batteries on the other hand, a major research focus is on the consideration of solid electrolytes (SE) such as $Li_7La_3Zr_2O_{12}$ (LLZO). The cycling behavior of the cell, however, is strongly influenced by the diffusion process on the metal anode side and the charge transfer driven morphological instability at the interface between both solids, i.e. lithium metal and LLZO. Thus, optimization of the kinetics at the interface is required for the development of solid-state batteries.

Impedance spectroscopy is particularly suitable to systematically investigate changes at the metal electrode|SE interface during operation. Individual impedance contributions such as the interface or transport signals, i.e. the grain boundary and bulk process, can be separated from each other if they differ in their frequency-dependent behavior. Krauskopf et al. recently demonstrated that the interfacial resistance is generally composed of a charge transfer (CT) and a constriction contribution.[1] The low exchange current densities frequently reported in the literature could be attributed to the pore formation at the interface since the CT resistance between lithium and LLZO is negligible. Despite the extensive study of the constriction effect in semiconductors or on solid|solid interfaces by Fleig and Maier[2-3], the phenomenon in ceramics with pronounced microstructure is not fully understood yet. Further research is required in order to understand the various dependencies of the phenomenon and how its behavior can be manipulated.

We developed an impedance network model to systematically investigate the impact of several factors such as the sample geometry, the microstructure of the SE or the interface design on the constriction effect and its derived transport quantities. Current constriction is not a migration process in the strict sense. It is related to the frequency dependent change of the electrode area actively contributing to the transport. The resistance is composed of constituents of all transport processes that occur around the interface. The activation energy is a mixture of the activation energies of the relevant transport processes. It is a geometric effect that has to be expected at different length scales. Stripping measurements were performed in order to compare the experimental behavior with the theoretical predictions. The results match quite well and the computations provide new insights into the dynamic change of the interface under anodic load.[4]

Keywords: solid-state battery, solid electrolyte, metal anode, interface, current constriction, LLZO.

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Linear stability analysis of a graphite multi-layer phase field model

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Graphite is for now the most commonly used active material for lithium battery anodes because of its very interesting properties like its stability, its reversibility and its low cost. It is a lamellar material made of graphene sheets. Lithium atoms insert between the graphene layers and can only move along these layers. They cannot cross the graphene sheets. In contrast, they interact with lithium ions in adjacent galleries. With this structure comes a staging phenomenon, which is that lithium in stage *n* will shape into islands of high concentration every *n* layers. This phenomenon influences critical properties of graphite like equilibrium potentials, lithium diffusion or insertion kinetics.

With a multi-layer phase field approach, one can simulate the emergence and the evolution of these stages in a graphite particle[1,2]. The underlying free energy model depends on interaction parameters that can greatly affect the way the stages form. In the present work, a linear stability analysis (LSA) is performed to investigate the impact of the free energy model parameters on the stage formation dynamics and growth rate. The simulation of the spinodal decomposition phenomenon shows different stages at a given time (Figure 1). The stages are identified using a discrete Fourier transform as a post-treatment, which allow to determine the average stage evolution over time (Figure 2). As expected from the LSA (Figure 3), stage *2* grows the fastest at early times.

Initial filling fraction $c = 0.3$
Taken at time $t = 28.8s$

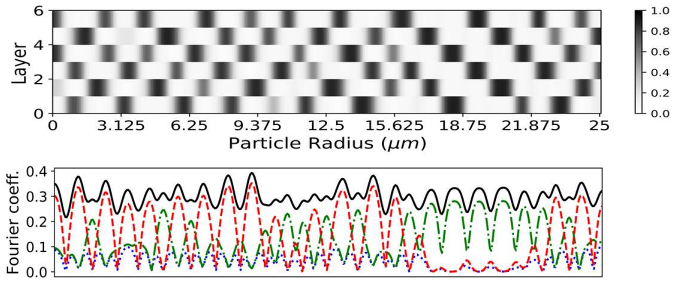

Figure 1 : Simulation of spinodal decomposition a graphite particle and stage identification with discrete Fourier transform

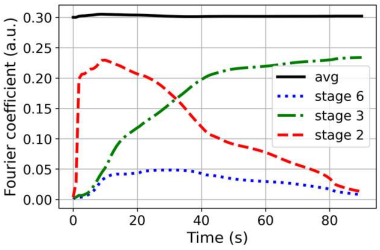

Figure 2: Stages evolution over time

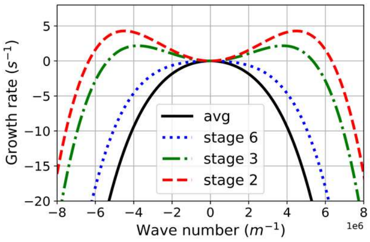

Figure 3 **:** Stages growth rate according to LSA

Keywords*:* Phase-field, graphite, linear stability analysis, modelling

1. R.B. Smith et al. J. Phys. Chem. C 2017, 121, 23, 12505 – 12523 DOI : 10.1021/acs.jpcc.7b00185
2. M. Chandesris et al. J. Phys. Chem. C 2019, 123, 38, 23711–23720 DOI : 10.1021/acs.jpcc.9b05298

Compensatory measures to overcome performance limitations of recycled Li-ion battery materials

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The increasing demand of lithium-ion batteries for electric vehicles, combined with the lack of critical raw materials and the necessity to dispose of spent batteries, is driving towards the use of recycled cathode active materials in the next generation of batteries. However, closed loop recycling solutions, such as direct recycling methods and co-precipitation, result in cathode materials which have a lower quality than those prepared from virgin precursors, which translate into smaller volumetric capacity and solid-state diffusivity. In order to meet the stringent requirements of the automotive sector, changes in the electrode design are thus required when recycled cathode active materials are used.

In this contribution we use a pseudo-2D thermo-electrochemical model to provide design guidelines to overcome the performance losses of recycled cathode active materials (namely, $LiNi_xMn_yCo_zO_2$, NMC). The model is first validated with discharge/charge data of a commercial cell (Samsung SDI 94 Ah used in the BMW i3 2016 model) by using a parametrization coming from a comprehensive survey of material properties [1], showing deviations smaller than 1 % in the prediction of capacity (Figure 1). The model is used to quantify the performance loss due to lower-quality NMC particles: a reduction in accessible capacity of 10 % is predicted by a 10 % reduction in maximum Li concentration in NMC, while a 1-4% capacity loss results from a halved solid-state diffusivity. In order to compensate for such losses, design guidelines are conceived and discussed (Figure 2). In particular, increasing the electrode thicknesses by 11 % as a maximum compensates the capacity loss given by recycled NMC, resulting in a minor decrease in specific energy density (from 141 Wh kg^{-1} to 136 Wh kg^{-1} at the battery pack level) without impacting the roundtrip efficiency and the fast charge capability (i.e., recovering 50 % of capacity in 15 min). A decrease in solid-state diffusivity can be compensated by reducing the NMC diameter from 8 mm to 6 mm, although a better strategy consists in increasing the electrode thicknesses by ca. 1 mm. In summary, results indicate that lower-quality recycled materials can be effectively used without compromising the performance of a Li-ion battery for electric vehicle applications.

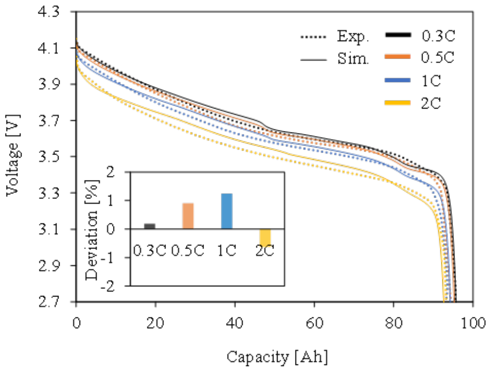

Figure 1: Model validation discharge curves

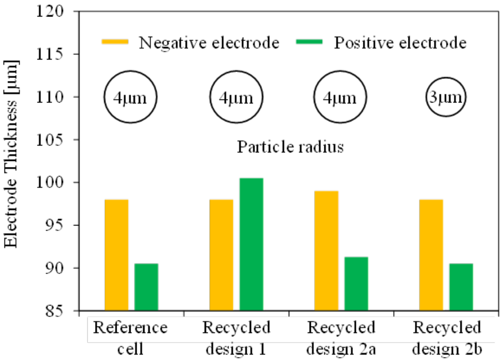

Figure 2 : Compensatory cathode designs comparison

Keywords: P2D model, battery recycling, nickel-cobalt-manganese oxide.

1. Lagnoni, M.; Nicolella, C. et al. *Electrochimica Acta* **2021**, *394*, 139098. DOI: 10.1016/j.electacta.2021.139098

Relating the morphology of hierarchically structured battery electrodes to rate capability

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Lithium-ion battery cells with a hierarchically structured positive electrode have the potential to improve cell performance. Their secondary active material particles are porous and consist of smaller primary particles. Short diffusion paths within the active material enable a higher specific capacity and an improved rate capability compared to conventional electrodes [1]. The performance of hierarchically structured electrodes depends on the electrode morphology. However, morphological properties are often interrelated, so their influence on the cell performance can hardly be distinguished with experimental studies. Furthermore, it is difficult to determine which processes within the cell cause the observed cell performance.

In this contribution, we offer an investigation of a hierarchically structured positive electrode by means of an electrochemical cell model to complement the experimental findings. We use a volume-averaged cell model for hierarchically structured electrodes developed by Birkholz et al. [2]. Two extensions of the model are presented. First, we introduce an alteration which allows to vary the specific surface area of the primary particles independent from their radius and the secondary particle porosity. Second, we assume that diffusion paths within the active material are longer than the particle size to account for partly blocked particle surface as suggested by Schmidt et al. [3]. With this modelling approach, we study the F900 cell, which was experimentally investigated by Wagner et al. [4] and contains a hierarchically structured NMC111 positive electrode. We demonstrate how different morphological properties influence the cell performance at various C-rates. In addition, we offer explanations for the observed changes based on the cell model.

Some results can be summarized as follows. For thick electrodes, rate capability is compromised due to salt depletion of the electrolyte close to the current collector. Furthermore, cell performance is highly dependent on the secondary particle porosity. Surprisingly, a low porosity of the secondary particle is favourable since the electronic conductivity within the secondary particles is the limiting factor for the cell performance. This can be attributed to the poor electronic conductivity of NMC. Better contact between the primary particles due to a low secondary particle porosity increases the electronic conductivity and thus the rate capability. The primary particle size is small enough to ensure small concentration gradients within the primary active material particles. Only for large primary particles a decrease in rate capability can be observed. A major contribution to this effect is the elongation of diffusion paths due to blocking of primary particle surface by contact with other particles. Varying the specific surface area of the primary particles has no influence on the cell performance. We conclude that the F900 positive electrode exhibits a sufficiently large specific surface area to ensure the electrochemical reaction kinetics do not limit the cell performance. Our results demonstrate that the small size of the primary particles and a high specific surface area are clear advantages of hierarchically structured electrodes. To best exploit the active material, we suggest to choose thin electrodes and secondary particles with a low porosity or add electronically conductive components within the secondary particles.

Keywords: lithium-ion battery, volume-averaged cell model, hierarchically structured electrode morphology.

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2. Birkholz, O.; Kamlah, M. *Energy Technology* **2021**, *9* (6), 2000910. DOI: 10.1002/ente.202000910
3. Schmidt, A.; Ramani, E. et al. *Energy Technology* **2021**, *9* (6), 2000881. DOI: 10.1002/ente.202000881
4. Wagner, A.C.; Bohn, N. et al. *ACS Applied Energy Materials* **2020**, *3* (12), 12565-12574. DOI: 10.1021/acsaem.0c02494

A guideline to the time-adaptive reduced order modelling of lithium-ion cells

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The numerical solution of continuum electrochemical models is one of the most widely used tools in lithium-ion cell and battery design. However, the use of these models in early stages of cell/battery design, cell optimisation or battery management systems is limited by their computational cost. In the past decade, some effort has been devoted to the development of reduced order models (ROMs) that can provide accurate results in real time. The ROMs derived in [1] and [2] from the electrochemical p2D model (obtained by Newman and co-workers in [3]), which utilise a Galerkin projection based on a proper orthogonal decomposition method (POD-based), are of particular relevance to the work discussed here.

Nevertheless, ROMs presented in the literature are based on a pre-processed approach, hindering their benefits in many tasks (such as early stages of design or optimisation) due to the very large computational cost of building a suitable solution database during the pre-process (off-line) phase. Adaptive ROMs, instead, are based on an on-the-fly ROM construction (using integration with the full order model, FOM, for some time intervals) and they do not need such costly pre-processes, making them much more efficient in a large range of applications (including battery/cell design and optimisation tasks). However, several difficulties must be overcome in order to develop an effective (time-)adaptive ROM. Some of these difficulties are shared with pre-processed ROMs (and were already detected, but not completely solved, in [2]) but some others are specific to adaptive ROMs.

In this presentation we discuss some guidelines for the derivation of an accurate and robust time-adaptive POD-based ROM. Special attention is paid to some critical features, such as criteria for automatic modes selection, ROM adaption strategies or (unexpensive) ROM error estimates. Although some aspects are discussed using a p2D cell model for the sake of clarity, the derived strategy is mainly intended to accelerate p4D battery simulations and its application to a p4D model for a graphite-NMC battery will be presented.

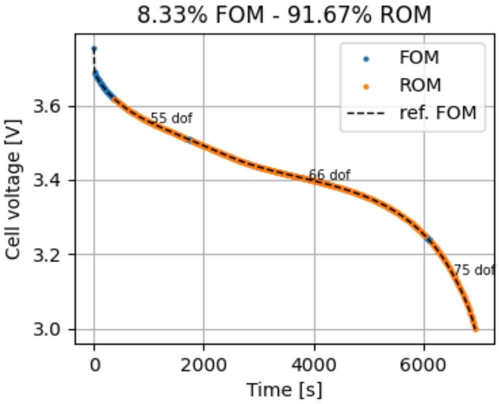

Figure 1: Time-adaptive ROM voltage curve of full 0.5C cell discharge

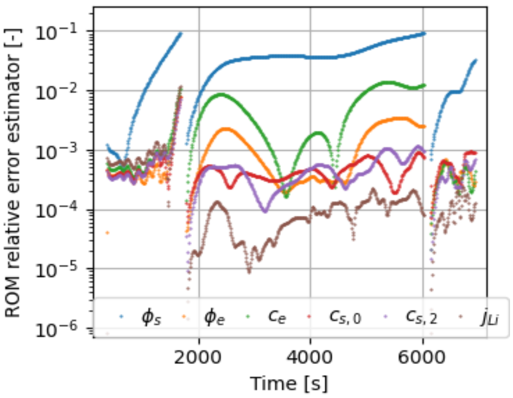

Figure 2**:** Time-adaptive ROM error estimators along 0.5C full cell discharge

Keywords*:* lithium-ion, cell, battery, reduced order model (ROM), adaptive ROM.

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Development and Verification of a Method to efficiently solve Discontinuous Thermal Transport Models

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Temperature has significant impact on the dynamic performance, the operating limits as well as the aging phenomena of Li-ion battery cells. The temperature within a battery cell is typically inhomogeneously distributed. This is caused by the complex interplay of the discontinuous heat transport, applied thermal gradients by thermal management systems, and the uneven heat release within the cell. Since it is also challenging to gain valid experimental access to the inner of the cell, numerical simulation models come into focus. These models are used to obtain a deep insight into the thermal behavior, especially the heat transport processes and temperature distribution. Moreover, the interaction between the heat transport paths within the cell, externally applied thermal management systems and the combined influence of both of them on the temperature distribution can be systematically examined in this way. However, simplifications and model reduction techniques like homogenization approaches need to be used to reduce simulation time caused by the high computational effort.

In this context, the development of numerical methods to efficiently solve battery cell models is of huge interest. The higher numerical costs, which are caused by mapping a large number of layers [1], are compensated by the use of efficient numerical methods. In the next step the method needs to be verified to proof its reliability and accuracy. Therefore, it is then required to set up evaluation criteria. [2]

This contribution presents a developed solver for the 3D thermal pouch cell model. The geometry consists of at least partially locally resolved material layers and locally assigned material properties as well as heat sources. Additionally, a verification strategy for such problems is introduced based on appropriate test problem, for which analytical solutions exist (Fig. 1). Furthermore, an analysis of thermal simulation results under different cooling scenarios will be demonstrated (Fig. 2). [1,2]

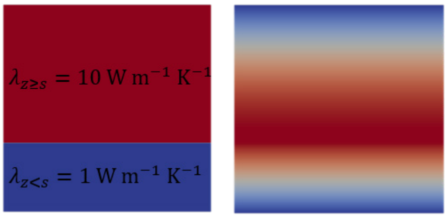

Figure 1: Schematic illustration of a discontinuous test problem (left) with its solution (right). [2]

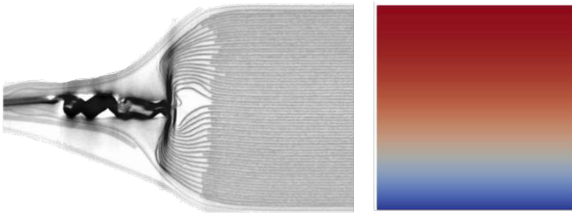

Figure 2**:** CT scan of a pouch cell (left) and temperature distribution with side cooling (right). [2]

Keywords*:* Li-ion battery, Numerical Thermal Modeling, Verification, Discontinuous thermal transport.

1. O. Queisser, L. Cloos, F. Boehm, D. Oehler, T. Wetzel, *Energy Technol*. **2021**, DOI:10.1002/ente.202000915.
2. Z. Veszelka, O. Queisser, M. Gontscharow, T. Wetzel, W. Dörfler, *Energy Technol*. **2020**, DOI: 10.1002/ente.202000906.

Investigation of Liquid Water Heterogeneities in Large Area PEM Fuel Cells using a Two-Phase Flow Multiphysics Model

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The Proton Exchange Membrane Fuel Cell (PEMFC) is a promising candidate for many applications particularly for the transportation in order to decarbonize this sector. Of the barriers, cost and durability represent two of the most significant challenges to achieving clean, reliable and cost-effective fuel cell systems. Proper management of the liquid water and heat produced in PEM fuel cells remains crucial to increase both its performance and durability. Indeed, large liquid water and temperature variations in the cell may accelerate long-term structural problems until irreversible degradation such as membrane micro-cracks [1].

A two-phase flow model of a large surface PEM fuel cell is developed with the commercial COMSOL Multiphysics® software using the Finite Element Method (FEM). The model considers the cell as a multilayered system where each layer is accurately in-plane discretized to allow the simulation of local thermodynamics heterogeneities with a reasonable computing time. The numerical results are compared to experimental liquid water measurement obtained from neutron imaging tests in several operating conditions. According to the good agreement, the model is used to predict the distributions of current density, species concentrations, water content, etc. in all the components of the cell, while taking into account the real flow-field designs. Figure 1 shows the liquid water thickness (a) and the saturation (b) for a dedicated 3 cells stack experimentally tested for a high power automotive. It appears that the liquid water accumulates at the anode Gas Diffusion Electrode (GDE) on the edges (dark red zone in Figure 1), inducing higher local current density and higher liquid water saturation in the external cathode channels, due to no-proper water convection by hydrogen gas (no anode channel in front of these zones).

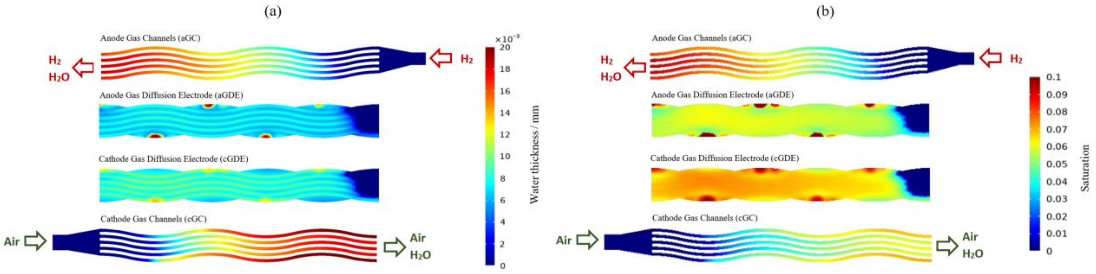

Figure 1. (a) Water thickness and (b) saturation distribution in the anode and cathode gas channels and gas diffusion electrode for a high-power automotive condition.

***Keywords**: Proton Exchange Membrane Fuel Cell, two-phase flow, water transport, computational simulation, hydrogen.*

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Representative Morphology Model for PEFC Catalyst Layer: *Operando* Water Saturation Determined via Small-Angle X-ray Scattering

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It is imperative to overcome the water management imperfections in the polymer electrolyte fuel cells (PEFC). Proper humidification of the membrane contributing to the performance relies on ionomer hydration. In contrast, excess water retention in the pores results in blockage of the gas diffusion to the active sites of the electrochemical reaction, thus reducing performance and efficiency.

Various measurement techniques suitable with the length scale of PEFC components have been explored to address the PEFC water management challenge. For gas diffusion layer (GDL), technological advances have permitted *operando* water saturation quantification and its mechanism with *X*-ray tomography with few microns resolution [1-4]. Furthermore, sub-voxel information contained in the *X*-ray tomography data has demonstrated accurate water quantification in the nano porous microporous layer (MPL)[5]. However, in the nanoscale regime of the catalyst layer, the quantification of water and its mechanism remains nontrivial. Studies involving imaging techniques dedicated to understand the water management in the catalyst layer have been carried out albeit with the limited spatial resolution[6]. Nevertheless, the pore-scale information has remained unresolved.

A non-destructive small angle *X*-ray scattering (SAXS) technique is proposed as a diagnostic tool to investigate the catalyst layer saturation in operating conditions. SAXS is well suited for diagnosing the presences of liquid water presence during *operando* experiments because of its sensitivity to electron density contrast, nanoscale observation window, high temporal resolution and adequate spatial resolution to distinguish the components in PEFCs. Herein, SAXS intensity profiles measured with a recently developed SAXS-compatible *operando* PEFC (Figure 1 middle and right) are interpreted using representative morphology models and assuming different water filling mechanisms (Figure 1 middle and left). The experiments were done at cSAXS, Swiss Light Source, Paul Scherrer Institut, Switzerland. The presentation will provide details on the structure morphology fitting and the implementation of the pore filling modelling that allows revealing the most probable pore filling mechanism.

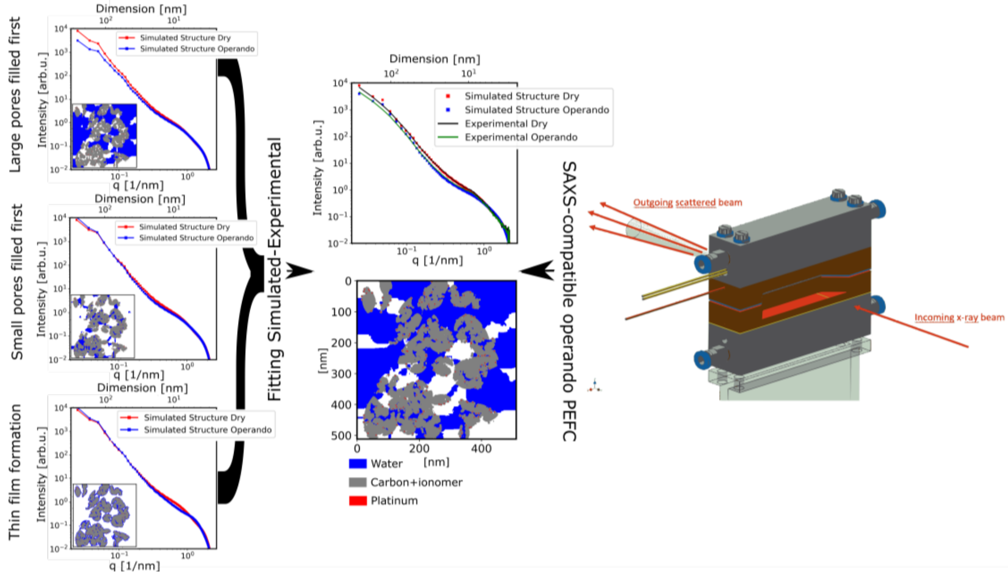

Figure 1 Left: Numerical SAXS intensity profiles derived from representative morphology model in different wetting scenarios. Cross section of 3D model used is shown as inset. Middle: Representative experimental operando SAXS data of partially saturated catalyst layer at constant voltage 100 mV fitted with the different wetting scenarios and the resulting fit. Right: Schematic design of SAXS-compatible operando PEFC used for the experiment.

Keywords: PEFC catalyst layer, water management, small angle *X*-ray scattering

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(2) Eller, J.; Rosen, T.; et al. *J Electrochem Soc* **2011,** *158* (8), B963-B970.
(3) Mularczyk, A.; Lin, Q. Y.; et al. *ACS Appl Mater Inter* **2021,** *13* (29), 34003-34011.
(4) Sabharwal, M.; Buchi, F. N.; et al. *J Power Sources* **2021,** *489*, 229447.
(5) Chen, Y. C.; Berger, A.; et al. *ACS Appl Mater Inter* **2021,** *13* (14), 16227-16237.
(6) Babu, S. K.; Spernjak, D.; et al. *J Power Sources* **2020,** *472*, 228442.

Rational approximation for electrochemical systems with constant phase elements: a preliminary study

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The characterization of electrochemical systems with impedance spectroscopy requires the interpretation of the measured data with the help of suitable models. Equivalent circuit models are most commonly used to interpret impedance data. These models contain passive elements such as, resistors, capacitors, and inductors and also so-called distributed elements such as, constant phase elements (CPEs), e.g., the (finite length) Warburg. In this study, we illustrate how to deal with identifying such elements from data, e.g., from samples of the transfer function of the underlying system. The method under consideration is purely data-driven, relies on rational approximation, and has been developed constantly in the last decade: it is known as the “the Loewner framework” (LF) [1] and is used to construct dynamical models from data. Here, we show the practical applicability of LF when applying it for data models with CPEs, and will also expose a potential challenge when dealing with such applications. The transfer functions of these models are indeed irrational (can be well approximated by rational functions) and may have branch points or even branch cuts [2]. The latter is illustrated in Fig. 2 (the negative real line is in this case a branch cut and it also contains the poles).

Modeling an electrochemical phenomenon with an ideal capacitor assumes that the surface under investigation is homogeneous which is normally not the case. This lack of homogeneity is modeled with a CPE element. In the current study, we are using a Randles circuit [3] to illustrate the rational approximation tool under consideration, i.e., the LF approach.

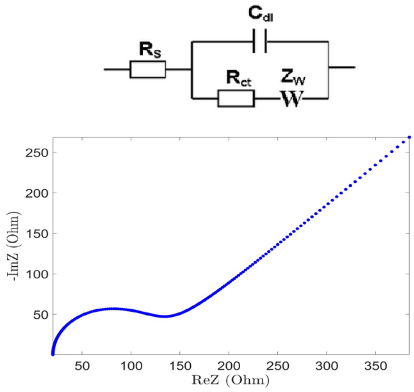

Figure 1: the Randles circuit schematic (up) and the Nyquist plot of the EIS spectrum (down).

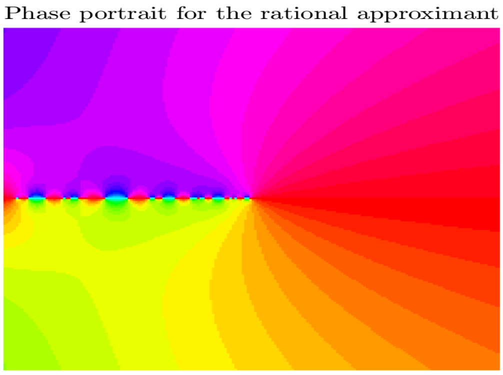

Figure 2**:** The phase portrait of the LF rational interpolant of order r = 16 (we have used the color scheme by Elias Wegert [4]).

Keywords*:* Constant phase elements, Warburg element, Data-driven approaches, Rational approximation, Loewner framework.

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Rapid and Local EIS on a Segmented Fuel Cell: Combining Spatial and Temporal Resolution

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Proton Exchange Membrane Fuel Cells (PEMFC) are expected to play a major role in the transformation of the mobility sector towards more sustainability. Automotive operation of PEMFC is highly transient and involves significant spatial inhomogeneities along the flow direction of an individual cell and in through plane direction of the membrane electrode assembly (MEA). Optimization of cell design and operation towards improved cost, lifetime and performance requires a profound understanding of the spatio-temporal distribution of internal states of a cell. One important internal state to be controlled is membrane humidification. This cannot be measured directly in-situ but can be inferred from membrane resistance R_{mem} that can be obtained via Electrochemical Impedance Spectroscopy (EIS). Schneider et al[1]. measured local EIS in a segmented PEMFC under steady-state operation and showed strong inhomogeneities in current density and membrane resistance along the channel that would not be revealed via global EIS. Shao et al.[2] measured temporally, but not spatially resolved membrane resistance R_{mem} at a constant frequency of $1\ kHz$. They showed how a cell averaged membrane resistance can lead to erroneous conclusions regarding membrane humidity. Thus, both, temporally and spatially resolved membrane resistance R_{mem} acquisitions are required to properly observe membrane humidity under automotive relevant operation. We developed a new diagnostic tool, Rapid and Local (RaLo) EIS, to close this gap. RaLo EIS offers the possibility to measure local resistance contributions including R_{mem} in a segmented cell under transient conditions, by conducting almost full spectra ($10\ kHz \rightarrow 50\ Hz$) in all segments simultaneously within less than a second. These spectra are used to study the spatio-temporal evolution of voltage loss contributions inside a PEMFC.

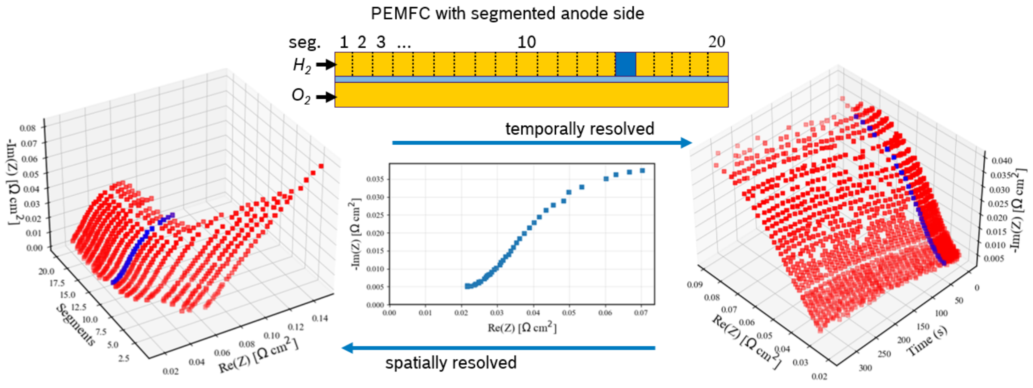

Figure 1: Schematic chart of the temporal and spatial resolution of RaLo EIS at Segment 15 of 20 for a jump in cathode and anode stoichiometry

Keywords: PEMFC, Fuel Cell, EIS, diagnostic

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Proton Conductivity in PEFC Catalyst Layers: Imaging-Supported Modeling

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[2] Robert Bosch GmbH, Corporate Research, Renningen, Germany.
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Polymer electrolyte fuel cells have already demonstrated their high level of technological readiness. However, the broad commercial adaption of this technology requires further advances in structure, composition and properties of the cathode catalyst layer (CCL). Amongst other transport properties, an efficient supply with protons must be achieved by fine-tuning the amount, type and dispersion of the ionomer.

Proton conductivity of the CCL is widely studied by both AC and DC measurements [1]. Several approaches are discussed to explain the dependence of proton conductivity on CCL structure and composition, random heterogeneous media theory [2] or agglomerate models that allow to explicitly consider an ionomer thin film covering the catalyst agglomerates [3].

This work aims to merge the different approaches by linking a new structure-based model [4] with an explicit image-based approach. Statistical descriptors, such as ionomer coverage and pore size distribution (see Fig 1b), are used to represent the structure of a CCL (Fig. 1c) that consists of partially ionomer-covered Pt/C agglomerates. From the obtained images, catalyst utilization, tortuosity of the proton-conductive network, and the effective proton conductivity were evaluated using *pytrax* [5] (Fig 1d).

The model reproduces and explains the experimentally observed dependence of proton conductivity on electrode structure. Parametric effects of ionomer content and dispersion will be discussed. We will present conclusions on 1) structural features of the CCL that determine proton conductivity and catalyst utilization, 2) the role of condensed water, and 3) the perspectives of combined statistical and physical-analytical modeling approaches to drive the design of CCLs for PEFCs.

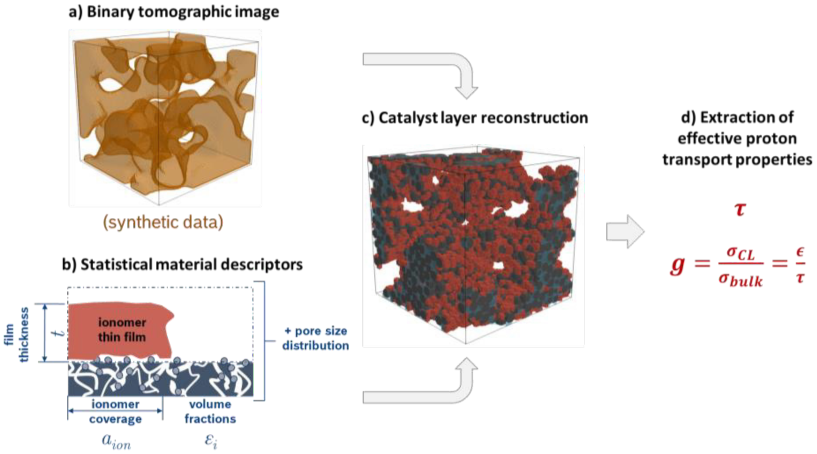

Figure 1: Illustration of the workflow combining tomographic data and statistical descriptors to generate a reconstructed image of the cathode catalyst layer structure. The ionic transport properties can be directly analyzed by running a random walk simulation in the image.

Keywords: polymer electrolyte fuel cell, cathode catalyst layer, ionomer, ionic conductivity, structure-based modeling, image reconstruction

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Assisted Cold Start of a PEMFC coupled with a Metal Hydride Reactor

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One challenge for the automotive application of polymer electrolyte fuel cells (PEMFC) is the start-up at sub-zero temperatures due to the freezing of water inside the cell. The temperature has to rise above 0 °C before the ice completely blocks the cathode pores and inhibits the oxygen reduction and species transportation. A promising solution to quickly increase the temperature of the fuel cell in a sub-zero environment is using a metal hydride reactor as a preheater. This thermochemical heater can exothermally absorb hydrogen and heat up the heat transfer fluid of a PEMFC stack.

This work presents a transient 2D numerical model of a single fuel cell thermally coupled to a metal hydride reactor via the heat transfer fluid (Figure 1). Both components are validated with experimental data. The simulation of the coupled system yields the necessary preheating time up to 0 °C to avoid any ice formation and potential damages due to ice in the cathode. Another cold start strategy is the potentiostatic start-up after a shorter preheating time, i.e. ice may be formed but a quicker cold start is possible (Figure 2). The criterion for a successful start in this work is an average temperature of 20 °C in the cathode catalyst layer, because the cold start can fail due to the blockage of the pores in the catalyst layer with ice but also with liquid water. For temperatures from - 5 °C to - 30 °C and cell voltages from 0.9 V to 0.1 V the preheating duration is varied to achieve the quickest cold start. Low voltages yield higher heat production inside the cathode catalyst layer and better cold start performance. Based on this parameter study, optimized cold start procedures are proposed.

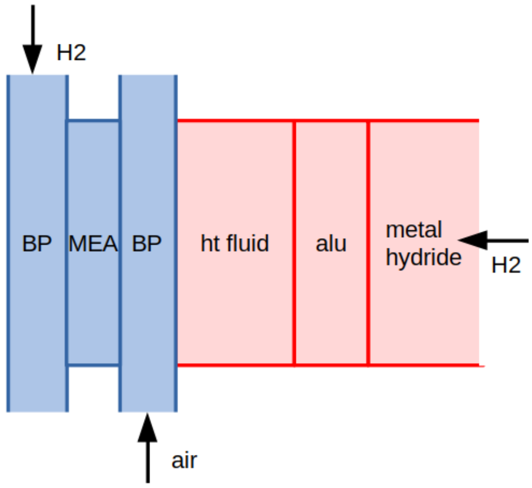

Figure 1: scheme of the fuel cell (blue) thermally coupled with a metal hydride reactor (red). Not to scale.

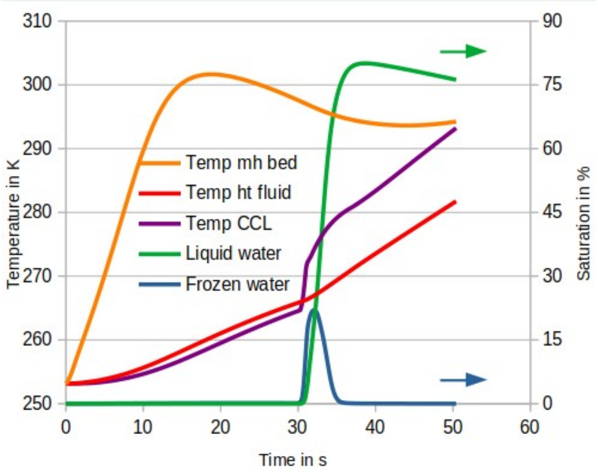

Figure 2**:** temperature of the metal hydride (orange), heat transfer fluid (red) and fuel cell (CCL, purple) for a successful cold start from - 20 °C with 0.3 V and 30 s preheating time. The saturations of liquid (green) and frozen water (blue) in the CCL are denoted by the right axis.

Keywords*:* PEMFC, cold start, metal hydride, preheating.

Optimal Catalyst Loading of Recombination Interlayers for PEM Water Electrolysis

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The gas crossover in polymer electrolyte membrane (PEM) water electrolysers leads to safety issues, degradation mechanisms and reduction of the faradaic efficiency.[1] Especially, the technically development towards thinner membranes, increasing operation temperatures and higher cathode pressures results in higher crossover fluxes that amplifies the previously mentioned crossover issues. Therefore, different mitigation strategies exist to reduce gas crossover or to reduce its negative effects.[1] One promising mitigation strategy is the use of recombination catalysts, such as platinum, within the membrane. This strategy is gaining focus recently.[2-5] It was successfully used at higher pressures[3,5] and for longer operations[2]. Within the literature different manufacturing processes were used[2,3,5] and different interlayer positions were investigated[3]. These are important screws to improve the recombination interlayer. Another very important key parameter is the loading of the recombination catalyst, which is the topic of this contribution: the target is to find the optimal loading of the recombination catalyst to achieve a good recombination efficiency while keeping the use of platinum group metals low to reduce the life cycle and economic costs.

For this purpose, we use model-theoretical investigations supported by experimental studies with different recombination catalyst loadings. The investigation leads to a closer examination of the recombination interlayer and results in a good description of the recombination reaction kinetics. By means of the validated one-dimensional model, we can determine the optimal loading and positioning of recombination interlayers at various operating conditions and design parameters to ensure a safe and economical operation of PEM water electrolysis systems.

Keywords: PEM water electrolysis, hydrogen crossover, recombination interlayer, mitigation strategies

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Effects of the Various Serpentine Channels on Proton Exchange Membrane Water Electrolysis Cell Performance with the Large Active Area

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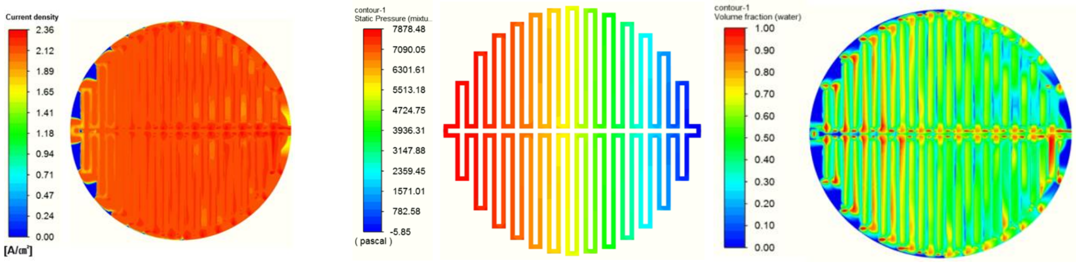
Renewable energies are attractive alternatives to fossil fuels. The main disadvantage of renewable energy sources is intermittent supply. Surplus electric energy can be stored as massive hydro-gen at a low cost [1]. Proton exchange membrane water electrolysis (PEMWE) is suitable for fluctuating energy conversion because of its fast transient response. PEMWE consists of the bipolar plates (BPP), porous transport layers (PTL), catalyst layers, and membranes. The anode channel in BPP provides the pathway for reactant water to the PTL through which water diffuses from the channel to the catalyst layer. Supplied water is decomposed into oxygen and hydrogen. The oxygen emitted from the catalyst layers accumulates in the outlet region, obstructing water flow and reducing electrochemical processes.

Three alternative channels with a 100 cm^2 active area were suggested in this study to improve oxygen removal. The concentric serpentine has arc shape channels with gradually extended lengths, whereas the length of the 2-path serpentine channel is shortened at the outlet. Oxygen is expected to be discharged without clogging the water channels, optimizing the pressure difference between the adjacent channels. The path of the ripple serpentine is stretched back and forth between the inlet and outlet regions, leading to the radial pressure gradient. The ripple-serpentine channel is expected to distribute water and oxygen uniformly throughout the active region. The two-phase flow model with electrochemical reaction depicts the current density distribution of PEMWE, which is proven by single-cell experiments.

The concentric and ripple serpentines have higher average current densities than the 2-path serpentine. Concentric channel design promotes under-rib convection, which raises the volume fraction of water in the PTL. Due to mass transfer in all directions, the ripple serpentine channel design uniformizes the volume fraction of water in the PTL. The proposed channel designs are found to improve performance by facilitating uniform reactant supply.



(a) (b) (c)

Figure 1 (a) Current denstiy distribution, (b) pressure field in channel and (c) volum fraction of water in PTL of PEMWE at cell voltage 1.8 V with the 2-path serpentine channel

Keywords: two-phase flow, 2-path serpentine, Concentric serpentine, Ripple serpentine

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Analytical Multiphase Flow Modeling of Parallel Plate Electrolyzers

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In this talk, we aim to further the understanding of multiphase flow in a parallel plate electrolyzer, as shown in Fig. 1. This configuration operates without a membrane, which has several advantages. Membranes add cost, ohmic resistance and are prone to degradation. In the absence of a membrane, it is critical to understand the multiphase flow behaviour to avoid product crossover to ensure safety and high product purity.

Using the mixture model equations[1] and assuming a gas fraction that decreases exponentially with distance to the wall, we derive accurate analytical expressions for the velocity profile and the relation between pressure drop and flow rate. Fig. 2 shows a reasonable agreement between the analytical results, the numerical solution obtained using COMSOL, and the experimental data[2]. Using our model, we find that buoyancy driven membraneless electrolyzers can be designed with a maximum height of 7 cm at 100 A/m^2 with an interelectrode gap of 3 mm and 98% product purity. At this gap the ohmic drop is lower than most zero-gap electrolyzers[3]. For a forced flow at Re=1000, the same electrolyzer can be made around 17 cm tall. These numbers show significant room for scale-up of such membraneless electrolyzers.

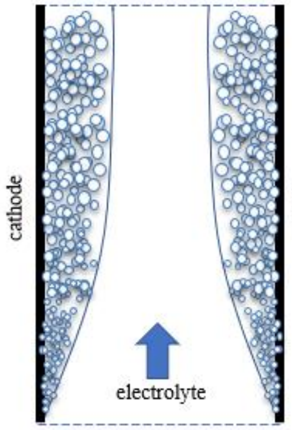

Figure 1: Configuration of a membraneless electrolyzer. The gas bubbles are generated at the electrode surface and move in a thin plume close to the electrode. The liquid electrolyte moves up – either by buoyancy or forced flow.

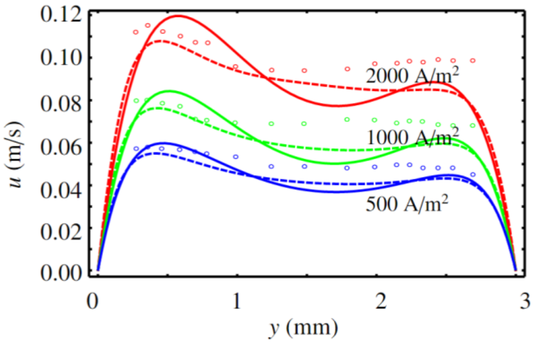

Figure 2: Velocity profiles for current densities: $j = 500$ A/m^2 (blue), $j = 1000$ A/m^2 (green), and $j = 2000$ A/m^2 (red). The circles represent the experimental measurements from Boissonneau and Byrne[1], the dashed line represents the numerical solution and the solid line represents our analytical solution.

Keywords: membraneless, multiphase flow, analytical solution

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Modeling and simulation of an alkaline water electrolyzer

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Detailed 3-D models of electrochemical components may be used to identify local behavior and characteristics that would be either very difficult, or not possible at all to measure in experiments. The information gained from such numerical simulations is an indispensable tool in the ongoing research and development of electrochemical devices, and can thus make a significant contribution to the optimization process. In this study, a comprehensive cell model was implemented in the object-oriented open-source package OpenFOAM® [1]. The model is able to consider single-phase and/or two-phase flows occurring in fuel/electrolysis cells with electrochemical reactions, mass and heat transfer. It is based on the continuum assumption, and employs the finite volume method.

A detailed calculation of a 3-D alkaline water electrolysis cell is presented and validated on the basis of in-house gathered experimental data. The two main objectives of the present work are the prediction of local differences in the concentration of the potassium hydroxide and the formation of the produced gases, which significantly influence the behavior and performance of the cell. The typical structure of the 'zero-gap' cell considered in the present study can be seen in Fig. 1. The simulations of the two-phase flow on the cathode and anode sides are based on the Eulerian-Eulerian approach, whereby the mutual mass transport, momentum exchange and heat transfer between the gas and liquid phases, is described together with local specie concentrations. The physically different regions are coupled with each other, by means of appropriate mapping functions. The electrochemical reactions are characterized by the Butler-Volmer equation that are presumed to take place on electrodes of finite thickness, i.e., within a defined volume (CCL, ACL, see Fig. 1). In addition, the properties within the different porous layers, such as tortuosities and permeabilities, are all assumed to be isotropic at this point. This is the first CFD code developed and used for an anisothermal 3-D alkaline electrolysis cell describing the gaseous and liquid phases as two individual and interacting phases based on an open-source platform. The simulations were performed on the HPC hardware of JARA, under grant JARA0070.

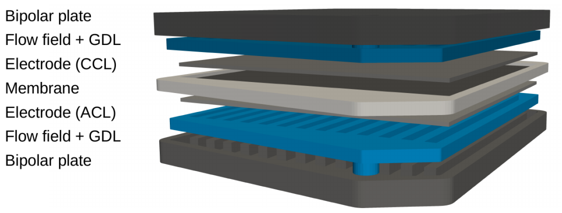

Fig. 1: Cell geometry and the different components

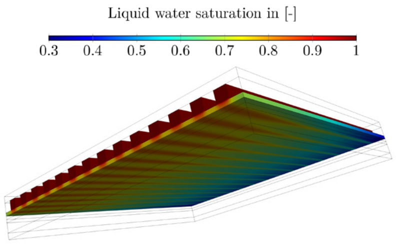

Fig. 2: Liquid water saturation at the anode side

Keywords: Finite volume method, Alkaline electrolyzer, Two-phase flow, Numerical simulation

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Validation of a dynamic alkaline water electrolyzer model with transient experiments

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The part-load range of conventional alkaline water electrolyzers is limited to 10-40% of the nominal load since the gas contamination increases with decreasing current density [1]. This phenomenon is caused by almost load-independent contamination fluxes, which determine the foreign gas content. The main gas contamination mechanisms are the mixing of dissolved product gases by the mixing of the electrolyte cycles and the diffusion of dissolved product gas species through the separator. However, the effect of the electrolyte mixing is often more dominant [2]. The foreign gas content can be critical as the lower explosion limit (LEL) of the product gases is at 4 vol.% hydrogen in oxygen. Therefore, industrial alkaline water electrolyzers perform a safety shutdown when reaching 50% of the LEL, lowering the plant availability [1]. However, the optimization of the process conditions and suitable dynamic operating concepts can be used to enhance the part-load range by lowering the gas contamination without a detrimental impact on the cell potential [3]. Since the experimental evaluation of operating concepts is very time-consuming, using process models is an efficient way to find optimum solutions. Hence, this contribution focuses on the validation of a dynamic alkaline water electrolyzer model with the help of transient experiments at various operating conditions, as displayed in Figure 1. The process model considers the dynamic mass and energy balances of an electrolyzer system to simulate the cell potential and the gas contamination, including the electrolyte concentration and the resulting system temperature according to the local constraints. Consequently, dynamic operating concept studies can be carried out.

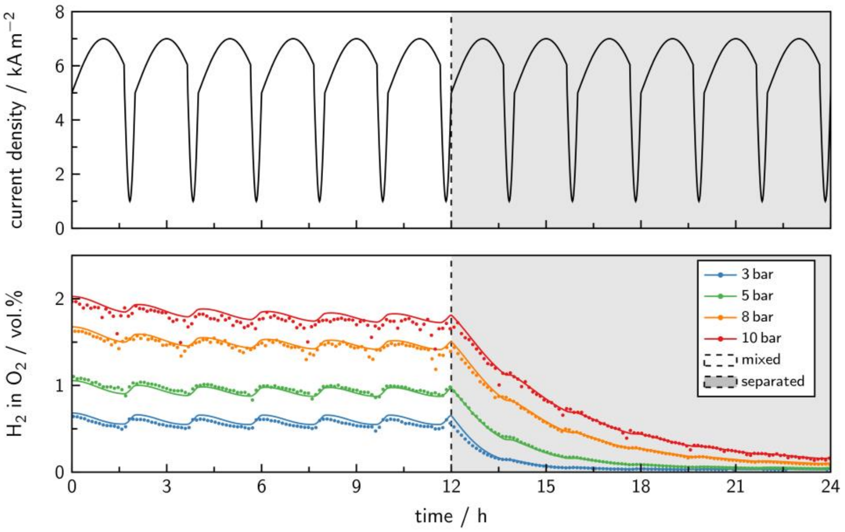

Figure 1: Results of the dynamic validation of an alkaline water electrolyzer model at various system pressures. A fluctuating current density profile combined with an electrolyte flow mode switching pattern was used as the input for the dynamic validation.

Keywords: alkaline water electrolysis, process model, dynamic, validation, gas contamination.

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Modeling direct ammonia anion exchange membrane fuel cells

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Anion exchange membrane fuel cells (AEMFCs) have attracted significant attention during the last decade. Recently ammonia has been proposed as a promising candidate fuel for AEMFC technology. Ammonia-fueled AEMFC is a carbon-free technology that combines the high energy density of ammonia with the high efficiency of the fuel cell. Currently, two major challenges facing this technology: ammonia crossover and sluggish ammonia oxidation reaction (AOR). A key factor for achieving higher performance is operating the cell at a higher temperature (above 100 °C) in order to eliminate the negative effects of ammonia crossover and enhance the AOR and ORR rate.

In this contribution, we will present the first numerical model of ammonia-fueled AEMFCs to investigate and understand the fundamental basics of this technology. Specifically, we will focus on the effect of ammonia crossover and the parasitic reaction (involving ammonia oxidation in the cathode) on cell performance and its stability.

First we will describe our modeling approach, properties, and parameters, where our one-dimensional and transient model of ammonia-fueled AEMFC including degradation kinetics capabilities is conceptually based on our previous studies of hydrogen-fueled AEMFCs[1,2,3,4]. The model captures species transport as well as significant electrochemical reactions taking place in the cell. Next, we present model validation against experimental data of AEMFC operated with KOH-free anode feed at high temperatures (100 and 120 °C). Following this, we present results concerning the effect of ammonia crossover on cell performance and performance stability of ammonia-fueled AEMFC. Analysis of the initial cell performance reveals a reduced AOR rate through the cathode, as the current density increases. More interestingly, the simulated results demonstrate a positive impact of ammonia crossover on cell longevity. A higher rate of crossover enhances the parasitic reaction (AOR) rate in the cathode resulting in high water generation. This leads to enhanced hydration levels through the cathode resulting in a slower degradation rate of the ionomeric material and, as a result, high-performance stability is obtained (albeit at the expense of performance).

Keywords: ammonia, anion exchange membrane, fuel cell.

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Modelling of the Anion exchange membrane based water electrolysis

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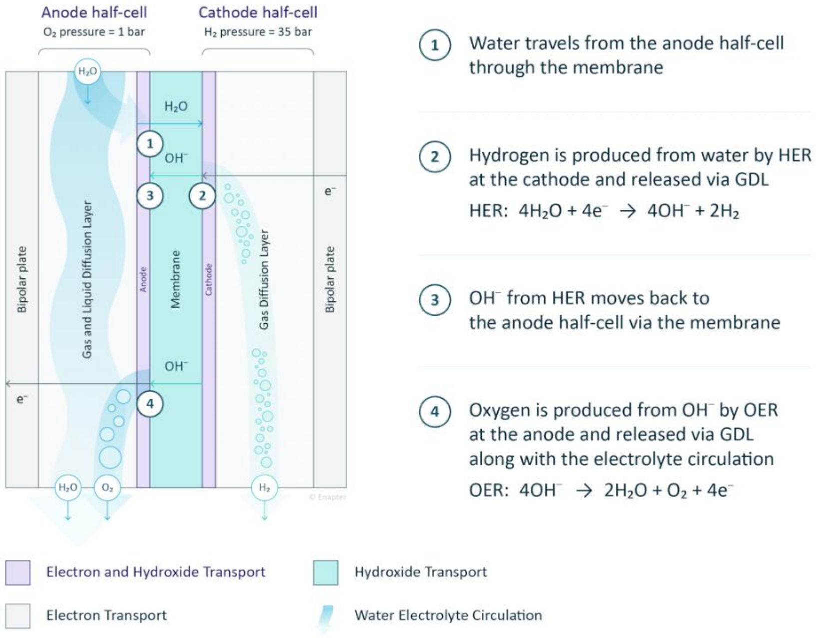
Anion exchange membrane (AEM) electrolysis is the method of hydrogen generation with an Anion Exchange Membrane, using electricity. One of the major advantages of AEM water electrolysis is the replacement of conventional noble metal electrocatalysts with low-cost transition metal catalysts. This device have been modelled in the code MePHYSTO-WE developed by CEA LITEN for the simulation of the electrolyzer performances. The model structure is based on the Bond Graph theory, in which each transport block is represented by a resistive element and each balance block is represented by a capacitive element. The developed multiphysics model for this device also incorporates the transport of liquid water and gaseous products through the porous layers.The equations were solved in MATLAB/ SIMULINK. Finally, the sensitivity analysis incorporates an evaluation and optimisation of the model geometry, operating temperature, concentration of the electrolyte fed into the device and internal characteristics such as porosity and tortuousity of the electrodes and membrane thickness. The main advantage of the model is the assessment of the phenomenon resulting in performance loss of the device, investigating the pH gradient and role of electrolyte concentration on operation as well as understanding the Schroeder paradox for its role on membrane water transport and assessing the key parameters to achieve the desired electrolyser performance. In terms of fabrication of components we also assess the role of membrane and catalyst size and the impact of ionomer content in the membrane and catalysts on the performance.



① Water travels from the anode half-cell through the membrane

② Hydrogen is produced from water by HER at the cathode and released via GDL
HER: $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$

③ OH^- from HER moves back to the anode half-cell via the membrane

④ Oxygen is produced from OH^- by OER at the anode and released via GDL along with the electrolyte circulation
OER: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Figure 1: schematic AEM water electrolysis

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Towards a Solid Oxide Fuel Cell microstructure evolution model calibrated using long-term performance experiment data

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Deterioration of Solid Oxide Fuel Cell (SOFC) microstructure is one of the key challenges to increasing the economic viability of high temperature fuel cell technologies The purpose of the research is to develop a calibration framework for a microstructure evolution simulation employing an interface tracking method, such as the Phase Field Model (PFM).

The calibration data is obtained from a concluded 3700h stack performance experiment [1]. In the proposed research scheme, Focused-Ion-Beam Scanning Electron Microscopy tomographic data from before and after the experiment is used to recreate the initial and the final state of the computational domain for a microstructure evolution model using the Cahn-Hilliard equation. A number of intermediary microstructure states is then used to compute parameters such as the tortuosity of sample phases and the triple phase boundary density. Sample tortuosity is computed using a finite-volume-method-based 3D diffusion simulation, and triple phase boundary density is estimated by means of the Volume Expansion Method. The aforementioned parameters constitute input to a microstructure-scale 1D model of electrochemical transport phenomena, in which Poisson differential equation set is implemented to model charge conservation, and Butler-Volmer model is used for the reaction kinetics. The gas transfer is accounted for using the Cylindrical Pore Interpolation Model [2]. The results are then compared to the terminal voltage readings gathered during the long-term stack experiment.

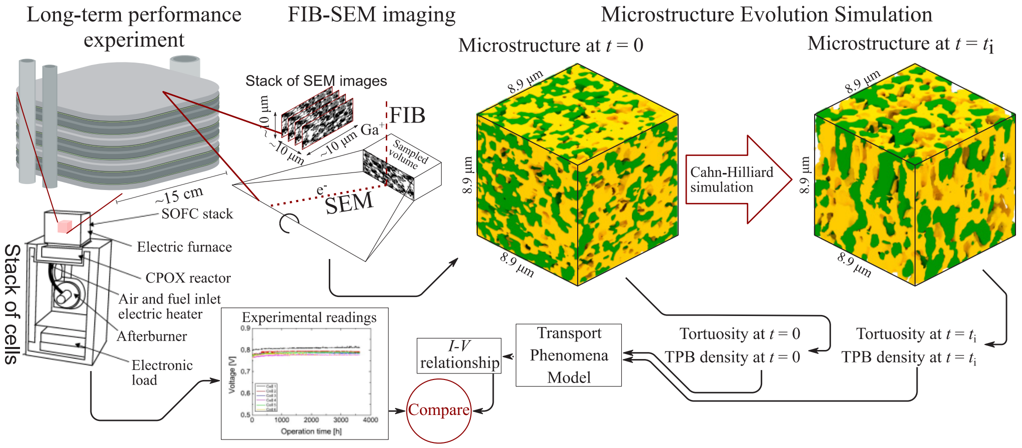

Figure 1: Model calibration scheme

***Keywords**:* Solid Oxide Fuel Cell, microstructure, FIB-SEM, evolution, degradation

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Segmented cell testing for local performance and degradation investigation in reversible operation

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A novel setup has been designed and mounted to investigate the local electrochemical and thermal behaviour of a cell from a 4-cells short stack under reversible operation SOFC/SOE. It consists in the partition of the cell's oxygen electrode into 20 segments, where each one is controlled by a specific electronic load (c.f. Fig. 1a). This allows to control the segments independently in galvanostatic or potentiostatic mode. The configuration also enables local electrochemical impedance spectroscopy (EIS) measurements of each segment. 20 thermocouples were added to measure the local temperature of the segments in order to gain a deeper insight into the cell thermal distribution. This helps correlating the local thermal and electrochemical answers to the operating parameters. This specific setup allowed mapping the cell's local behaviour based on a multidimensional operating conditions matrix, including current density, temperature, feed gas composition, sweep gas flow and polarization (c.f. illustration in Fig. 1b). Moreover, an ongoing durability test (currently >1500h) will help investigating the local long-term degradation in a reversible (day SOE, night SOFC) configuration. Besides, an electrochemical model was developed and validated on a single cell setup to simulate the local electrochemical properties and thus support the experimental investigations. Finally, post-test examinations, via scanning electron microscopy (SEM), will help understand the degradation mechanisms. These results are of significant importance towards optimal operation of a reversible SOC with enhanced durability.

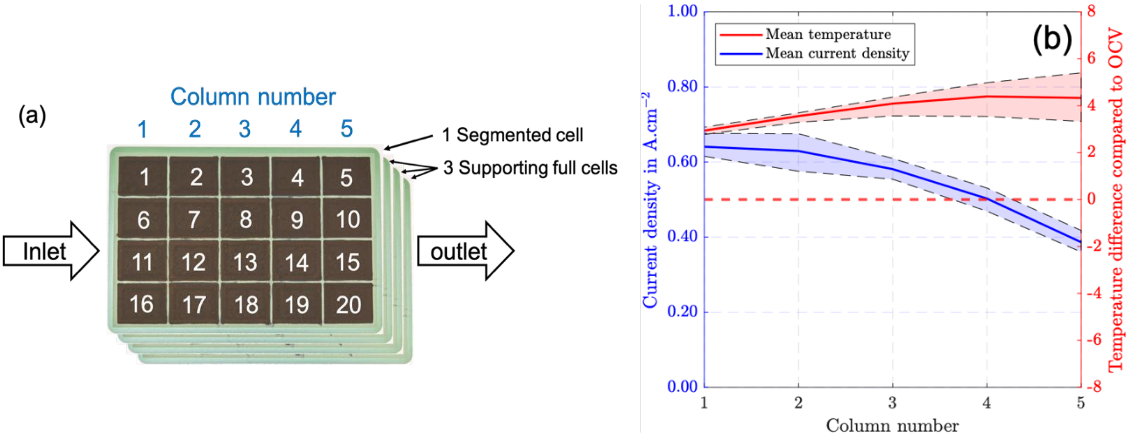

Figure 1: (a) Overview of the segmented cell: each segment has a surface area of 3.5 cm^2. (b) Illustration of the current density and temperature distribution in a SOE experiencing steam starvation (1.28:0.14 NL/min H_2O:H_2) at 1.4V, stack temperature 760ºC, total current 39 A, and steam conversion of 83.9% (Column 1 is the row next to the gas inlet, and 5 near outlet. Shaded area represents the measurements' standard deviation).

***Keywords**:* Segmented Reversible Solid Oxide Cell, local electrochemical investigations, Durability testing, Electrochemical Modelling, Scanning Electron Microscopy.

Optimization of MIEC-based SOFC anodes by Digital Microstructure Design (DMD)

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Fully ceramic anodes such as LST-CGO offer some specific advantages compared to conventional Ni-based cermets. Ceria- and titanate-based phases are both mixed ionic and electronic conductors (MIEC), which leads to very different reaction mechanisms and associated requirements for the microstructure design compared to e.g. Ni-YSZ. In MIEC anodes, the reaction mainly takes place on the two-phase boundaries of ceria (instead of the three-phase boundaries). Due to the MIEC-property of both solid phases, the transports of neither the electrons nor the oxygen ions are limited to a single phase. This leads to an effective composite conductivity (for electrons as well as for ions), which is much higher than the (hypothetical) single phase conductivity. In such a system, the charge carriers can reach the reaction sites even when the phase volume fraction(s) is/are below the percolation threshold.

In this contribution, methodologies for the digital materials design (DMD) are presented to investigate the much larger design space opening for composite MIEC electrodes. Stochastic digital twins representing the 3D microstructure are constructed based on Gaussian random fields for real structures obtained from 3D-tomography. Based on stochastic parameters of digital twins, a large variation of virtual 3D microstructures is then realized using massive simultaneous cloud computing (MSCC) with GeoDict software. All relevant microstructure characteristics are determined by image analysis and/or transport simulation (e.g. the relative ionic composite conductivity (Fig. 1 a) and the specific pore-CGO interface area (Fig. 1 b)). The effect of the microstructure properties on the cell-performance is then determined with a suitable multiphysics model (see Marmet et al.[1]). This combination of DMD-methodologies (3D imaging and image analysis, stochastic modelling, numerical simulation) allows for a systematic and data driven optimization to provide robust design guidelines for MIEC-based anodes.

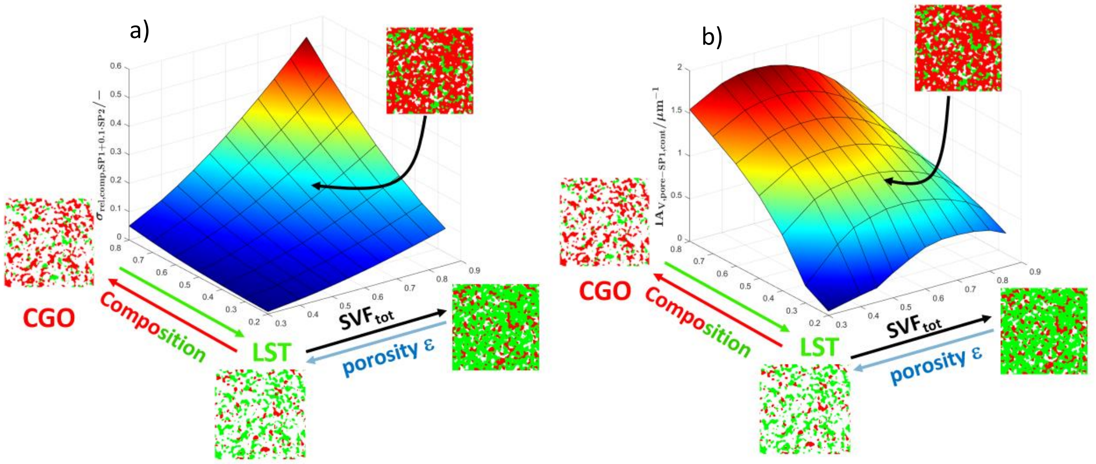

Figure 1: Important microstructure properties of the LST-CGO material system as a function of composition and porosity from a virtual microstructure variation: a) Relative ionic composite conductivity and b) specific CGO-pore interface area. 2D-slices of the virtual 3D-microstructructues are shown for the corner points for illustration.

Keywords: SOFC, MIEC, CGO, titanates, virtual microstructures, digital materials design.

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Capacitance of the blocking YSZ|Au electrode

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Yttria-stabilized zirconia (YSZ), $xY_2O_3 + (1-x)ZrO_2$, is a solid ionic conductor used as an electrolyte in high-temperature solid oxide cells. In an YSZ crystal, the oxides O^{2-} can hop to neighboring oxide vacancies, created by the lower valency Y^{3+} doping. Although the concentration of oxide vacancies in the volume of the YSZ is bound to a constant, electroneutral, value; a concentration gradient forms near the crystal terminations. In particular, near a triple-phase boundary, the non-constant oxide vacancy concentration influences the electrode reactions.

In this work, we measured impedance spectra of an YSZ single crystal electrolyte with a blocking Au electrodes for biases between -1V and +1V. We fitted the obtained spectra with an equivalent R-RCPE circuit and extracted approximate values of the space-charge layer capacitance for all the biases, see Figure 1. First, the obtained capacitance is two orders of magnitude lower than in comparable studies [1]. Second, the obtained capacitance profile has a double-hill profile.

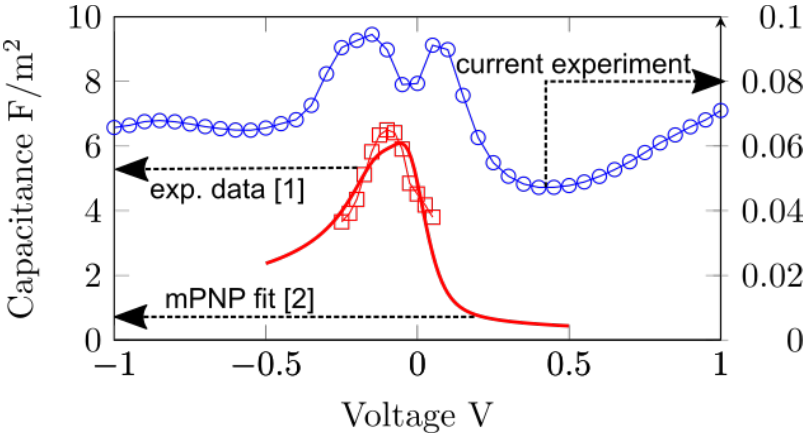

Figure 1: Capacitances of YSZ|Au interface at 600°C. Current experiment (blue circles), ten Elshof's experiment [1] (red squares), mPNP fit of [1] presented in [2].

Based on our previous work [2,3], we develop a modified Poison-Nernst-Planck (mPNP) model that qualitatively replicates the extracted capacitances. The mPNP model resolves the vacancy concentration and electrostatic potential across the blocking YSZ|Au interface. The oxide vacancies are modelled as a charged, interacting, lattice gas. In particular, the model assumes a vacancy concentration limit in the double layer, which the newly obtained data help to estimate. We enhance the mPNP model with interface species with aim to capture also the double-hill profile.

***Keywords**: solid oxide cell, yttria-stablized zirconia, blocking electrode capacitance, double layer*

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Modelling and experimental investigation of a reversible SOC using Total Harmonic Distortion Analysis as an advanced online monitoring tool

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To support the ever-increasing energy transition towards renewable sources, flexible, affordable, and reliable energy storage solutions should be made available. Solid oxide cells (SOCs) have great potential for becoming a key technology in this frame, however their durability is yet to be improved for large-scale deployment. On-field statistical data reveal that the intrinsic degradation is not the most limiting obstacle, but rather in-situ identification of faulty conditions at their reversible stage. The early detection and identification of faults are of central importance to act timely and minimize any damage by applying relevant mitigation and recovery strategies.

In this study, the applicability of Total Harmonic Distortion (THD) as an online monitoring tool to identify specific processes and faulty conditions in running SOCs was examined. First, a SOC was tested in normal conditions to acquire a performance map that will serve as a reference for the following analysis. Second, on-purpose faults were induced to simulate the most common failures that occur in reversibly operated SOCs, namely fuel and oxygen starvation in fuel cell mode and steam starvation in electrolysis mode. Thorough online characterizations have been made to identify the failures' footprint. This included Electrochemical Impedance Spectroscopy (EIS) complemented by Distribution of Relaxation Times (DRT), and THD analysis (c.f. illustration in Fig. 1). The second section of this work consisted of developing a 2D MATLAB® model to support the experimental results by simulating the local electrochemical properties. Finally, the experimental investigations together with the modelling approach, helped to achieve a clearer understanding of the behavior of SOCs under some frequent faulty conditions, thus providing guidelines towards optimal operation.

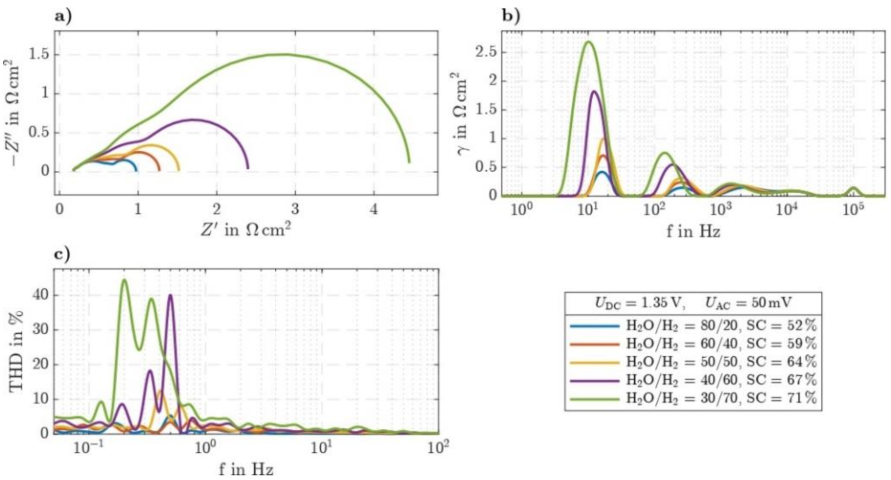

Figure 1: Illustration of the a) EIS, b) DRT and c) THD results for the failure mode of steam starvation.

***Keywords**:* State-of-Health, online monitoring, failure modes, fuel starvation, air starvation, steam starvation, total harmonic distortion, solid oxide cell durability, 2D steady-state model.

Optimizing innovative Power-to-Methane plant concepts with integrated SOEC module via multi-scale modelling

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Power-to-Methane (PtM) could become one of the core concepts to realize the transformation to a sustainable energy network, with CH_4 being a versatile energy carrier that can be readily applied as chemical feedstock in industry, or in residential and transportation sectors.

In this work, we develop system models for a detailed energetic assessment of various innovative PtM plant concepts with integrated solid oxide electrolysis cell (SOEC) unit [1] and different CO_2-sources and catalytic methanation technologies. A multi-physics 3D-stack SOEC model, which has been built upon an experimentally validated 2D single cell model of state-of-the-art electrolyte-supported (ESC) and cathode-supported cell (CSC) designs is coupled to the MATLAB®-based system models, such that a high-fidelity modelling approach close to the real-world application is realized. Subsequently, optimization algorithms are employed to maximize the PtM plant efficiency and the stacks' H_2 production rate whilst accounting for practical stack operation constraints such as thermal management issues.

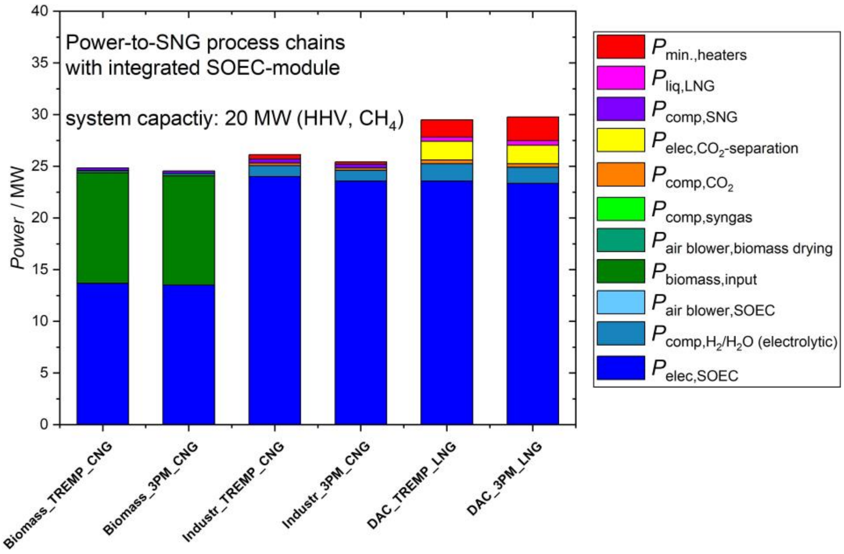

Figure 1: Breakdown of the energy consumptions of different Power-to-SNG plant concepts with integrated SOEC module and varying CO_2-sources and catalytic methanation technologies.

Keywords: SOEC, 3D-stack model, Power-to-Methane, system model, optimization

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3D printed electrodes for redox flow batteries

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To resolve the production-consumption profile imbalance that arises with renewable intermittent power sources such as solar panels and wind mills, electricity storage solutions are required to stabilise the electricity grid if our society wants to become fossil fuel independent.[1] In this regard, redox flow batteries (RFB) are an interesting solution. By actively pumping the electrolyte through the battery cell, the storage capacity is no longer dependent on the battery size. By simply increasing the electrolyte volume, which can be stored in cheap vessels, the capacity is enlarged. To minimise local current density and maximise the power output, redox flow batteries are often equipped with felt electrodes.[2] However, having a disordered 3D geometry, the energy required to pump the electrolytes through the RFB is adversely affected.[3]

In this work, for the first time, we have studied different all metal 3D printed structured static mixer electrodes for an iron-zinc RFB (Figure 1) and compared its performance to the typical used felt electrode (Figure 2). Based on the most common static mixer designs, these electrodes have an ordered geometry, diminishing preferential flow paths and minimizing pressure drop. Moreover, they induce mixing effects which maximises mass transport towards the electrode surface. As a result, similar battery performance was obtained in terms of cell voltage, but at a pumping cost that was three orders of magnitude lower. These results show the impact structured 3D electrodes can have in the field of batteries, allowing to minimize transport losses and maximize battery efficiency.

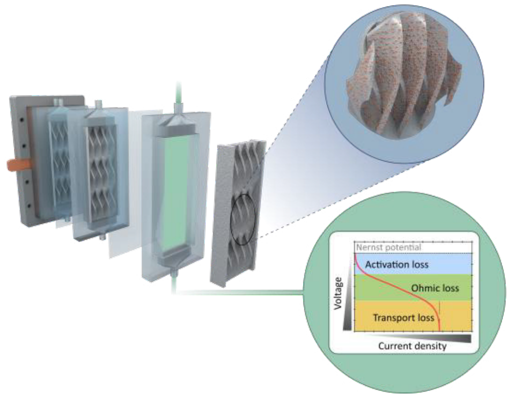

Figure 1: Representation of the RFB.

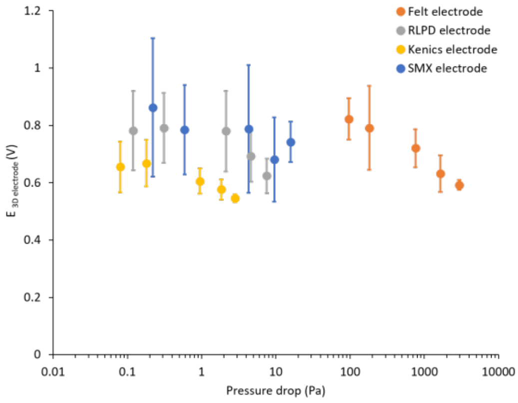

Figure 2: Electrode potential vs Ag/AgCl at 100 mA/cm² for different electrode designs.

***Keywords**: Redox flow battery, 3D electrode, mass transfer, pressure drop*

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Modelling and Simulation for the Search for New Active Materials for Redox Flow Batteries - Results of the International Project SONAR

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Xinjie Guan[2], Jan Hamaekers[5], Astrid Maaß[5], Chris Menictas[2], Gael Mourouga[6], Hermann Nirschl,
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Due to the characteristics of flow batteries, this technology is ideally suited for low-cost storage in the range of a few hours and thus for load balancing as stationary storage in grids with high amounts of renewable energy [1]. Today, a large number of different active materials for flow batteries are known, although only a few have been commercialised [2]. Basically, the energy supply and thus also the required storage should be sustainable, i.e. not cause resource problems and not be harmful to humans and the environment. A potential for a huge range of possibilities is offered by organic active materials, which should be used especially in aqueous solutions. Due to the immense possibilities, classical synthesis and testing is extremely lengthy and costly. An alternative can be model-based high-throughput screening, where by simulating the properties of active materials in the electrolyte and the battery itself, computer-based simulations can be used to conduct the search.

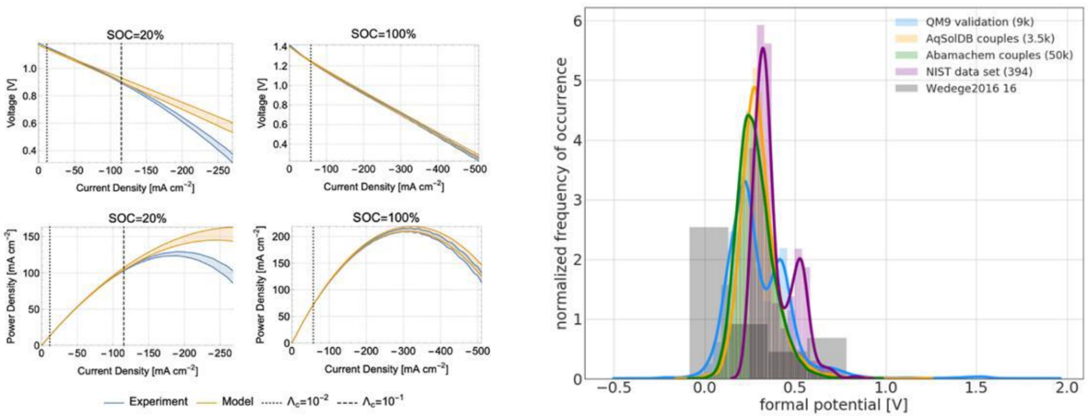

Figure 1: left) Simulated vs. experimental polarisation curves based on a 0D cell modell for MV/TMA-TEMPO, right) ML-based calculated formal potentials vs. database-based potentials of a dataset with 9000 quinone based redox couple

The SONAR project is an EU-funded project in which 7 different institutions from the EU, Switzerland and Australia are developing a high-throughput screening method capable of finding new active materials for redox flow batteries. The principle is a serial coupling of different size scales, combined with molecule generation and machine learning. The chemical structure of a candidate is generated by a molecule generator and then its atomistic properties, kinetics, side reactions and cell properties are iteratively calculated with exclusion criteria.

In this talk we will give an overview of 2 years of research in this project in the areas of machine learning for high throughput screening, DFT based quantum mechanics modelling, kinetics Monte Carlo methods for meso-scale, 0D cell modelling, 3D cell modelling, stack modelling and techno-economics.

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Non-solvent Induced Phase Separation: A Versatile Synthetic Method for High Performance Redox Flow Battery Electrodes

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Carbonaceous porous electrodes are ubiquitous to advanced electrochemical systems where they are responsible for multiple critical functions in the cell. However, our current arsenal of materials is limited to carbonaceous fibrous electrodes which are manufactured using various mechanical methods (e.g. paper making, weaving, hydro-entangling) resulting in idiosyncratic structures such as papers, cloths, and felts. These fabrication methods involve multiple complex subprocessing steps impacting the final manufacturing cost and offering limited versatility to control the electrode microstructure and surface composition, which ultimately limits the performance of the electrochemical cell. Thus, there is a need to develop novel material sets with precise control over microstructure and composition while employing synthetic methods that are compatible with large scale manufacturing. In this work, we focus our efforts on designing tailored electrodes for redox flow batteries (RFBs), which are promising for grid-scale energy storage if their costs can be significantly reduced[1].

Here, we introduce the non-solvent induced phase separation (NIPS) as a simple and versatile fabrication method for carbonaceous porous electrodes for redox flow batteries[2]. Drawing inspiration from membrane technology, the NIPS method has been leveraged to synthesize morphologically-diverse microstructures (e.g., isoporous, macrovoids, porosity gradient) which are appealing to electrode manufacturing[3]. A polymer solution, containing polyacrylonitrile (PAN, carbon-containing) and polyvinylpyrrolidone (PVP, pore-forming agent) dissolved in N,N-dimethylformamide (solvent) was casted in a mold and subsequently immersed in water (non-solvent). Finally, the polymeric scaffold is carbonized under inert conditions to form a conductive network. Microstructural characterization revealed a multimodal pore size distribution composed of fine, interconnected microvoids (pore diameter ≈ 2-15μm) coupled with through plane, finger-like macrovoid channels (throat diameter > 50 μm) forming honeycomb networks. The unique microstructure, not attainable with traditional carbon-fiber manufacturing techniques, enables large surface area at the membrane-electrode interface and fast electrolyte replenishing which reduces mass transfer resistance within the electrode. In the final part, we demonstrate the use of NIPS-electrodes in a full all-vanadium RFB which results in a significant improvement in power density compared to the baseline material, which can be attributed to reductions in the charge transfer and mass transport overpotentials. Although nascent, NIPS emerges as a promising platform to engineer porous electrodes for RFBs and other convection-enhanced electrochemical systems.

Keywords: porous electrodes, redox flow batteries, mass transfer.

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In situ and in operando detection of redox reactions during vanadium transport in ion exchange membranes

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The global shift from fossil fuels to renewable energy requires energy storage devices for balancing the associated fluctuations in energy supply. In recent years, the vanadium flow battery (VFB) has received increasing attention and has demonstrated to be a promising energy storage system for stationary applications. Even though VFBs are commercially available, further performance improvements are mandatory to achieve widespread implementation. In particular, the problems related to the capacity fade due to vanadium species crossover through the membranes require greater attention. It is proven that reactions between these ions do occur inside the membrane, a phenomenon which is not considered in state-of-the-art crossover models[1]. Therefore, it seems very likely that the neglect of redox reactions inside the membrane has led to significant inconsistencies in the estimated diffusion parameters for the different vanadium ions. This results in an apparent lower performance than calculated using current crossover models.

In our work, we present for the first time a time-resolved in situ and in operando method to measure the potential distribution inside membranes during operation of a VFB. This practical method can be used to gain better insights into the complex processes occurring within membranes and to determine transport parameters more accurately. The experimental method is supplemented by a dynamic model, which describes the ion transport as well as the reactions between the vanadium species within the membrane. The validation of the model focuses on the crossover phenomena, which is done with a series of measurements of the potential distribution as well as the conductivity of the membrane.

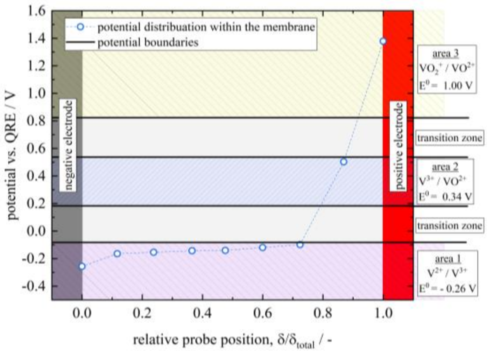

Figure 1: Distribution of quasi stationary potentials vs. QRE (quasi-reference electrode) as a function of the relative probe position.

Keywords: Vanadium flow battery, crossover, membrane transport phenomena, redox reactions, potential probe.

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Pore-scale resolved 3D simulation of aqueous organic flow batteries

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Three-dimensional pore-scale continuum models resolve the real geometry of the electrode to gain insight of the microstructural processes inside the flow battery. They offer great capability to obtain information about the microstructure and how it affects transport processes within the electrode and the overall cell performance[1].

Most of the flow battery modelling approaches to date have concentrated on volume-averaged or macroscopic calculation of transport processes within porous electrodes captured by using empirical relations e.g. Darcy's law or Bruggeman correction. Hence, the behaviour of key parameters like ionic diffusivity or permeability on performance is not represented correctly, as well as the coupled species and charge transport. Pore-scale resolved models overcome these disadvantages and provide spatial characteristics of velocity, concentration or current density depending on the complex structures of the electrode. Therefore, a spatially resolved continuum model is set up to gain insight into the microstructural processes inside the flow battery[2].

The three-dimensional half-cell model is parameterized with the known model chemistry of the organic 4-OH-TEMPO system[3] and accounts for electrolyte flow, mass and charge transport. The electrochemical reaction is implemented using Butler-Volmer type kinetics to couple the solid and electrolyte region. The simulations consider galvanostatic and isothermal operating conditions comprising laminar and steady-state flow.

Simplified structured electrodes are used as computational domain to numerically investigate the influence of the initial active material concentration, the current density and the active surface. Furthermore, a digital twin of the real electrode microstructure is generated by experimental image reconstruction from X-ray computed micro-tomography and used to investigate the impact of different flow rates on the concentration distribution within the electrolyte and on the half-cell potential.

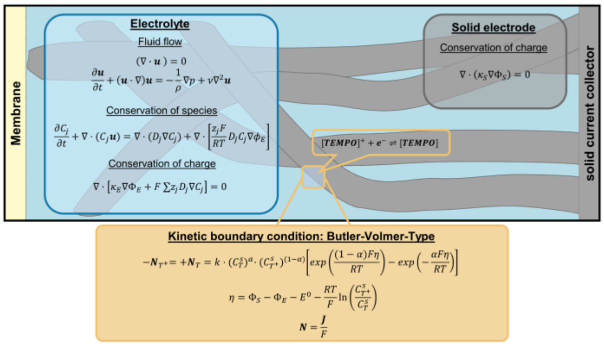

Figure 1: Electrochemical Model

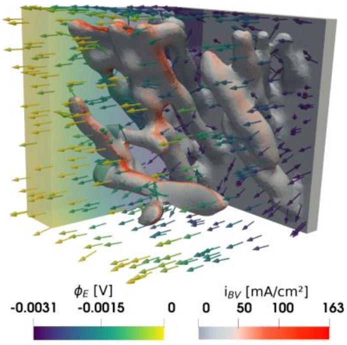

Figure 2: Simulated half-cell compartment of the electrode microstructure

Keywords: flow battery, direct numerical modelling, pore-scale, electrode microstructure, digital twin.

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Macroscopic simulation of 1000 PEMFC ageing cycles

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In the frame of the UE project Id-Fast, a new automotive cycle has been proposed to study the fuel cell ageing during realistic operations (figure 1). This cycle has been applied until 1000 times to single cell and to stack. From the stack polarisation curves, the semi-empirical law for the electrochemical response of the MePHYSTO code has been calibrated. The evolution of the electrochemical surface area and of the Platinum particles sizes distribution between BoT (beginning of test) and EoT (end of test) have been obtained by cyclic voltammetry and Transmission Electron Microscopy. Thanks to all these data, the MePHYSTO code has been used to simulate the catalyst degradation associated with the dissolution/deposition of platinum (Ostwald mechanism). Thanks to the use of a coarse meshing, we have been capable to simulate 1000 Id-Fast cycles in a reasonable CPU time. This simulation provides the active surface area reduction induced by the Ostwald mechanism and can be used as a tool to help for the definition of new cycles that accelerate the degradation realistically.

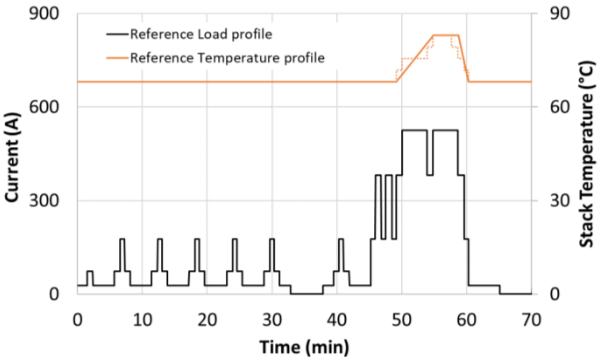

Figure 1: ID-FAST DLC – Load and stack temperature profiles
adapted to S3 design from the proposed automotive drive cycle.

Keywords: Ostwald, catalyst degradation, AST, simulation, fuel cell.

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Modeling of platinum oxides formation and reduction: a performance model for O_2 reduction reaction

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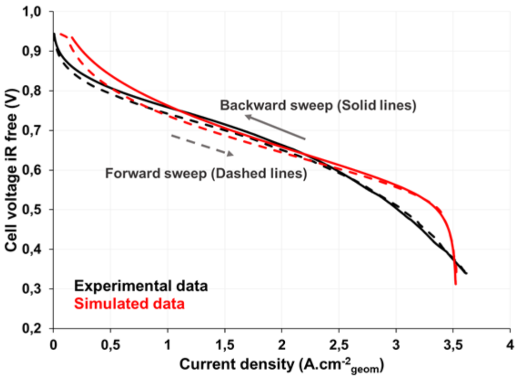
Despite many improvements, PEMFC systems still suffer technological limitations, such as their initial cost and overall durability in real life operation, which prevents widespread industrial deployment. Some of these limitations can be overcome by combining experiments and modeling to characterize and better understand the behaviour of the carbon-supported platinum (Pt/C) electrocatalyst, its utilization/effectiveness in PEMFC catalyst layers and to be able to predict the performance and durability of PEMFC. This should help making the most relevant choices to accelerate the development processes of PEMFC.

In this work, physico-chemical and electrochemical measurements are performed from the scale of the raw Pt/C materials up to the complete catalyst layer, to gather as much information as possible on the catalytic layer micro-structure and its operating properties. Coupling experiments in classic RDE and in PEMFC differential-single cell (1.8 cm² under high reactant stoichiometry) enables to fully characterize the electrochemical properties and behaviour of our materials. During experimental performance measurements, reversible performance gains/losses can be observed. This behaviour is often ascribed to variable hydration state of the ionomer in the catalyst layer and the bulk membrane and also to the evolution of platinum surface states due to oxides partial formation/reduction.

In parallel; several models have been developed to simulate one or combined mechanisms leading to the performance[1] and degradation of cell components[2,3]. Based on our experimental work and data sets, the behaviour of the Pt/C electrocatalysts has been studied in order to introduce new electrocatalytic features and especially the Pt surface oxide formation and reduction which is linked to Pt surface state as well as Pt 'bulk' oxide formation via chemical place exchange reaction. This preliminary step was then further developed into a complete performance model for the O_2 reduction reaction at the cathode to better describe the physical and electrochemical phenomenon involved in catalyst layers during fuel cell operation. With this new description, the position of the main adsorption/desorption peaks monitored by CV under inert atmosphere and the hysteresis phenomenon on the polarization plot during real fuel cell operation are well captured by the simulation compared to experiment keeping complete physical meaning.



***Keywords**: Performance model, Hysteresis phenomenon, Reversible degradation, Modeling, Fuel cell.*

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Modeling the effect of membrane electrode assembly microstructure on thermal and water transport in polymer electrolyte fuel cells

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The effect of water management on oxygen transport plays a critical role in the design of high-performance polymer electrolyte fuel cells (PEFCs) for the automotive industry, especially at low cathode Pt loading [1,2]. In this regard, optimizing the hierarchical pore structure of the membrane electrode assembly (MEA) is crucial to alleviate cathode flooding while ensuring good membrane hydration [3]. However, this task is complicated due to the small dimensions involved in the problem. Mathematical modeling plays a crucial role to understand transport in the thin layered assembly used in PEFCs, including the catalyst layer (CL), microporous layer (MPL) and gas diffusion layer (GDL).

In this work, oxygen and two-phase water transport in the MEA are examined by means of a continuum bundle of capillary tubes model. Experimental pore size distributions (PSDs) are considered for the GDL/MPL/CL assembly. The model predictions are validated against previous experimental data for various operating conditions and MEA materials (see Figure 1). The results offer precise information on the coupling between heat and water transport, and the impact of operating conditions and transport properties on the saturation distribution through the MEA. The continuum bundle of capillary tubes model is also used to determine optimal PSD-dependent effective transport properties to produce improved MEA microstructures.

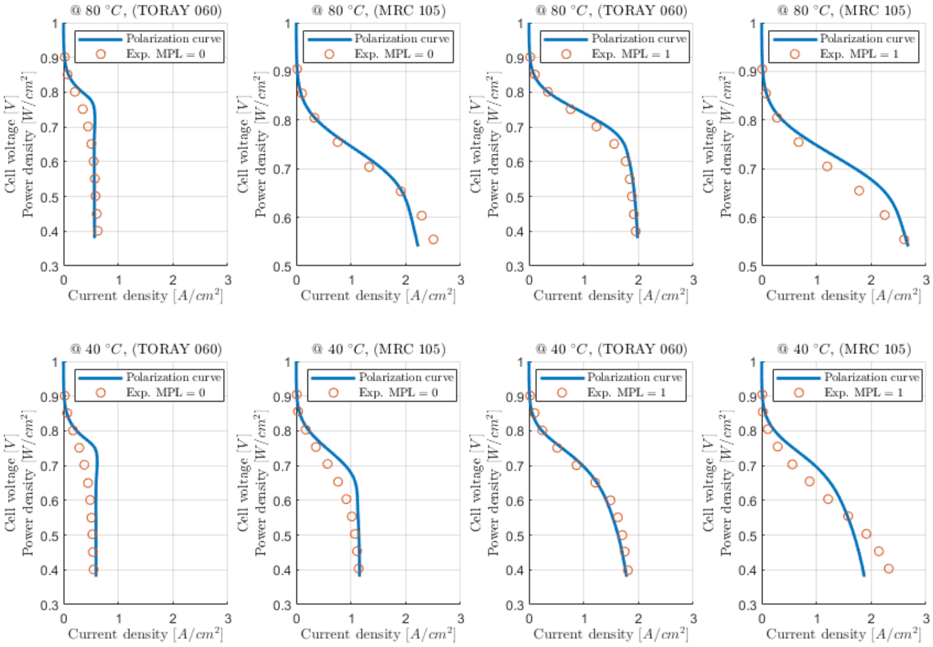

Figure 1. Validation of the continuum bundle of capillary tubes model under different conditions. The results include temperatures of 40ºC and 80ºC for two GDLs, Toray 060 and MRC 105, with and without MPL.

***Keywords**:* continuum bundle of capillary tubes model, pore size distribution, membrane electrode assembly microstructure.

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Predicting optimal catalyst layer microstructures in low Pt loading PEMFCs

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Negative environmental impacts from transportation emissions have resulted in a push to design newer vehicles with cleaner technologies. Fuel cell electric vehicles (FCEVs) are one such technology that utilize proton exchange membrane fuel cells (PEMFCs) to power electric motors. The optimization of cheap, efficient, and durable PEMFCs is likely to increase wide-spread adoption of FCEVs. Therefore, identifying and addressing performance limitations in PEMFCs fabricated with low Pt loadings is the focus of this work. Previous studies have agreed that poor device performance is linked to complex physiochemical processes in the cathode catalyst layer (CL) [1]. More specifically, poor performance with low Pt-loading is attributed to sluggish proton and/or oxygen transport through the nano-thin films of Nafion ionomer in this layer. Because direct *operando* measurements of these processes are challenging, we have developed a half-cell model to investigate how CL transport processes contribute to the overall cell performance. After validating the model, we perform a parametric study on the microstructure to find optimal CL designs with low Pt loading. Within this study we include novel, functionally graded CLs in which Pt and/or ionomer loadings vary as a function of depth, as in figure 1.

For this presentation, we will provide a discussion on limiting phenomena and optimal CL designs. In addition, we will discuss first-of-their-kind structure-property relationships included in the model. In contrast to studies which use property relationships from bulk Nafion membranes, structure-property relationships are informed by neutron reflectometry [2] and conductivity measurements [3] on thin films. Using these relationships, ionic conductivities and oxygen diffusion coefficients are locally resolved, based on the water absorbed in the Nafion ionomer. Results demonstrate that these transport properties more accurately predict performance under low Pt loading, and enable new insights into catalyst layer design for high-performance, cost-effective PEMFCs.

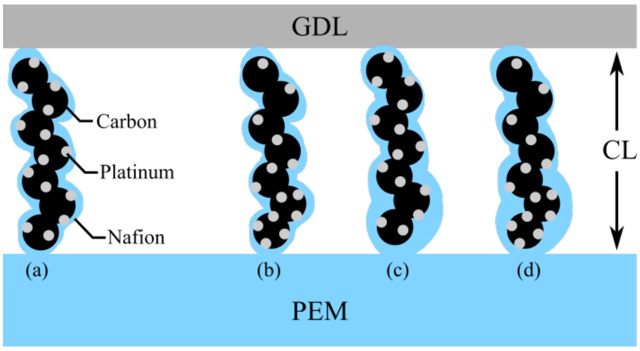

Figure 1: Illustrated CL designs with: (a) uniform, (b) graded Pt, (c) graded ionomer, and (d) combined graded Pt/ionomer loadings.

***Keywords**:* proton exchange membrane fuel cell, Nafion, structure-property relationships

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Automating Image Analysis for Electrochemical Materials Characterization with Deep Learning

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The performance of polymer electrolyte fuel cells largely depends on the structure and processes in membrane electrode assemblies (MEA) and their components, particularly the catalyst layers (CLs). Transmission electron microscopy (TEM) imaging has become the standard technique to study the microstructure of MEA components before cell assembly or post-testing. To expedite further advances in the design and fabrication of CLs, it is essential to accelerate the analysis of the TEM imaging data. While the applications of routine methods for image processing in materials research are often indiscriminate, empirical, and expensive, deep learning (DL) algorithms based on deep convolutional neural networks (ConvNets) offer promising capabilities for the high-throughput analysis. We first present a novel DL-based approach to automate the particle size distribution analysis from TEM images of carbon-supported catalysts for polymer electrolyte fuel cells [1]. This will follow by an application of ConvNets for the high throughput screening of catalyst ink imaging data [2]. We discuss the importance of model pre-training and data augmentation that works on multiple scales in training robust and accurate methodical pipelines.

Keywords: Characterization, Automation, Fuel Cell, Deep Learning

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High-fidelity pore-level simulation of the flow in the channel and GDL of a micro-PEFC

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The flow field in a serpentine channel and the under-laying porous gas diffusion layer (GDL) of a micro polymer electrolyte fuel cell (PEFC) is investigated numerically using high-fidelity lattice Boltzmann Method (LBM) simulations. The geometries of serpentine channel and GDL are obtained with a high-resolution 2.9 μm X-ray tomography [1]. This study focuses on two conditions, a) partially saturated (operating) fuell cell wherein the flow Reynolds number is not high enough to move the liquid droplets (Fig. 1); and b) dry fuel cell where the inlet Reynolds number is higher and it pushes the liquid out of the channel and GDL.

The simulation results show that liquid water formed in the serpentine channel improves the fuel cell performance under the ribs by blocking the channel and leading the flow towards the GDL. Due to the channel blockage, more gas flows inside the GDL pores and this becomes the dominant transport mechanism. In addition, the cross flow in wet GDL is noticeably higher than in dry GDL, especially where the serpentine channel is blocked by water. Pressure drop and velocity field at different cross sections of the serpentine channel and GDL are finally compared for the two operating conditions.

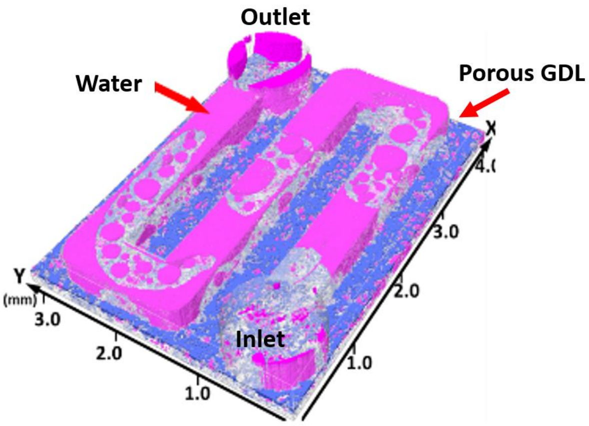

Figure 1: Porous GDL and serpentine Channel

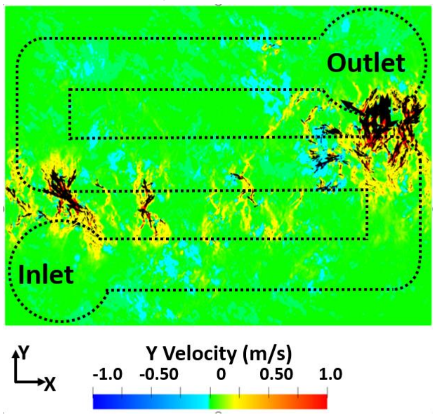

Figure 2: Cross flow Y-velocity distribution averaged over GDL thickness

***Keywords**:* Polymer electrolyte fuel cells (PEFCs), Pore-scale numerical simulation, Mass transport in gas diffusion layers (GDLs), Flow field in serpentine channel and GDL.

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