

19th
SYMPOSIUM

BOOK OF ABSTRACTS

ModVal 2023

Symposium on Fuel Cell & Battery Modeling & Experimental Validation

21 - 23 March 2023 / Mercatorhalle - Duisburg, Germany

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2 MARKET

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Day 1 - 21 March 2023

- 2:30 p.m. **Sitetour (optional)**
- presentation and tour of ZBT - The Hydrogen and Fuel Cell Center
 - presentation and tour of the European headquarters of Plug Power
- 7 p.m. **Welcome Dinner (optional)**
-

Day 2 - 22 March 2023

- | | | | |
|------------|--|-----------|------------------------------|
| 8 a.m. | Registration | 1:10 p.m. | Technical sessions |
| 9 a.m. | Welcome address
Plenary Session I | | - Battery fabrication I |
| | Coffee break | | - Redox flow batteries |
| | | | Coffee break |
| 10:20 a.m. | Technical sessions | 3:50 p.m. | Technical sessions |
| | - Battery degradation | | - Data driven battery models |
| | - SOFC / SOEC / Methods | | - PEM-Systems / Degradation |
| | Lunch buffet | 5:30 p.m. | Poster session |
| | | 7 p.m. | Conference dinner |
-

Day 3 - 23 March 2023

- | | | | |
|------------|---|-----------|---------------------------|
| 9 a.m. | Welcome
Plenary Session II | 1:00 p.m. | Technical sessions |
| | Coffee break | | - Battery fundamentals |
| | | | - PEM / Microstructure I |
| | | | Coffee break |
| 10:20 a.m. | Technical sessions | 3:30 p.m. | Technical sessions |
| | - Battery microstructure | | - Battery fabrication II |
| | - AEM, PEM and Alkaline | | - PEM / Microstructure II |
| | Electrolysis | | |
| | Lunch buffet | 4:50 p.m. | Closing |
-

	Sitetour (optional)
2:30 p.m.	Start at Mercatorhalle and transfer to ZBT by coach
3:00 p.m.	Presentation and tour of ZBT - The Hydrogen and Fuel Cell Center
4:30 p.m.	Transfer to Plug Power
5:00 p.m.	Presentation and tour of the European Headquarters of Plug Power
6:00 p.m.	Transfer to Mercatorhalle
6:30 p.m.	Drop-off at Mercatorhalle
	Welcome Dinner (optional)
7:00 p.m.	Dinner at Mercatorhalle



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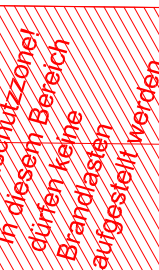
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	Room 4+5	Room 6
8.00 a.m.	Registration	
9.00 a.m.	Welcome Plenary Session I Climate modelling: fundamentals, evaluation, and storyline simulations Helge Goessling	
9.50 a.m.	Coffee break	
	Battery degradation Chair: t.b.c.	SOFC / SOEC / Methods Chair: André Weber
10.20 a.m.	Modelling OER and HER in NiZn battery cells Britta Doppl	Simulation of electrode diffusion models for solid oxide fuel cells Zhang Xiaoliang
10.40 a.m.	Silicon-graphite composite electrodes: modelling state-of-charge and current distribution, and experimentally determining degradation rates Niall Kirkaldy	Predicting the SOFC anode performance from microstructure using convolutional neural networks Pascal Plettenberg
11.00 a.m.	Simulation of Li plating in Si/Graphite composite electrodes Lioba Boveleth	Multiscale and Multiphysics Modeling of an SOC Stack Zhang Shidong
11.20 a.m.	Monitoring battery degradation using acoustic signatures Elias Galiounas	Modeling and simulation of an anion-exchange membrane electrolyzer using a unified open source platform for electrochemical systems Xavier Raynaud
11.40 a.m.	Health-aware battery fast charging optimisation Nicola E. Courtier	Ontology-based graph data model for scalable data management in catalyst layer fabrication Max Dreger
12.00 p.m.	Lunch break	
	Battery fabrication I Chair: Ilona Glatt	Redox flow batteries Chair: Antoni Forner-Cuenca
1.10 p.m.	KEYNOTE 3D multiphysics model for large format lithium-ion cells and its application in an agile cell production André Weber	KEYNOTE Advancing redox flow batteries through porous electrode and reactor engineering Antoni Forner-Cuenca
1.50 p.m.	A new approach for state of charge and state of health diagnosis of batteries using voltage-controlled models Wolfgang G. Bessler	Starting from the bottom: Coupling a genetic algorithm and a pore network model for redox flow battery porous electrode optimization Maxime van der Heijden
2.10 p.m.	Pore-scale Modeling and Validation on the Calendar of Lithium-Ion Battery Cathodes Xu Jie	Optimizing electrode geometry for improved mass transfer in redox flow batteries: a CFD simulation and experimental study Michiel De Rop
2.30 p.m.	Modelling and experiments on porous electrodes with lithiated bin Tanmay Dev	Combining electrochemical and imaging analyses to understand the effect of electrode microstructure and electrolyte properties on redox flow batteries Catalina A. Muñoz
2.50 p.m.	Electrode Structuring and its Effects on Battery Production and Performance Benjamin Kellers	System-level performance modelling of regenerative fuel cells Ye Minnan
3.10 p.m.	Coffee break	
	Data driven battery models Chair: Nicola Courtier	PEM-Systems / Degradation Chair: Steven Beale
3.50 p.m.	Battery Aging Identification Tool, a new Simcenter Amesim feature on electric storage library Rémy Mingant	Modeling of Carbon Corrosion in PEM Fuel Cells applied to 3D Simulation Clemens Fink
4.10 p.m.	Machine learning for the classification of equivalent circuit models from solid-state electrochemical impedance spectra Joachim Schaeffer	Simulating cathode catalyst morphology and degradation on porous carbon supports Anne-Christine Scherzer
4.30 p.m.	Operando EIS applied to commercial Li-ion batteries Noel Hallemans	Numerical modelling and simulation of metal interconnect oxidation of SOC stacks Yu Shangzhe
4.50 p.m.	Modelling Battery Behaviour with Physics informed neural Networks Josü Yeregui	Investigation of scaled-down fuel cell system components by means of the IPEK X-in-the-loop approach Jan Haußmann
5.10 p.m.	Quantifying the impact of charge rate and number of cycles on particle cracking in Li-ion battery cathodes Orkun Furat	Studies on Operational and Failure Dynamics of a Phase-Change Cooled Aviation PEM Fuel Cell System using Flownex® Gao Xin
5.30 p.m.	Poster session	
7.00 p.m.	Conference Dinner	

	Room 4+5	Room 6
All day	Poster exhibition	
9.00 a.m.	Welcome Plenary Session II Climate modelling: fundamentals, evaluation, and storyline simulations Gregory Offer	
9.50 a.m.	Coffee break	
	Battery microstructure Chair: t.b.c.	AEM, PEM and Alkaline Electrolysis Chair: Moritz Pilaski
10.20 a.m.	Li-ion battery in high C-rate conditions: improving the temperature prediction Volkan Kumtepel	Multiphase zero-gap electrode simulations for alkaline water electrolysis Wouter Leen van der Does
10.40 a.m.	Microstructure-resolved simulation of three-dimensional electrodes for sodium iodine batteries Felix Gerbig	CFD modeling of a PEM water electrolyzer: relationship between flow regime and performance Cheng Tianliang
11.00 a.m.	Understanding the Dynamics of Lithium-Ion Transport in Graphite-Silicon Composite Electrodes through Model Analysis Eduardo Jané	Transient hydrogen crossover in dynamically operated PEM water electrolysis cells - a model-based analysis Tobias Franz
11.20 a.m.	Homogenized monolayers based 3D-model of a thermal event in a lithium-ion battery pouch cell Marcel Silas Tumelero	Structure-performance relationship of IrO ₂ nanoparticles during oxygen evolution: Investigation by dynamic microkinetic modeling Gözde Kardeş
11.40 a.m.	Multiphase-field modelling of layered-oxide compounds for intercalation batteries Simon Daubner	Membrane electrode assembly simulation of anion exchange membrane water electrolyser Suhas Nuggehalli Sampathkumar
12.00 p.m.	Lunch break	
	Battery fundamentals Chair: Gregory Offer	PEM / Microstructure I Chair: Michael H. Eikerling
1.00 p.m.	KEYNOTE Translating entropy measurements to next-generation battery materials Michael Mercer	KEYNOTE Unraveling the role of ionomer and water in cathode catalyst layers of PEM fuel cells Michael H. Eikerling
1.40 p.m.	Electrode material design booster using a statistical digital twin Ilona Glatt	Noninvasive local impedance determination in polymer electrolyte fuel cells stacks Jens Eller
2.00 p.m.	ENMR-derived Transference Numbers in Different Reference Frames Franziska Kilchert	Experimental and modelling analysis of liquid water and current density distribution in a PEMFC stack Pierrick Balestrieri
2.20 p.m.	Advances in LiS Model Validation and Prediction Michael Cornish	Spatial Distribution of Loss Processes in PEMFC Philipp Oppek
2.40 p.m.	Why diffusion coefficients in active materials are not constants – On the importance of state-of-charge dependent input parameters in battery simulation Anja Bielefeld	Electrochemical pressure impedance spectroscopy for PEM fuel cells: Model-based signal interpretation Lutz Schiffer
3.00 p.m.	Coffee break	
	Battery fabrication II Chair: Michael Mercer	PEM / Microstructure II Chair: Michael H. Eikerling
3.30 p.m.	Cell design on target – maximum performance at optimal cost in minimal time Jan Richter	Machine learning for the characterization of fibrous gas diffusion layers Dieter Froning
3.50 p.m.	Coupled EIS-FIB/SEM analysis of wet mixing effects on performance of Li-ion battery Saeed Abdolhosseini	Multiscale simulation of nanostructured electrocatalytic systems by coupling neural network surrogates and continuum models Younes Hassani Abdollahi
4.10 p.m.	DEM-Simulation of Drying and Calendaring of Lithium-Ion Battery Electrodes Carsten Schilde	A coupled diffusion-mechanics model to investigate the interfacial mechanical damage at the microscale in block copolymer-based solid-state battery cathodes Soheil Bazazzadeh
4.30 p.m.	Identification of SEI growth models during Li-ion battery cell formation Felix Schomburg	Advancement and validation of OpenFOAM PEMFC toolbox on automotive PEMFC design Sabina Schneider
4.50 p.m.	Closing	

Status: 16 March 2023







Helge Goessling

Helge Goessling examines the functioning of the physical climate system and its predictability on scales from days to centuries. Since his graduation in biophysics at Humboldt University Berlin in 2008, global coupled climate models have been one of his main research tools. During his doctorate at the MPI for Meteorology 2009-2012, he researched the global water cycle and land-atmosphere interactions. Since 2012 at AWI, his focus has been on the prediction of sea ice conditions. His research also includes global aspects of climate change, extreme events, the earth's energy balance, and geo-engineering. Since 2022, Helge Goessling has been leading a joint project of the Helmholtz Earth-and-Environment Centers, in which observed extreme events of the recent past are simulated in different background climate states in order to better understand the influence of climate change on extremes.

Gregory Offer

Gregory Offer is Professor of Electrochemical Engineering at Imperial College London, is based in the Department of Mechanical Engineering, and helps lead the interdepartmental Electrochemical Science and Engineering Group. His research focuses on both the experiments and modelling of batteries, supercapacitors, and fuel cells. Greg was a co-founder of the Faraday Institution in 2017, and is the PI of the Multi-Scale Modelling project, >£20M over 7 years including 9 institutions. Greg co-founded and organises the Future Propulsion Conference series in the UK, attracting over 600 delegates and exhibitors each year. Greg also co-founded and is Director of multiple spin-out companies, including Breathe Battery Technologies Ltd.





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Michael Mercer

Michael Mercer is a laboratory lead in the Faculty of Mechanical Engineering at the Helmut-Schmidt-University, Hamburg, supporting the Chair for Computational Materials Design. After a degree in physics at the University of Warwick, UK, he did a PhD at the University of Bristol as part of the Bristol Centre for Functional Nanomaterials. As a postdoc at Lancaster University, he joined the Faraday

Institution-funded Multi-Scale Modelling project in 2018, and has since led advanced thermodynamic characterisation and atomistic/statistical thermodynamics modelling of battery materials, developing new insights into lithium- and sodium-ion intercalation. In his new role at Helmut-Schmidt, he is leading a new battery lab which will integrate high-throughput physical vapour deposition (PVD) and computation to screen candidate materials for next generation batteries with a focus on coupling these techniques with advanced electrochemical characterisation.

Michael H. Eikerling

Michael Eikerling is Professor at RWTH Aachen University and Director of the Institute of Energy and Climate Research in Forschungszentrum Jülich, heading the new sub-Institute for Theory and Computation of Energy Materials (IEK-13). Moreover, he is the Scientific Coordinator of the Centre for Advanced Simulation and Analytics (CASA) in Jülich. Previous important stages of

his career were at Simon Fraser University and the National Research Council in Vancouver, Canada. Research in IEK-13 explores how electrochemical energy materials form, function, fade and fail, focusing on interface theory, electrocatalytic phenomena, nanopore transport, statistical physics of materials aging, porous electrode theory, and modeling and diagnostics of electrochemical devices. In 2017, Michael was awarded the Alexander Kuznetsov Prize for Theoretical Electrochemistry of the International Society of Electrochemistry, in recognition of his groundbreaking work on modeling polymer electrolyte fuel cells.





Antoni Forner-Cuenca

Antoni Forner-Cuenca leads the Electrochemical Materials and Systems Laboratory at Eindhoven University of Technology. The ultimate goal of his research is to accelerate the deployment of transformative energy technologies into the real world. To do so, his group employs fundamental principles at the convergence of (electro)chemical engineering, materials science, and physical chemistry to design, synthesize, characterize, and simulate materials and reactors. Areas of application include large-scale energy storage with flow batteries, energy conversion with hydrogen fuel cells, and decarbonization of the chemical industry with electrolysis. Before starting his independent career, Antoni was a postdoctoral fellow in the Department of Chemical Engineering at the MIT and received his Ph.D. from ETH Zürich and the Paul Scherrer Institute. His work has been recognized by multiple awards including the ERC Starting Grant, NWO Veni, ETH Zurich Medal, the Electrochemical Society Graduate Student Award, and the Hydrogen Europe Young Scientist Award.

André Weber

André Weber is working as senior scientist and academic counselor at the Institute for Applied Materials – Electrochemical Technologies (IAM-ET), an institute in the faculty of electrical engineering and information technology at the Karlsruhe Institute of Technology (KIT). He is heading two research groups related to fuel cells and electrolyzers and batteries and is the scientific manager of the “Fuel Cell Test Laboratory”, a lab designated to fuel cell system testing. His research is related to electrical testing and modeling of fuel cells and batteries, with a special emphasis on electrochemical impedance spectroscopy. Experimental and theoretical work ranges from fundamental studies on model systems to the analysis of commercial products, aiming at an understanding of the complex coupling of electrochemical reactions and transport mechanisms with material-, microstructural- and design-parameters of these electrochemical devices.



Climate Modelling: Fundamentals, Evaluation, and Storyline Simulations

H.F. Goessling^{1*}

¹Alfred Wegener Institute, Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany

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Mitigation of climate change is a fundamental socio-economic challenge and calls for a new Great Transformation of human societies and economies. Research and development of technologies for renewables and electrification as a backbone of deep decarbonization, including battery and hydrogen technology, are driven substantially by the climate crisis. Here, I will outline our current understanding of climate change and possible climate futures. A focus will be on climate models, how they work, how they are evaluated, and how they are used to support the assessments of the Intergovernmental Panel on Climate Change (IPCC). Moreover, I will present a new concept toward climate change attribution and projection that overcomes some limitations of the classical probabilistic approach: so-called storyline simulations. In these, the atmospheric large-scale circulation in a climate model is forced (“nudged”) to follow the observed evolution of the real atmospheric circulation, while all other physical processes are computed by the model as usual. This way, instead of simulating its own quasi-random realization of weather-related variability, real extreme events like the July 2019 European heat wave can be reproduced in a climate model, and the fidelity of a model to reproduce specific events can reveal model deficiencies. By modifying the climatic background conditions such as greenhouse-gas concentrations in the model, specific events can be translated into different counterfactual climates, including the pre-industrial or possible warmer future climates. The storyline approach can help understand how climate change depends on weather patterns and how it impacts extremes. The approach also bears considerable potential for effective communication by making climate change more tangible, and to inform climate adaptation measures.

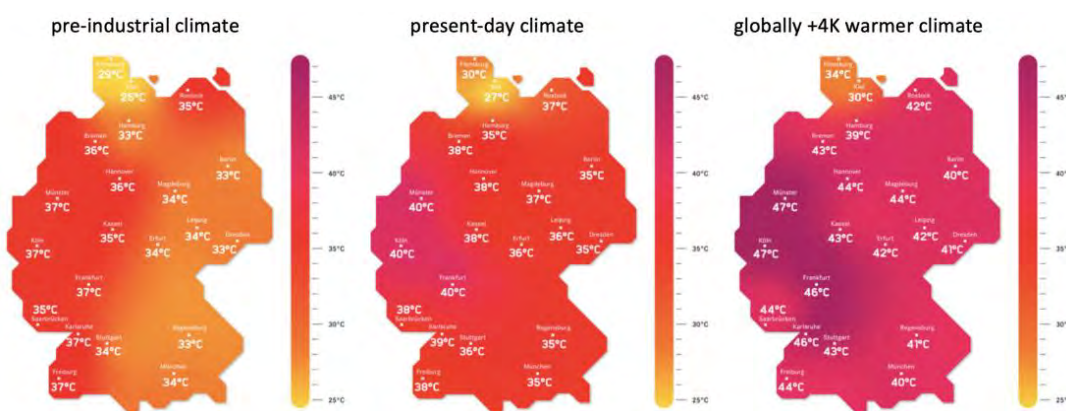


Figure 1: Temperatures during a heat wave in Germany on July 25th 2019, translated into different climate background states by means of storyline simulations with the AWI Climate Model [1].

1. Sánchez-Benítez, A.; Goessling, H.F. et al. *Journal of Climate* **2022**, 35 (8), 2373-2390. DOI: 10.1175/JCLI-D-21-0573.1

Understanding, modelling, validating, and predicting lithium-ion battery degradation.

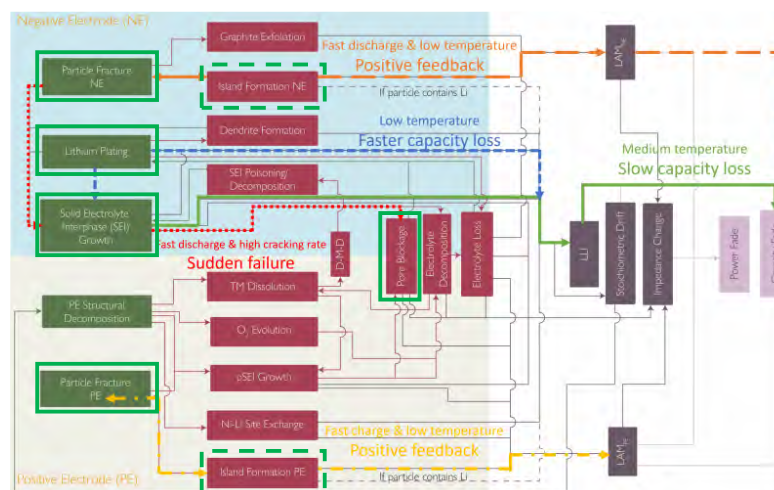
G.J. Offer^{1*}, *co-authors acknowledged in the presentation & papers below.*

¹ Electrochemical Science & Engineering Group, Mechanical Engineering Department, Imperial College London, SW7 2AZ, UK, * gregory.offer@imperial.ac.uk

Professor Gregory Offer will present the research his group have done over the past ten years in understanding lithium-ion battery degradation, how to model it, and how close those models are getting to usefully predict lifetime. The journey began with pioneering work demonstrating how different thermal management approaches strongly affected the degradation rates of lithium-ion pouch cells¹. At around the same time the group began working on understanding and modelling the physical mechanisms of degradation.

The group have demonstrated how understanding non-uniform temperature and heat generation is essential in cell design²⁻³. This gives rise to non-uniform degradation which is critical to understanding and explaining multiple experimentally observed phenomenon. If this strong positive coupling between the thermal and electrochemical behavior is not properly considered, then any model of a battery risks being very wrong except under the most benign conditions.

Over the same period, the group have published multiple ground-breaking papers on understanding⁴ and modelling multiple coupled degradation mechanisms⁵. The group's work also includes advancing our understanding of lithium plating⁶, positive electrode (cathode) decomposition^{7,8}, unequal degradation in silicon carbon composite electrodes^{9,10}, particle cracking¹¹, electrolyte consumption and cell dry-out¹², and how multiple degradation mechanisms are coupled with each other and contributed towards accelerated degradation (the knee point/cliff-edge/etc).



1. Hunt, I. et al. ECS, Vol 163, Pages A1846-A1852 (2016). DOI: 10.1149/2.0361609jes
2. Zhao, Y. et al. ECS, Vol 166, A2849 (2019). DOI: 10.1149/2.0501913jes
3. Li, S. et al. JPS, Vol 492, Page 229594 (2021). DOI: 10.1016/j.jpowsour.2021.229594
4. Edge, J. S. et al. PCCP. (2021), 23, 8200-8221. DOI: 10.1039/D1CP00359C
5. O'Kane, S.E.J. et al. PCCP. (2022), 24, 7909-7922. DOI: 10.1039/D2CP00417H
6. O'Kane, S.E.J. et al. ECS, Vol 167, Page 090540 (2020). DOI: 10.1149/1945-7111/ab90ac
7. Abir Ghosh et al. ECS, Vol 168 Page 020509 (2021). DOI: 10.1149/1945-7111/abdc71
8. Zhuo, M. et al. JPS, Vol 556, Page 232461, (2023). DOI: 10.1016/j.jpowsour.2022.232461
9. Kirkaldy, N. et al. ACS Appl. Energy Mater. (2022), 5, 11, 13367 DOI: 10.1021/acsaem.2c02047
10. Ai, W. et al. JPS, Vol 527, Page 231142, (2022), DOI: 10.1016/j.jpowsour.2022.231142
11. Ai, W. et al. ECS, Vol 167, 013512, (2020), DOI: 10.1149/2.0122001JES
12. Li, R. et al. ECS, Vol 169, Page 060516, (2022). DOI: 10.1149/1945-7111/ac6f84

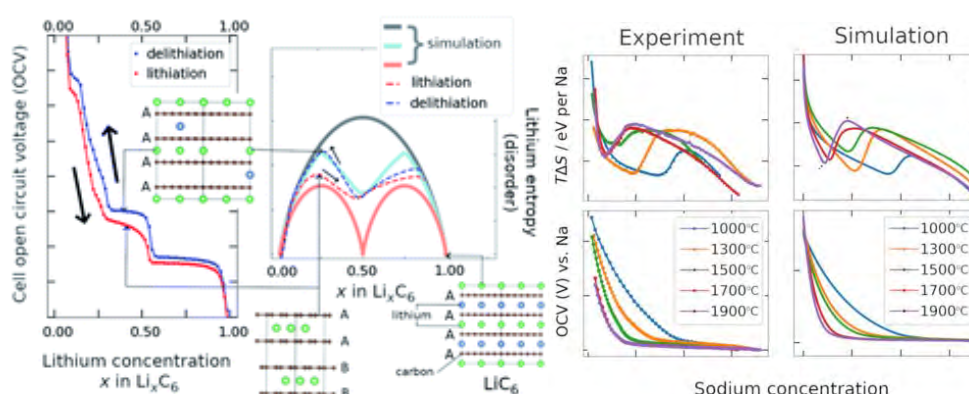
Translating entropy measurements to next-generation battery materials

M.P. Mercer*

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Accurate parameters informed by physically realistic models are important for description and diagnosis of current battery technologies. These descriptors, including the cell open circuit voltage and its variation with respect to temperature (the partial molar entropy) also provide insights into atomic scale transitions within the battery materials, which can guide materials design efforts for the next generation of batteries as well. Exploitation of these techniques to battery technologies beyond lithium-ion that are needed for the Energy Transition remains an almost untapped area that we have recently started to explore and understand.

In this presentation, we will discuss how we have put together an integrated suite of techniques, including fast, accurate entropy measurement¹⁻⁶, mean field (Bragg-Williams) and Monte Carlo statistical mechanical approaches²⁻⁶, and density functional theory (DFT)^{2,3}, to provide physical and quantitative insights into host/guest transitions. Even within the relatively well understood lithium-ion intercalation electrodes, an essential proving ground for model validation, we generated fresh insights into the origins of the lithiation/delithiation hysteresis in graphite² and the role of point defects in disrupting ordering transitions in cathode materials^{3,4}. Further, the methods are applicable even to highly non-ideal structures lacking long range order, including hard carbons, for which we generated new insights into relationships between the energetics of sodiation and pore morphology^{6,7}. We also touch on the likely next direction of travel with these techniques, including integration with high throughput physical vapour deposition (PVD) and computational techniques, which will systematise the search for new anode materials in next generation batteries and generate rich detail into their properties.



1. P. Osswald et al., *Electrochim. Acta* **2015**, 177, 270
2. M.P. Mercer et al., *J. Mater. Chem. A* **2021**, 9, 492
3. M.P. Mercer et al., *Electrochim. Acta* **2017**, 241, 141
4. S. Schlueter et al., *PCCP* **2018**, 20, 21417
5. M.P. Mercer et al., *Electrochim. Acta* **2019**, 324, 134774
6. M.P. Mercer et al., *ChemPhysChem* **2022**, 23, e202100748
7. M.P. Mercer et al., *J. Mater. Chem. A*, *in press*

Unraveling the role of ionomer and water in cathode catalyst layers of PEM fuel cells

Michael H. Eikerling

¹*RWTH-Aachen University, Faculty of Georesources and Materials Engineering, 52056 Aachen, Germany*

²*Forschungszentrum Jülich, Institut für Energie und Klimaforschung, IEK-13: Theorie und computergestützte Modellierung, 52425 Jülich, Germany*

Polymer electrolyte fuel cells (PEFC) will become a crucial technology in a future energy economy based on renewable hydrogen. Among the components that are needed for a highly performing, durable and affordable PEFC, the cathode catalyst layer (CCL) continues to stand out. The main function of the CCL is to expedite the oxygen reduction reaction (ORR), entailing an intricate interplay of transport and reaction that spans several scales, as illustrated in Figure 1. In this realm, physical modeling has gained vital importance in rationalizing structural effects on properties and performance of CCLs. In the first part of this presentation, I will briefly review capabilities of model-based analyses to deconvolute voltage loss contributions, determine and correlate parameters obtained, develop a spatially resolved activity map, and evaluate the overall effectiveness factor of Pt utilization in the CCL.^{1,2} Recognizing the importance of a well-balanced water-distribution for CCL operation, the focus of modeling has shifted towards the consistent treatment of pore size distributions and pore network morphologies as well as wetting phenomena. Clumps or aggregates of ionomer, embedded into the CCL, play a vital role in this context. At the microscopic scale, ionomer films at interfaces with the water-covered catalyst-support surface determine the local reaction environment and the kinetics of interfacial processes involved in ORR and platinum dissolution. Moreover, the structure and distribution of ionomer determines the water sorption behaviour of the CCL, which in turn affects oxygen and water transport. Forays in modelling that strive to unravel the intertwined impacts of ionomer and water will be presented.^{3,4} Besides, a CCL cannot be understood and optimized as a stand-alone component. At the PEFC level, balances of reactant, charge, water, and heat fluxes must be considered. Comprehensive modeling approaches must account for the coupling of the corresponding local equilibria and transport phenomena across the whole cell, including polymer electrolyte membrane, diffusion media and flow fields. In this context, recent efforts to rationalize the coupled water phenomena will be discussed.

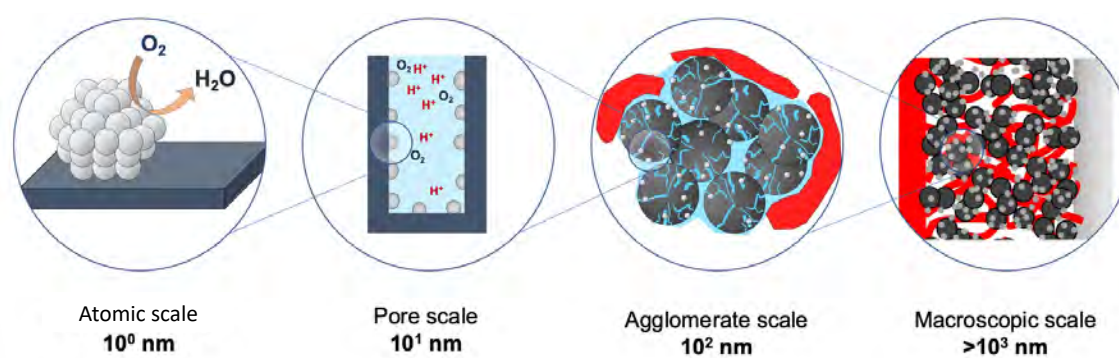


Figure 1. Main levels of the structural hierarchy in a catalyst layer.

1. T. Muzaffar, T. Kadyk, and M. Eikerling, *Sust. Energy Fuels* **2** (2018) 1189-1196.
2. M. Eikerling and A.A. Kulikovskiy, *Polymer Electrolyte Fuel Cells – Physical Principles of Materials and Operation*, CRC Press Taylor & Francis Group, 2014.
3. W. Olbrich T. Kadyk, U. Sauter, and M. Eikerling, *J. Electrochem. Soc.* **169** (2022) 054521
4. W. Olbrich, T. Kadyk, U. Sauter, and M. Eikerling, *Electrochim. Acta* **431** (2022) 140850.

Advancing redox flow batteries through porous electrode and reactor engineering

A. Forner-Cuenca

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Redox flow batteries are a promising technological platform for grid-scale energy storage, but their deployment is limited by elevated costs. At the core of the stack, the porous electrodes and flow fields determine the overall performance by distributing the liquid electrolytes, providing the active area for electrochemical reactions, facilitating mechanical compression, and conducting electrons and heat. Thus, advancing electrochemical reactors is an effective strategy to decrease cell overpotentials, pumping losses, and improving the overall cost-competitiveness.

In this lecture, I will discuss our efforts to fundamentally understand the influence of porous electrodes and flow fields in the performance of redox flow batteries by using a suite of electrochemical methods, advanced manufacturing of materials, and computational modeling. First, I will discuss the impact of the porous electrode microstructure of carbon fiber-based electrode materials. Using a set of commercially available electrodes, we find that woven electrodes provide outstanding electrochemical performance and lower pressure drop than non-woven electrodes. Motivated by these findings, I will then introduce a synthetic platform for porous electrodes using non-solvent induced phase separation, which enables the formation of new electrode architectures difficult to obtain with traditional methodologies. Using iron- and vanadium-based electrolytes, we demonstrate the potential of these electrodes as alternative to fiber-based substrates. Third and finally, I will describe the coupled influence of flow field geometries and porous electrode microstructures. Through systematic experiments, we elucidate relationships between prevalent flow field geometries (flow through, flow by, and hybrid) and porous electrode microstructures (woven, non-woven). On the basis of these learnings, we conceptualize and manufacture new flow field geometries providing improved mass transfer rates and lower pressure drop.

3D Multiphysics Model for Large Format Lithium-Ion Cells and its Application in an Agile Cell Production

A. Weber*, M. Schiffler, A. Schmidt

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Large format lithium ion cells face electrochemical, electrical, thermal and mechanical gradients on different scales during operation. To analyse the cell behaviour, a multi scale multi domain (MSMD) model for large format cells was developed applying homogenization on two scales (i) from the particulate electrodes to homogenized electrode materials by an extended Newman model [1] and (ii) from individual cell layer materials to a homogenized battery material with anisotropic electrical and thermal transport properties [2]. As mechanical stress/strain, resulting from reversible chemical expansion of active materials and irreversible formation of solid reaction products from SEI-growth and Li-plating, affect performance and durability of lithium ion cells, in a first step the electrochemical-thermal model is extended to cover the impact of mechanical strain during Li-intercalation on the transport parameters of the electrodes [3]. Next to the MSMD-model, implemented in Comsol Multiphysics, experimental approaches to determine the model parameters and validate the model will be presented in this contribution.

Considering the agile production of format flexible lithium ion cells differing in their application oriented cell geometry, a multiphysics cell model covering electrical, thermal and mechanical cell properties is supportive for cell and battery design. The application of the model in an agile cell production process at KIT will be discussed.

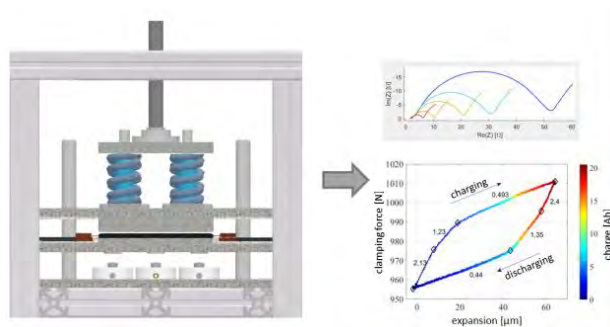


Figure 1: Test setup for combined electrical/mechanical testing of pouch cells

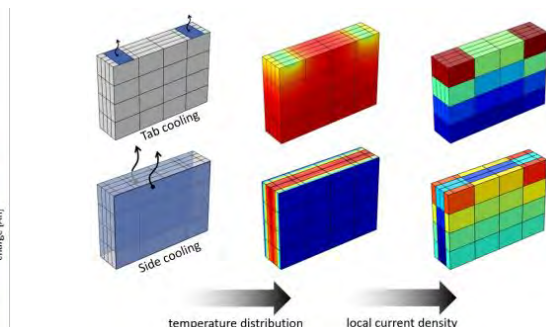


Figure 2: Heterogeneities for different cooling conditions

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SESSION ABSTRACTS

1. Battery Degradation

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Modelling OER and HER in NiZn battery cells

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In view of the transition to renewable and environmentally friendly energy sources, zinc-based battery technologies have increasingly become the focus of research in recent years, as part of the development of next-generation energy storage technologies^{1,2}. Nickel-zinc batteries (NiZn) are a promising candidate for stationary applications. The theoretical, physicochemical-based description and simulation of battery systems contribute to a more profound understanding of the phenomena that occur within battery cells, and thus to an improvement in battery design and performance¹.

We have developed a model based on thermodynamics to describe the electrochemical reactions shown in Figure 1 and to simulate the performance of a nickel-zinc cell. The 1D+1D continuum model describes the electrochemical reactions at the electrodes, transport in the electrolyte and resulting local concentration changes, as well as local volume changes of solid, liquid and gas fraction.

The lifetime of rechargeable nickel-zinc batteries is limited to a large extent by unwanted side reactions during cycling. In this contribution we focus on those involving gas formation. At the nickel hydroxide cathode, especially at the end of charge, oxygen is evolved³ (OER); and at the zinc anode hydrogen is evolved (HER). The gas evolution leads to a pressure increase inside the cell and consumes the electrolyte. To mitigate the negative effects of the gas evolution side reactions, we additionally model the gas recombination at a catalyst in the head space of the battery cell.

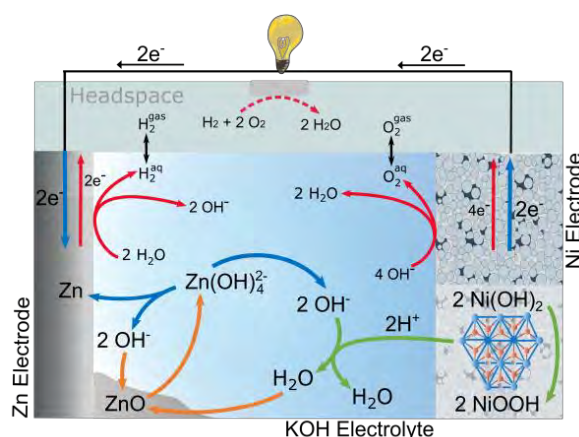


Figure 1: Modelling scheme for a nickel zinc battery cell during charge including zinc deposition (blue), zinc oxide dissolution (orange), deintercalation of protons (green), oxygen and hydrogen gas evolution (red, solid) and oxyhydrogen recombination reaction (red, dashed) at a catalyst

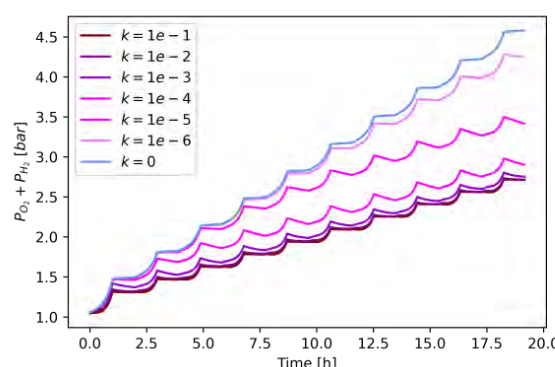


Figure 2: The increase in the summed partial pressure of oxygen and hydrogen on a catalyst as a function of time during cycling was modelled. The material-specific recombination rate was varied over seven orders of magnitude

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Silicon–graphite composite electrodes: modelling state-of-charge and current distribution, and experimentally determining degradation rates

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Many commercial lithium-ion battery cell manufacturers are adding silicon to graphitic negative electrodes in an effort to increase energy densities. However, most models of silicon-graphite (Si-Gr) composite electrodes treat it as a single “lumped” material, offering limited understanding of the behaviours of the individual materials and thus limited design capability. Further, silicon is known to age at faster rates than graphite during battery cycling, in part due to the large volumetric expansion of silicon during lithiation, leading to drastic changes in the active material composition. Here we present our efforts to model the electrochemical interactions between silicon and graphite in these composite electrodes, and our experimental work to determine their degradation behaviour.

We developed a multi-material electrode model for Si-Gr which can reproduce voltage-hysteresis effects and reveals the state of charge (SoC) variation in the two active materials during (de)lithiation.¹ The model can be used to investigate the effects of changing the silicon-to-graphite ratio and how it impacts performance. SoC and current distribution across the two phases are also observed in our Si-Gr full cell model, showing that silicon is more active at lower cell-level SoCs, and experiences far higher interfacial current densities than graphite.²

Finally, we investigated how the SoC-dependent activity of the two materials affects degradation on a full cell level by performing an experimental cycle ageing study.³ In this, we cycled a commercial 21700 cell (LG M50) over different SoC ranges and temperatures, and tracked the loss of each active material using degradation mode analysis. This allowed us to quantify the losses of silicon and graphite separately. We found that silicon capacity is lost at far greater rates than graphite capacity under all ageing conditions, but especially when cycling the cell at low SoC.

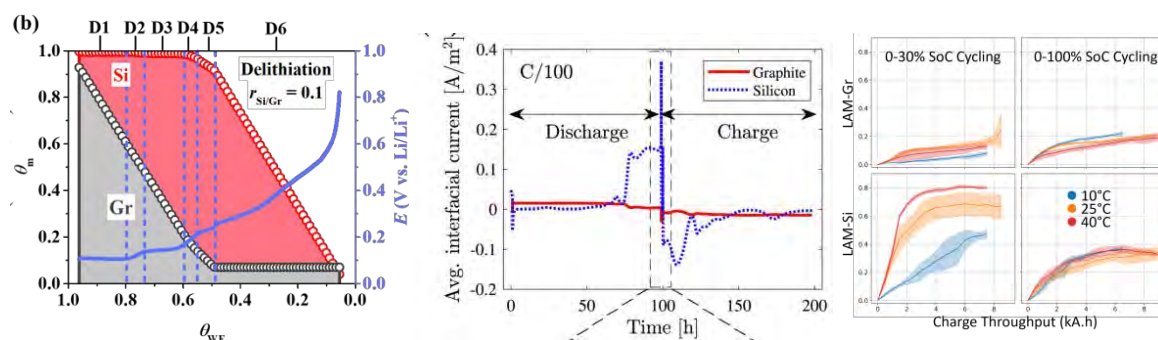


Figure 1 (left to right): Material-level SoC during delithiation of a composite Si-Gr electrode; current density on the two materials during (dis)charge; temperature and SoC dependence of the loss of each active material during cycle ageing.

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Simulation of Li Plating in Si/Graphite Composite Electrodes

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It is a common perception that the demand for high-performance batteries is constantly increasing. While the primary characteristics depend on the application, decisive criteria are energy density, safety, cost, and sustainability of the batteries.

Here, Li-ion batteries play a key role especially for electric vehicles and portable electronics. However, additional improvements are needed, for example, to achieve the fast charging criteria given by the automotive industry. The performance characteristics of the batteries such as high energy or power density can be tuned by the electrode microstructure, composition, or choice of materials. One such promising material for the negative electrode is Silicon: Si exhibits a high theoretical capacity and is very abundant. On the other hand, Si shows a large volume expansion and low Li mobility. Thus, to take advantage of the high theoretical capacity and to limit the deformation during cycling, Si is mixed with Graphite to produce more practical Si/Graphite composite electrodes.

In order to increase the cycle life of Si containing electrodes, it is critical to trace the degradation processes responsible for their performance loss. One major aging mechanism causing fast degradation and fundamental safety risks is Li plating. This deposition of a metallic lithium phase on the surface of Si/Graphite anodes is barely studied in the literature yet crucial to improve the performance and safety of state-of-the-art Li-ion batteries.

In our contribution we present simulation results of Si/Graphite composite electrodes including models for Li plating on Graphite [1] and Si particles in 3D microstructure-resolved simulations. While focusing on the differing lithiation behaviours of Graphite and Si, the findings are validated with experimental results from our project partners. More specifically, we compare our simulations to multiple complementary techniques such as neutron depth profiling (NDP) [2], post-mortem glow discharge optical emission spectroscopy (GD-OES) depth profiling [3], and X-ray diffraction analysis (XRD) [4]. Under examination are commercial and self-manufactured full and half cells containing varying amounts of Si or SiC blend. Furthermore, we developed a homogenized p2D model of composite electrodes which also includes the volume changes during lithiation and delithiation of representative Si particles and the effect on transport processes [5]. The studies serve as a starting point to understand Li plating in Si containing electrodes and, eventually, the design of better Si/Graphite composite electrodes.

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Monitoring battery degradation using acoustic signatures

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The application of ultrasonic waves for the inspection of batteries has gained increasing popularity since 2015 [1]. The speed and attenuation of sound propagating through the internal structure of a battery is influenced by the mechanical properties and thickness of its constituent layers, including the stiffness, density and porosity of the electrodes. The natural variation of such parameters during battery operation, and as a battery ages, provides a coupling between its acoustic signature and internal states which can be utilised for state estimation. Successful demonstrations of state-of-charge estimation can be found in the literature [2], nevertheless, the correlation of the acoustic response to state-of-health indicators is less well explored. In this work we present experimental findings of through-life acoustic and electrochemical characterisation, which delineate the coupling between the acoustic signature of a cell and its level of degradation. Accelerated ageing tests were performed on a 210mAh pouch cell comprising a graphite negative electrode and a lithium cobalt oxide (LCO) positive electrode. Combined acoustic and electrochemical characterisation was performed periodically, including the acquisition of electrochemical impedance spectra (Fig. 2) followed by a slow cycle and a series of pulse-relaxation events (Fig. 3). Acoustic data was processed by isolating the time-of-flight (ToF) of the final acoustic peak (Fig. 1) and tracing it throughout the experiment (Fig. 3). Changes in the ToF between cycles were found to be highly pronounced compared to changes in the voltage response, with the ToF shifting to higher values as the cell ages. This progressive shift can be viewed as a powerful state-of-health indicator with high signal-to-noise ratio, exhibiting high sensitivity to changes in the state.

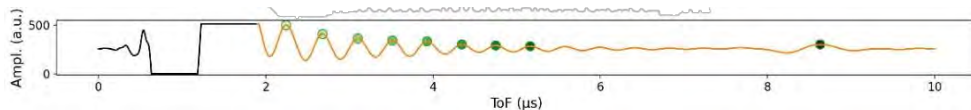


Figure 1: Example acoustic waveform with identified peaks

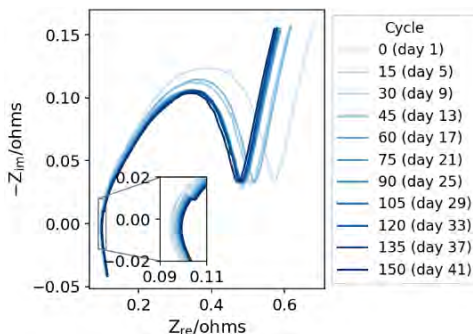


Figure 2: EIS spectra obtained periodically at the top-of-charge

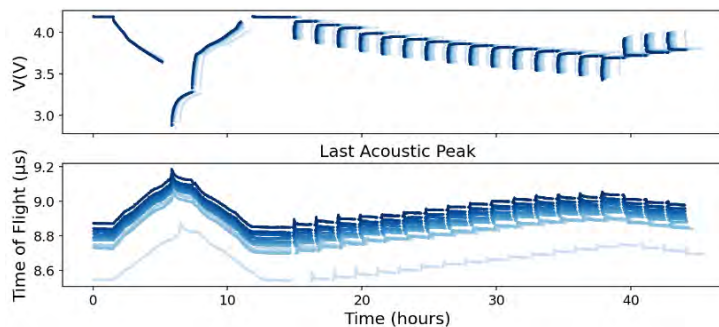


Figure 3: Concurrent electrical and acoustic characterisation results obtained periodically after EIS

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Health-aware battery fast charging optimisation

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Safe and reliable battery fast charging algorithms have the potential to accelerate the global transition to clean energy in the transport sector. Recent work [1,2] has shown that optimal charging trajectories commonly follow a sequence of active path constraints. Therefore, safely pushing a battery to its limits requires precise and accurate knowledge of these constraints throughout the lifetime of the battery. This work combines battery modelling, control engineering and numerical optimisation.

We develop a consistent approach to cell-level parameterisation and fast charging protocol optimisation based on a single reduced-order model. We employ the equivalent hydraulic model (EHM) proposed by Couto et al. [3,4] which is a reduction of the single particle model (SPM) for a lithium-ion battery [5]. Crucially, this model retains states and parameters which have a physical meaning, whilst also being almost as simple to solve computationally as a low-order equivalent circuit model. Our approach is designed to ensure safety and maintain battery health by updating physically meaningful parameters and constraints as the battery ages.

For validation, cycling and characterisation experiments have been carried out at ULB on energy-dense commercial NCA/graphite cells. We compared standard and optimised charging profiles. For the optimised profiles, we included a state-dependent constraint on the anode overpotential, intended to prevent lithium plating. Our approach can achieve higher capacity retention than standard 1C constant current/constant voltage (CCCV) in an approximately equivalent charge time. The choice of constraints (e.g. for different chemistries and/or degradation pathways) has a direct impact on the optimal charging profile and therefore the total charge time.

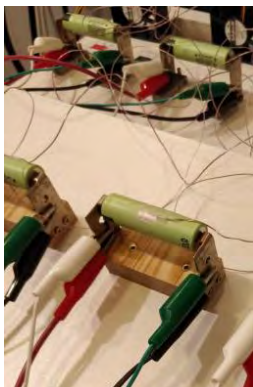


Figure 1: Battery testing experimental set-up.

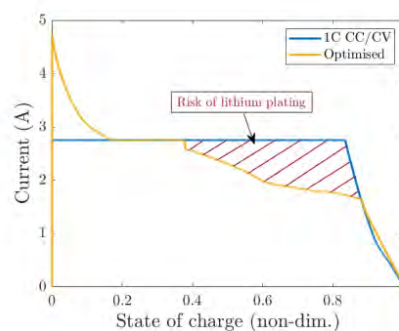


Figure 2: A standard 1C CC/CV charging profile vs. SOC and an optimised profile designed to avoid lithium plating.

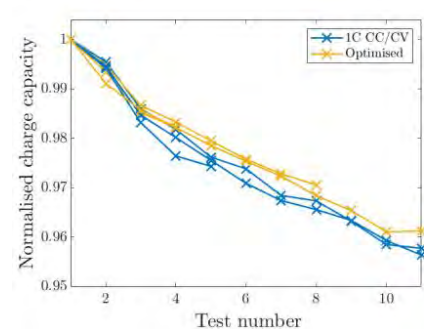


Figure 3: Charge capacities measured by reference performance tests every 11 charge/discharge cycles.

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SESSION ABSTRACTS

2. Battery fabrication I

2.1 A new approach for state of charge and state of health diagnosis of batteries using voltage-controlled models	27
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A new approach for state of charge and state of health diagnosis of batteries using voltage-controlled models

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State of charge (SOC) and state of health (SOH) diagnosis is commonly based on measuring battery current and using it in Coulomb counters or as input for a current-controlled model. Here we introduce a new algorithm [1] based on measuring battery voltage and using it as input for a voltage-controlled model, see Figure 1. This is achieved by taking the governing equations of an equivalent circuit model which are usually formulated in terms of $V(I)$, and inverting them mathematically or numerically to $I(V)$. This is a paradigm shift in the field of model-based state diagnosis.

In this contribution we will show that this approach leads to significant advantages compared to the state of the art. For SOC diagnosis, (a) only voltage, not current, is required as measurement input. This reduces measurement cost and complexity in practical application. (b) The algorithm is self-calibrating – no initial state estimation nor “full” or “empty” battery states are needed. (c) The algorithm is robust with respect to partial cycling and does not exhibit SOC drift in case of inaccurate current measurement. (d) The algorithm is numerically simple, no filter or observer is required, and it can be easily implemented on standard microcontrollers. For SOH diagnosis, (a) SOH can be estimated from regular battery operation without requiring artificial full cycles. (b) The model does not require aging-adaptive parameters. (c) The SOH is obtained based on simple computational rules; no filter or observer is needed.

We demonstrate the algorithm using fresh and pre-aged commercial NMC/graphite 20 Ah lithium-ion battery pouch cells operated under well-defined laboratory conditions on full cycles (0...100 % SOC), shallow cycles (25...75 % SOC), and a dynamic battery electric vehicle load profile (based on the WLTP protocol). We show that both SOC and SOH are accurately estimated using the new algorithm in combination with a most simple V0-R equivalent circuit model. Due to these advantages, we believe that the new algorithm is a promising approach towards battery state diagnosis.

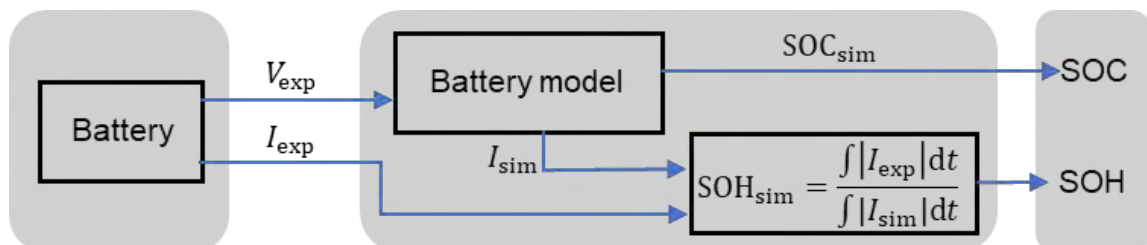


Figure 1: New approach for SOC and SOH diagnosis. The battery model uses experimental voltage as input and gives SOC and current as output. The output current is used together with the experimental current for SOH calculation.

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Pore-scale Modeling and Validation on the Calendering of Lithium-Ion Battery Cathodes

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The cathode of lithium-ion batteries (LIBs) has a crucial influence on cell performance and durability. In making the cathode, the separator is first coated with a cathode slurry, dried, and then undergoes a hard-pressing by rollers, i.e., calendering process. In the present study, the effects of calendering on the cathode's effective transport properties and its impact on the battery's charging performance are investigated using a multiscale approach. This work includes the following steps: sample preparation, characterization, reconstruction, pore-scale simulation, and macroscopic simulation, see Fig. 1. The $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) cathode sample is prepared by coprecipitation and high-temperature sintering. Microscopic images of the sample are obtained using XCT and SEM. The 3D microstructure of this material is generated using a numerical reconstruction algorithm based on the distribution characteristics of active particles, additives, and pores observed from the microscopic images. The reconstruction algorithm is verified to render the simulated domain that preserves similar features to the experimental domain. Five 3D models that respectively set for calendering ratios (CRs) of 0, 10%, 20%, 30%, and 35% are numerically reconstructed. Pore-scale simulations are performed on these models to evaluate the pore distribution, effective lithium-ion diffusivity, and electron conductivity of the cathode material at different CRs. The computed effective transport properties of the cathode are applied to a macroscopic model to study the charging performance of LIBs at various CRs. The present study demonstrates a multiscale approach combining experiment characterization and pore-scale simulation for investigating the effects of calendering on LIB cathode. This approach can be employed for the future optimization of LIB fabrication processes.

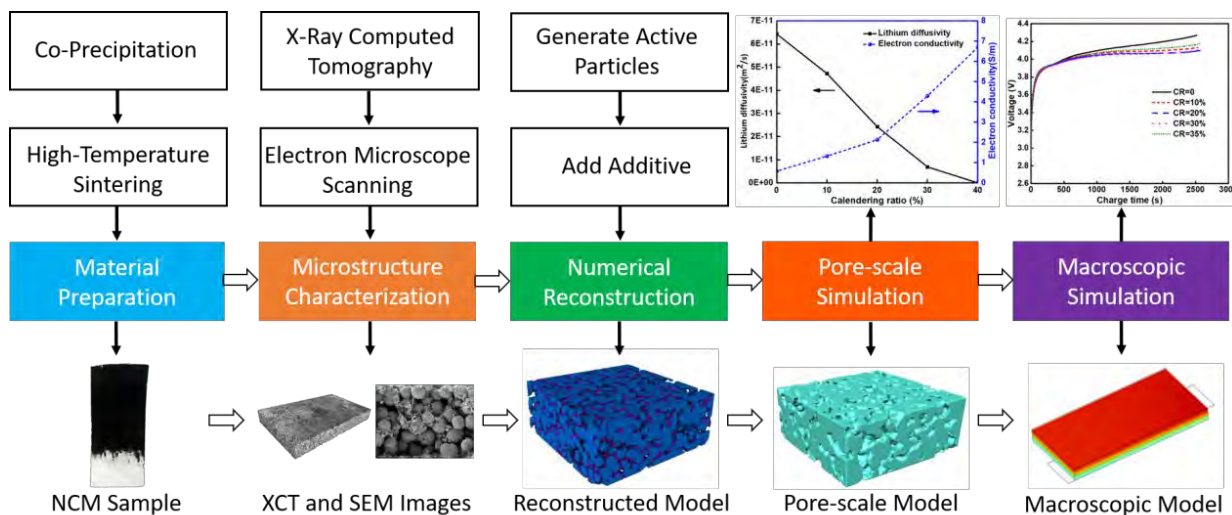


Figure 1. Schematic of the present multiscale approach.

Modelling and experiments on porous electrodes with lithiated binder

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It is well known that low ionic diffusivities cause high concentration and potential polarization across thick, porous cathodes at high current rates. Furthermore, the rapid depletion of Li⁺ ions at the reaction surface limits the rate capability of thick electrode-based Li-ion batteries. Using numerical simulations and experiments, this research aims at investigating the influence of ionic additives in the porous carbon-binder network for improving the rate capability.

Thick electrodes of standard size were fabricated using standard (inactive) binder, and their performance was tested at various C-rates. Cathodes made with lithiated (active) binder were tested to verify improvements in discharge capacity and voltage.

A mesoscale computational model was developed. A porous carbon-binder domain filled with electrolyte is modeled as a homogeneous continuum domain, with an interface at the electroactive materials surface. The electro-chemo-mechanical response of porous electrode Li-ion batteries is simulated through a set of Partial Differential Equations, which describe the behavior in the electrochemical cell domains, as well as through proper reaction interface conditions. COMSOL Multiphysics was used to implement the weak form of the governing equations.

The Multiphysics model has been validated against experimental observations, see Fig 1. From numerical simulations we determine the ionic concentration fields, the electric potential across the components, and the terminal voltage at the current collector. The ionic flux at the active material surface is highlighted in Fig. 2. Non-uniformity is more pronounced at high C-rates. Hotspots of high reaction current are observed across the electrode. Numerical simulations show limited ionic depletion and electric potential drop for cathodes with lithiated binder. A nonuniform Li dissolution at Li anode, leading to an uneven anodic surface prone to dendrite initiation, is emerging from the numerical results.

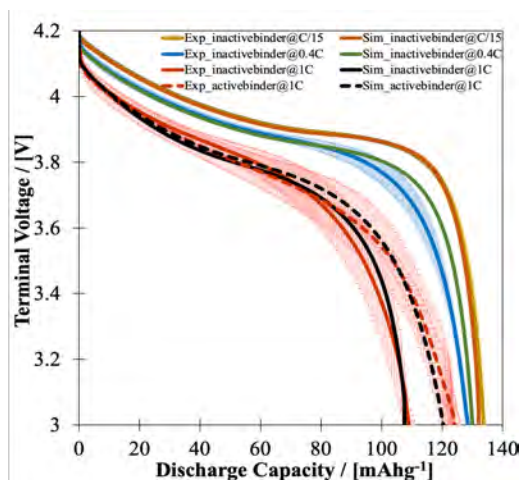


Figure 1: model validation

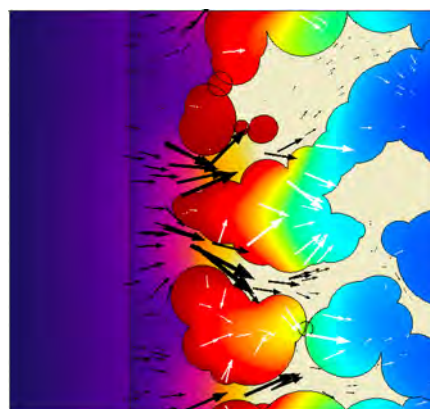


Figure 2: Li distribution and flux

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Electrode Structuring and its Effects on Battery Production and Performance

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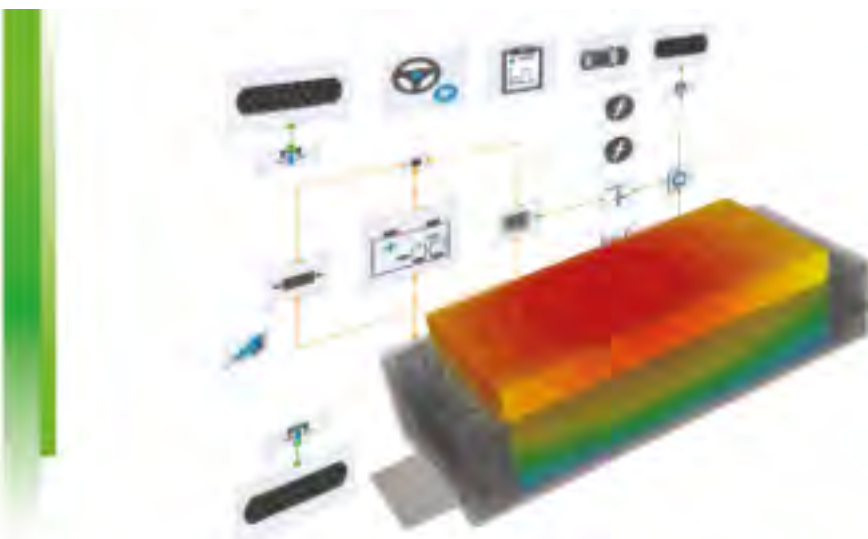
**corresponding author email address: Benjamin.Kellers@dlr.de*

Many open questions in the manufacturing of Lithium-ion batteries concern the electrolyte filling process and the related entrapment of air inside the pores of the electrodes. In this context, the effect of the entrapped air on the performance of the battery is still unclear. Moreover, it is not known how much air is entrapped at all and how well this could be avoided by adjusting the manufacturing process.

The present work aims to fill some of the gaps in our current understanding. Thus, the influence of structural properties as well as additional electrode structuring on gas entrapment and the performance of Lithium-ion batteries is investigated. Multiple physical models are combined into a joint multi-scale multi-physics workflow to simulate the electrolyte filling process before performing electro-chemical simulations on the resulting heterogeneously filled electrodes. The lattice Boltzmann method and pore network modelling provide input to the simulation framework BEST. The results are compared to experimental data linking electrolyte wetting to the saturation of the pore space.

The workflow is computationally very efficient as it reduces the size of the total parameter space allowing for identification of the most promising parameter combinations and ranges. Thus, it can be used as an important supplementary tool for improving battery design and development.

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Battery Aging Identification Tool, a new Simcenter Amesim feature on electric storage library

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Batteries, particularly Li-ion batteries, are key components for new electric vehicles. They are well suited for automotive applications as they offer both high energy and power densities. However, unlike internal combustion engine vehicles, battery aging leads to energy retention decrease over time and with external stress factors. By comparison, it is as if the fuel tank of a gasoline vehicle were to shrink with use.

Modelling battery aging is essential for sizing batteries and optimizing their use. Many underlying mechanisms are at play and physical models struggle in considering all aging mechanisms since some of them remain unknown. Some empirical or semi-empirical aging models can adequately model battery aging without prior knowledge of the aging mechanisms, using data from battery aging campaigns.

Generally, calibrating aging models for batteries requires a long and costly cell aging campaign. In a joint development, IFP Energies nouvelles (IFPEN) and SIEMENS have developed, as part of the Simcenter Amesim software, a battery aging model which is calibrated using aging data through a tool called the Battery Aging Identification Tool. The principle of this calibration is based on the use of a complete model with many parameters, and the progressive reduction of these parameters using the statistical significance p-value¹ to reduce the risk of over-learning. Finally, we obtain a complete and valid battery model for long and complex aging profiles², like what an electric vehicle may experience in reality. Compared to the experimental data, the model simulates the capacity loss value with less than 1% error. This new functionality should be available in the next releases of Simcenter Amesim. The goal of this presentation is to show the entire approach and the associated Simcenter Amesim tools.

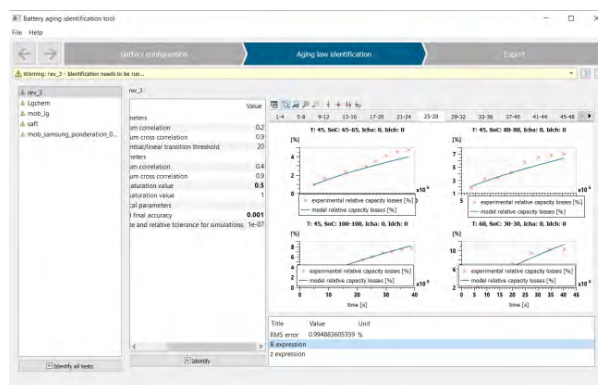


Figure 1: Screenshot of the Battery Aging Identification Tool user interface

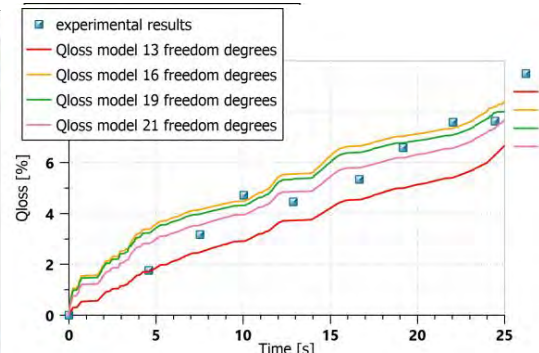


Figure 2: Validation curves of the Battery Aging Identification Tool process

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Machine learning for the classification of equivalent circuit models from solid-state electrochemical impedance spectra

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Machine learning is commonly used to build models and make decisions for electrochemical systems. Electrochemical Impedance Spectroscopy (EIS) is a powerful method to investigate processes that occur at different timescales and is widely applied to Lithium-Ion Batteries (LIBs) [1]. The analysis of EIS data commonly consists of defining an Equivalent Circuit Model (ECM) [2], which is time-consuming for large data sets and typically requires expert knowledge.

This work is based on a large dataset of about 9300 EIS spectra from solid-state batteries provided by QuantumScape (QS), ranging over 10 years of research and development [3]. Each spectrum is labeled with an ECM, defined by experts from QS. The data were provided for the BatteryDEV hackathon. We present different supervised machine learning approaches for automating the identification of ECMs that were suggested during the hackathon and developed afterward. The best-performing model is an XGBoost model based on features calculated by the tsfresh feature automation library, achieving a weighted F1-score of 0.51 on the hold-out test set. A random forest model that was learned from the raw spectral data performed slightly worse. Furthermore, we transformed the spectra into boolean images (Fig. 1), to explore Convolutional Neural Networks (CNNs), drawing on similarities with the MNIST digit classification challenge. The CNN approach had lower performance than the other approaches and could be improved further by considering the frequency information and optimizing the model's architecture. The results of the classification models form a benchmark for further studies.

Using machine learning methods in the analysis of EIS data can reduce the time engineers spend on selecting models for electrochemical impedance spectra, allowing them to focus on modeling and drawing informed conclusions.

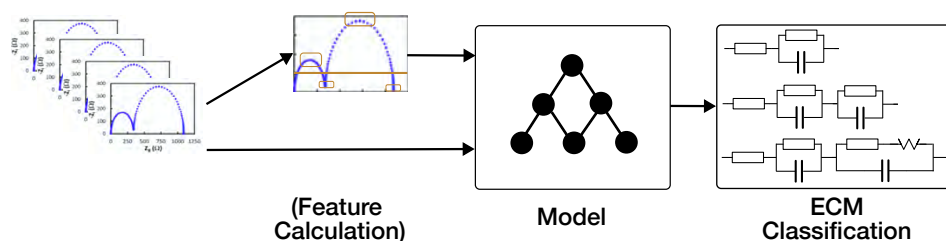


Figure 1: Visualization of the machine learning pipeline.



Figure 2: Visualization of 60 EIS spectra used as Boolean images for the CNN.

Acknowledgments: We would like to thank the authors of the manuscript containing the results outlined above [3].

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Operando EIS applied to commercial Li-ion batteries

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Data-driven modelling of Li-ion batteries is a crucial step for the design of smart-charging protocols and state-of-health (SOH) prognosis [1,2]. Often, the impedance is chosen as a model, which can be estimated from current and voltage data using electrochemical impedance spectroscopy (EIS). This powerful tool, implemented in potentiostats and cyclers, measures the frequency-dependent impedance in a set of selected frequencies. However, EIS is limited by the constraints of linearity and stationarity, while Li-ion batteries inherently behave in a nonlinear and nonstationary way. With regards to linearity, the voltage over the electrodes is a nonlinear function of the current through the electrodes, due to the Butler-Volmer kinetics. However, linearity can be achieved by applying a small amplitude zero-mean current excitation around an operating point. Regarding time-variation, the impedances of fully charged and fully discharged cells are different, as it is for pristine and aged cells, or cells kept at room temperature and in freezing environments. This means that EIS experiments should be performed in steady-state at a specific state-of-charge (SoC) and temperature, that is, at an *operating point*.

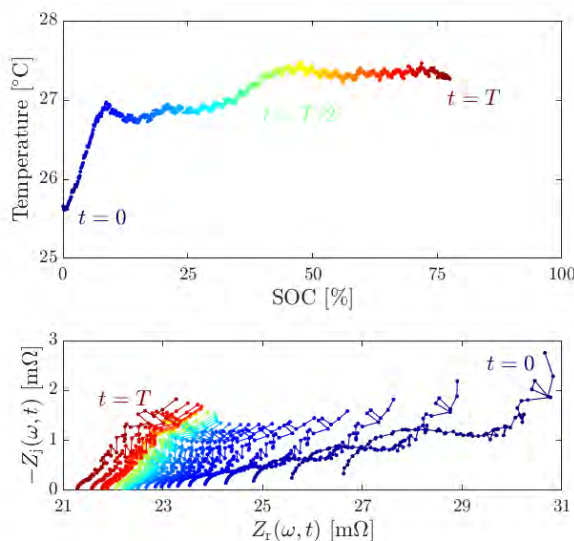


Fig. 1: Time-varying impedance along a trajectory.

To overcome the constraints of linearity and stationarity, we have developed *operando* EIS [3,4]. This method estimates time-varying impedance along an *operating trajectory* of the battery, for instance while charging or discharging (see Fig. 1). A constant current is applied through the battery to drive the SoC operating condition, with a multisine superimposed to excite the battery's dynamics. The time-varying impedance is estimated in the frequency domain based on the voltage response to the current excitation. Also, the level of nonlinear distortions and noise are each quantified. Moreover, for batteries low frequency information is crucial. In *operando* EIS we suppress drift signals, such as the increasing open-circuit voltage while charging the battery, nonparametrically. As a result, low frequency time-varying impedance data can be measured too, while it would be hidden by the drift signal otherwise [3].

Experiments are performed on commercial LG M50 batteries, demonstrating that the impedances while charging, discharging and resting are different. Next, we study how certain parameters of an equivalent circuit model (ECM), such as the charge-transfer resistance, vary over time during charging and discharging. Since the model estimated from *operando* EIS is valid over a *trajectory* instead of at an *operating point*, it contains novel information, which can be used for smart-charging protocols [5] or for SOH prognosis.

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Modelling Battery Behaviour with Physics Informed Neural Networks

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The recent development in Deep Learning (DL) has brought promising solutions to model the behaviour of batteries. These models can obtain accurate estimations of the battery parameters, using data that can be acquired directly from the application. Nevertheless, the fact that they are built as pure statistical models makes them act like black boxes, with little to no interpretability on their decisions. In this context, other research areas (especially fluid mechanics) have found a workaround to this problem with the introduction of Physics Informed Neural Networks (PINN) [1]. Here, the equations governing the system are introduced into the model architecture, in this way ensuring that the decisions made by the Neural Network (NN) will consider these dynamics. Considering how existing physics-based modelling proposals in batteries capture their internal phenomena during operation, we can design a model architecture that combines physics-based equations with the benefits of the data-driven approaches.

In this work, we present a PINN approach to model the behaviour of a Li-ion battery. Our proposed solution is built around the Single Particle Model (SPM) proposed in [2]. The DL model estimates the concentration of lithium in each electrode and infers the voltage following the SPM equations. This estimation and the governing Partial Differential Equations (PDE) are then evaluated to compute the loss value in order to train the NN. Besides the behaviour estimation, which could be obtained from a purely data-driven model, this method provides information of the internal state of the battery. Once trained, the model solutions follow the SPM dynamics accurately without the need of any numerical differential equation solver, thus improving the computational cost and avoiding convergence problems.

The developed PINN is trained and evaluated with the LG M50 cylindrical cell, whose electrochemical parameters are implemented in PyBaMM [3]. This way, constant current charges and discharges are applied to the cell with a more complex pseudo-two-dimensional (P2D) model to obtain the training and testing data. Our model's performance is then tested against the SPM model solved with numerical methods, both compared in terms of computational cost and accuracy.

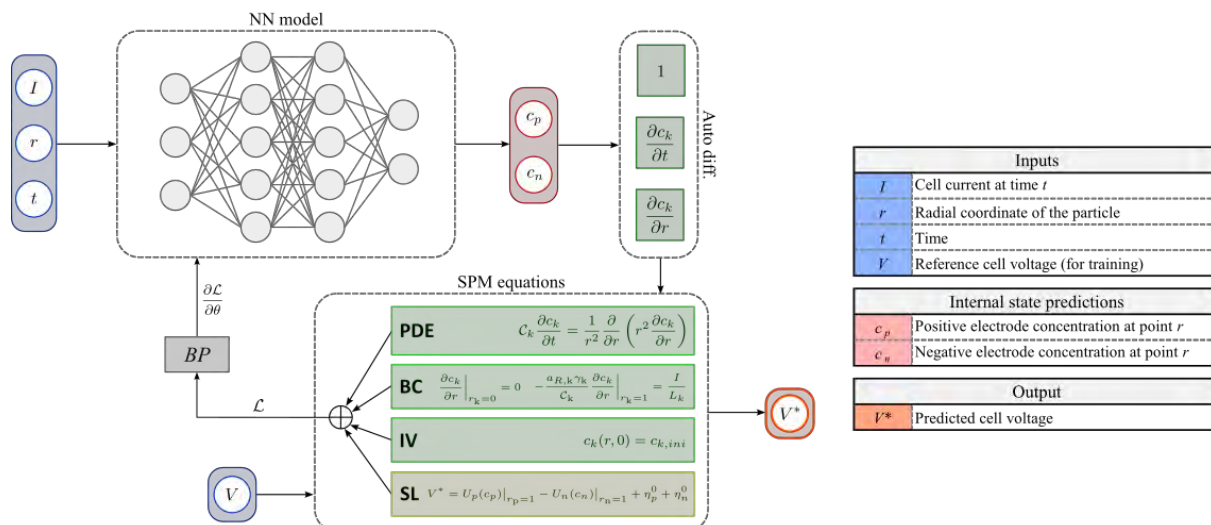


Figure 1: Proposed PINN battery modelling solution.

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Quantifying the impact of charge rate and number of cycles on particle cracking in Li-ion battery cathodes

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Quantitative relationships that link the effect of repeated cycling of Li-ion batteries on the structural degradation of cathode particles are not well established. In this talk, we present a computational method for quantifying cracks within electrode particles from scanning electron microscopy (SEM) image data of cross-sectioned NMC 532 electrodes. More precisely, generative adversarial network (GAN) is trained to super-resolve SEM images, i.e., the trained network can increase the resolution of lowly resolved SEM images—allowing for a more reliable quantification of fine features such as cracks, while leveraging the statistically representative field of view of the lowly resolved image data [1]. Then, a second neural network is deployed to segment the super-resolved image data into background, particles and cracks, see Figure 1, such that crack statistics on particle porosity or crack size/width/length distributions can be computed [2]. The proposed computational method has been deployed for the crack quantification of cathodes that have been cycled with various charge rates (1C, 6C, 9C) and cycle numbers (25, 225 and 600 cycles), see Figure 2. We observed that the crack size increases co-monotonously both with the number of cycles and with the charge rate, where the former has a more significant effect on the crack length, whereas the latter influences the crack width. Additionally, the computed crack statistics have been compared to electrochemical data from full and half cells of NMC532 cathodes [2]. This comparison indicated that the capacity fade correlates strongly with the structural degradation within the first 25 cycles, however, for larger numbers of cycles this correlation decreased.

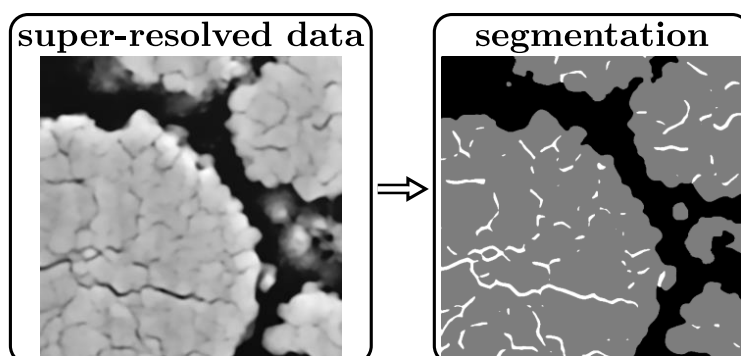


Figure 1: Cutout of a super-resolved SEM image (left) of a cycled cathode and corresponding segmentation (right). Figure is adapted from [2], used under CC BY 4.0.

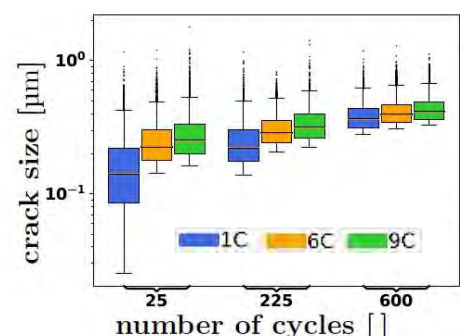


Figure 2: Cutout of a super-resolved SEM image (left) of a cycled cathode and corresponding segmentation (right). Figure is adapted from [2], used under CC BY 4.0.

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SESSION ABSTRACTS

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Li-ion battery in high C-rate conditions: improving the temperature prediction

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Knowledge of the temperature distribution within a Li-ion cell is needed to ensure its safe and effective operation. It is desirable to be able to charge electric vehicles as fast as possible, perhaps up to 10C, but unfortunately current battery models fail to capture the electrochemical and thermal responses above 6C.¹ Although the literature justifies the use of a simple lumped thermal model for low C-rate applications, higher C-rates accelerate local reaction rates, promoting greater and more non-uniform heat generation, and thus invalidating lumped modelling assumptions. Given the complexity of processes at higher C-rates, both equivalent circuit models and conventional Doyle-Fuller-Newman derived models are unable to capture temperature evolution accurately above 6C.²

In this work, we propose an adaptation of a 3D reduced continuum thermal-electrochemical model previously developed by Jie et al.³ To verify model performance, experimental data was collected from an 8 Ah A123 Systems LFP/Gr pouch cell, cycled from 1C to 10C constant current and subjected to a square wave excitation proposed by Chu et al.⁴ An infrared camera was used to record temperature across cell surface.

Model parameters were identified by maximum likelihood estimation minimising the errors in battery surface temperature and output voltage, where a high-fidelity simulation was performed across different C-rates using COMSOL LiveLink™ for MATLAB®. Due to the high computational cost of the simulation, we employed surrogate optimisation to reduce the number of cost function evaluations. Lastly, we explored the feasibility of dynamic mode decomposition,⁵ a data-driven method, to reduce simulation time by extrapolating the remaining surface temperature data.

Simulations show promising results across the full range of tested C-rates. A clear relationship was observed between the C-rate and optimised value of diffusion time, which points towards diffusion assumption limitations used in the model.

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Microstructure-resolved simulation of three-dimensional electrodes for sodium iodine batteries

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The need for safe, eco-friendly, low-cost batteries for large scale implementation rises in the presence of the expansions of renewable energy sources. High-temperature liquid sodium batteries (e.g. sodium-sulfur) are a well-established technology for large-scale grid storage. Combining the molten sodium anode with an aqueous iodine cathode overcomes the problems of thermal losses and sealing by reducing the operating temperature to about 100°C. This leads to higher cost efficiency, energy density and a simplified cell design.

Here we present a novel modelling approach for complex carbon-based cathode structures and its limits and abilities on enhancing the utilizable capacity. Due to their sustainability and high efficiency, which is comparable to Li-Ion batteries, mid-temperature sodium-iodine batteries are a promising candidate for small and medium scale stationary energy storage applications. With a high specific energy of around 200 Wh kg⁻¹, sodium-iodine batteries have the ability to meet the growing demand of short-term energy storage caused by the integration of renewable energy sources into the power grid. Up to this day, the detailed processes inside the battery are not well-understood. Quantities like initial species concentrations, C-rate, cell design and cathode geometry have large impacts on the overall battery performance. A deeper understanding of these processes is inevitable for enhancing the battery performance by choosing the optimal abovementioned quantities. We set up a fully resolved 3D Simulation model to gain insight into microstructural processes inside the battery, as experimental studies are limited to macroscopic quantities like electronic current and potential. The methodology is based on continuum hypothesis by using an open-source CFD software, which is rewritten accordingly. The proposed spatially resolved three-dimensional simulation model takes charge and mass transport, heterogeneous and homogeneous reactions as well as the electrochemical processes into account. Results show that transport limitations confine the utilizable capacity of the battery [1].

This contribution focuses on enhancing the battery energy density and efficiency by including open-pored glassy carbon foam structures in the cathode half-cell [2]. We state simulation predicted, optimal morphology properties of such a structure. The results indicate that a high porosity of the cathode structure is crucial for utilizing the full battery capacity while the specific surface area is insignificant.

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Understanding the Dynamics of Lithium-Ion Transport in Graphite-Silicon Composite Electrodes through Model Analysis

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In recent years, many efforts have been devoted to the development of composite electrode materials for lithium-ion batteries. Particularly, graphite-silicon (G-Si) composite anodes stand out among them due to their enhanced energy density and low open circuit voltage. However, the electrochemical modelling of these electrodes [1, 2] raises several questions regarding the identification of model parameters and relies on assumptions that require novel experimental validation. Moreover, the introduction of additional active particle scales makes these models exceptionally computationally expensive. In this presentation, we use a G-Si half-cell single particle(s) model, in which a pure G particle and a composite particle consisting of Si nanoflakes embedded in a G matrix are considered, to gain understanding on the different dynamics that occur during a galvanostatic intermittent titration technique (GITT) experiment. We focus on analysing the effects that the lithium-ion exchange kinetics between G and Si in the composite particle, which may result in the development of moving reaction fronts during (de)lithiation and relaxation of the electrode (see Figs. 1 and 2), can have on the dynamics at a cell voltage level. This, in combination with the electrochemical balancing between the two types of particles during relaxation, makes deriving active material diffusion properties from conventional GITT experimentation no longer straightforward. To effectively tackle this problem, we show how the analytical solution to the associated linearised model, together with dimensional analysis, constitutes a powerful tool that allows identifying the dependency of GITT relaxation dynamics with respect to the parameters of the model.

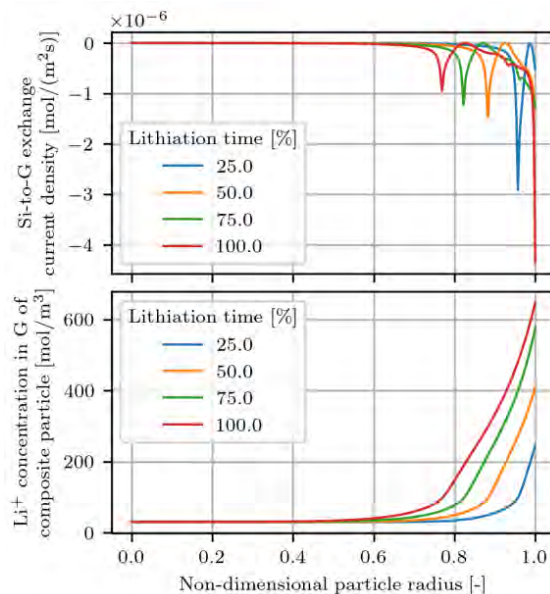


Figure 1: Lithiation dynamics in G-Si particle

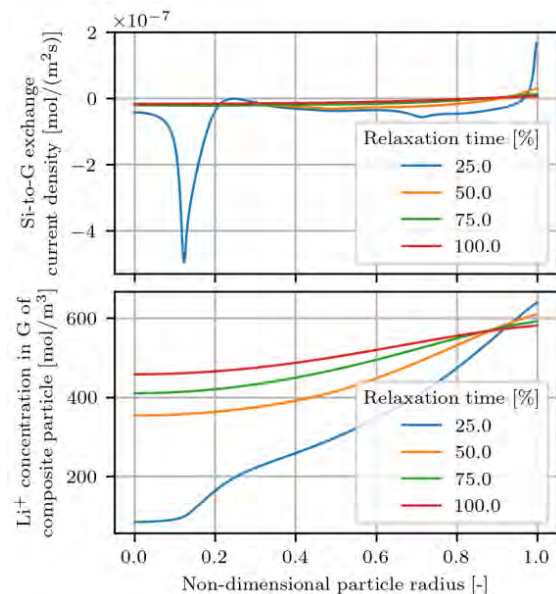


Figure 2: Relaxation dynamics in G-Si particle

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Homogenized monolayers based 3D-model of a thermal event in a lithium-ion battery pouch cell.

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The assessment of battery cell safety is an important part in the development of a battery pack. This is especially valid for the application of high-energy density active materials in lithium-ion batteries. A series of abuse tests can be used to obtain a better understanding of the physical phenomena and triggers during a thermal event. Furthermore, experiments must be used to evaluate counter measures to prevent the hazardous character of a thermal event. Direct consequences of elaborate testing are high costs and waste production. These problems can be reduced by integrating numerical models in the battery cell development and testing process, which leads to an in-depth and quantitative understanding of all cell safety aspects.

In this work, a three-dimensional numerical model is developed to investigate and identify possible phenomena that influence a thermal event. The chemical conversion rate was modelled by Arrhenius equations using power-law kinetics. A virtual upscaling workflow was developed to advance the 0D-model published by Baakes et al. [1] to a 3D multi-layer pouch cell model. To decrease the computational requirements, a reduced multi-step reaction mechanism was employed for a cell consisting of LiCoO₂ cathodes and graphite anodes. First, kinetic parameters were calibrated by using literature values. Then an optimization with a 3D model consisting of homogenized monolayers was implemented to further increase accuracy, which includes heat conduction and dissipation. Finally, for the validation numerical results were compared with the experimental temperature evolution of an ARC measurement conducted by Maleki et al. [2]. The developed model replicated the overall experimental temperature curve up to the assumed opening of the test cell. As isobaric conditions were assumed the model is not capable of realizing a cell opening and, thus, slight temperature deviations after cell opening are expected. Nonetheless, it can accurately define the onset temperatures of the pouch cell, once at the start of self-sustaining exothermic reactions and once at the start of the so-called thermal runaway. Further analyses on external applied heating, heat conduction, and heat dissipation revealed a significant change to the overall thermal behaviour and influence on the chemical reactions. To summarize, this work presents an important step towards a fully discretized thermo-chemical model applicable for safety assessments in an early development stage of battery cells.

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Multiphase-field modelling of layered-oxide compounds for intercalation batteries

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The research of new electrode materials such as sodium ion intercalation compounds is key to meet the challenges of future demands of sustainable energy storage. Many commercial as well as promising electrode materials exhibit strongly anisotropic properties and are synthesized as polycrystalline agglomerates. The interplay of chemical, electrical and mechanical forces strongly drives the intercalation behaviour on the microscale and, thus, influences the overall cell performance. The multiphase-field method [2] is a suitable tool to study these multi-physics on the nano-scale [1] and micro-scale [3] to identify the dominant processes and computationally guide research towards batteries with longer lifetime and improved performance.

Our previous work [3] highlights the importance to consider pre-existing grain boundaries for nucleation at higher-order junctions, heterogeneity of the intercalation fluxes and grain-by-grain filling behaviour. Anisotropic elastic deformation leads to high stresses at the evolving phase boundaries, especially at high misorientations between neighbouring grains. The maximum principal stress is used as an estimate for degradation by fracture in polycrystals. Furthermore, the extension to layered-oxide materials such as LNO and $\text{Na}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ encompasses the modeling of multiple first-order phase transformations during cycling, corresponding to an OCV with multiple potential steps.

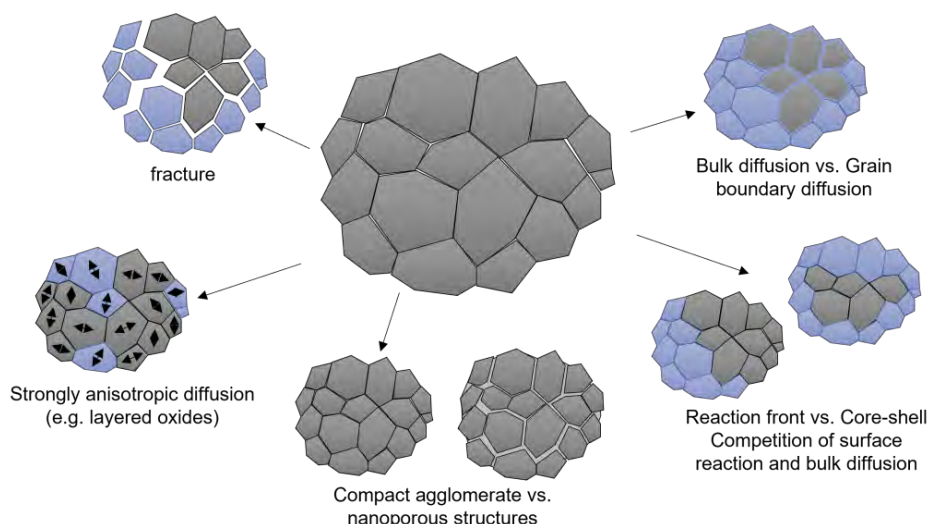


Figure 1: Modelling aspects of agglomerated cathode particles

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2. S. Daubner, P. G. Kubendran Amos, E. Schoof, J. Santoki, D. Schneider and B. Nestler, 2021, Multiphase-field modeling of spinodal decomposition during intercalation in an Allen-Cahn framework. *Phys. Rev. Materials* 5, 035406.
3. S. Daubner, M. Weichel, D. Schneider and B. Nestler, 2022, Modeling intercalation in cathode materials with phase-field methods: Assumptions and implications using the example of LiFePO_4 . *Electrochim. Acta*, 421, 140516.

SESSION ABSTRACTS

5. Battery fundamentals

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Electrode Material Design Booster Using a Statistical Digital Twin

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For current operations, batteries must be fast-charging, durable, sustainable and cost-effective to manufacture, while also offering high-storage capacity. An essential piece of this challenging puzzle is to improve the microstructure of the electrodes.

Direct experimental approaches are difficult at this scale and are also expensive and time-consuming. Alternatively, performing simulations to specifically improve batteries at these scales is extremely useful. Our work is carried out using a complete, commercially available software environment called GeoDict.

Reliably reproducing the original material with a digital model is a starting point to improve the microstructure. We call this model a statistical digital twin. We start with importing a microCT image stack and segmenting the material phases to reconstruct the 3D structure. Subsequently, the statistical properties of this imported 3D structure are calculated, such as open and closed porosity, tortuosity, or diffusivity. Based on this data and starting from grains with a certain shape and size distribution, the volume fraction of these grains is determined and their shape is adjusted to create a statistical digital twin of the original 3D structure. Finally, the binder-and-carbon black domain (CBD) is added to the structure. The resulting statistical digital twin is validated by comparing its porosity, tortuosity and diffusivity with the same parameters of the original imported 3D structure.

As an application example, we present a case study showing how batteries can be improved by 3D microstructuring approaches. We simulate the structuring of a graphite anode with a laser and describe how these changes affect crucial parameters of the material, such as tortuosity and diffusivity. This work was carried out as part of the BMWK's structur.e project [1].

[1] <https://math2market.com/math2market/publicly-funded-projects/structur-e.html>

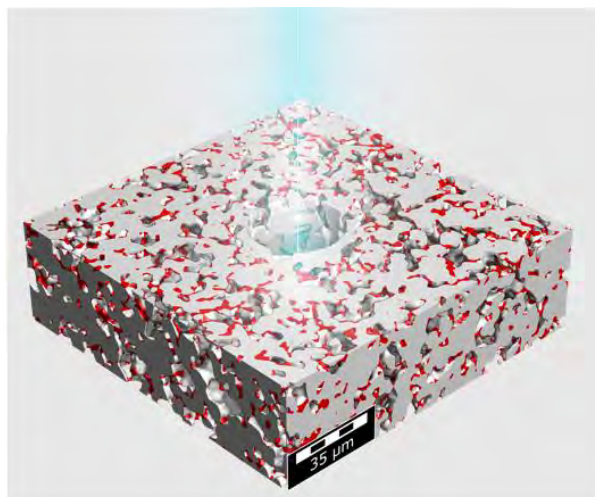


Figure 1: Illustration of a laser perforation of an anode

ENMR-derived Transference Numbers in Different Reference Frames

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With the powerful measurement technique of electrophoretic NMR (eNMR) direct insight into ion movements in liquid electrolytes is possible. This direct access to ion mobilities allows for the calculation of important transport parameters like the transference number of ionic species.[1] The transference number is a valuable performance indicator for batteries and a necessary input parameter for physics-based battery simulations. However, their reference frame dependence has to be carefully considered.

With our transport theory for highly concentrated electrolytes we can describe transport processes in different reference frames. It was originally developed in the center-of-mass representation.[2] However, we recently showed how eNMR measurements on ionic liquid mixtures can be better described via the volume-based frame of reference assuming local molar volume conservation and a vanishing volume flux as boundary condition (Fig. 1).[3,4]

We derived rules to transform between different reference frames. We apply these transformation rules to transference numbers of ionic liquid mixtures and assess them quantitatively in different representations, like the center-of-mass-, volume- or species-fixed reference frames (Fig. 2). This rationalizes the role of transference numbers in highly concentrated electrolytes and adds to recent discussions about their frame-dependence.

This work is supported by the European Union's Horizon 2020 research and innovation programme via the "Si-DRIVE" project (grant agreement No 814464).

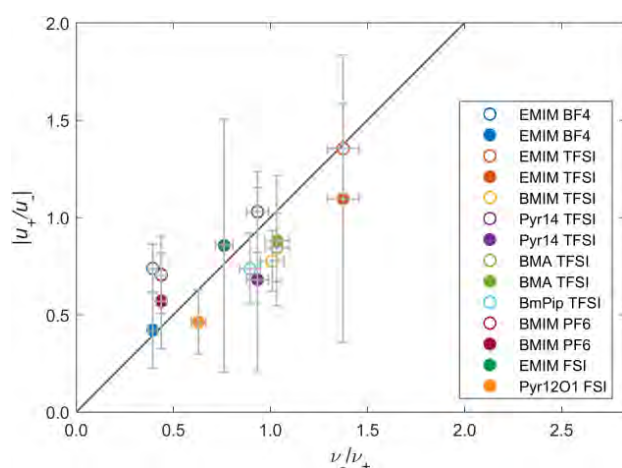


Fig. 1: The volume-based reference frame describes eNMR results better than the mass-based representation.

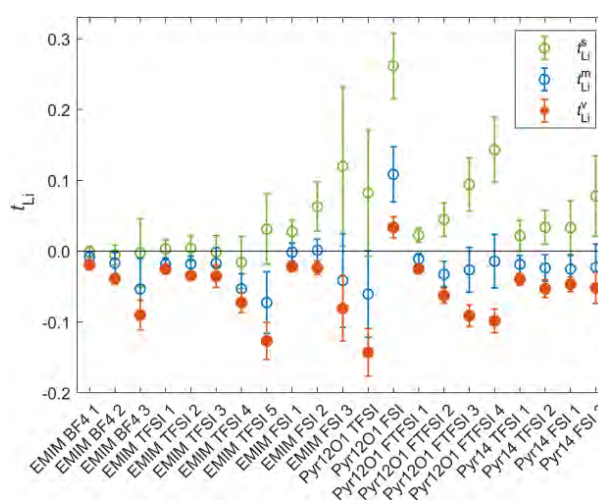


Fig. 2: Transference numbers in different reference frames for various ionic liquid mixtures.

- [1] Gouverneur, M. et al. *Phys. Chem. Chem. Phys.* **2018**, 20(11), 7470–7478. DOI: 10.1039/c7cp08580j
- [2] Schammer, M. et al. *J. Electrochem. Soc.* **2021**, 168(2), 026511. DOI: 10.1149/1945-7111/abdddf
- [3] Lorenz, M. et al. *J. Phys. Chem. Lett.* **2022**, 13(37), 8761–8767. DOI: 10.1021/acs.jpclett.2c02398
- [4] Kilchert, F. et al. **2022** arxiv.org/abs/2209.05769

Advances in Li-S Model Validation and Prediction

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Li-S battery models can be useful tools for battery diagnostics as well as the optimisation of both cell operation and design parameters. Well-validated models can be trusted to provide accurate, precise, and informative information of the cell physics. However, the many proposed models for Li-S batteries have few predictions which are compared to experimental data, thereby making model validation quite difficult as well as the comparison of proposed mechanisms. A recently published paper [1] has proposed a minimum set of testing procedures for Li-S model validation. Such a procedure will allow future models to be more easily validated and compared with competing models. Moreover, a zero-dimensional model is proposed which is validated across the set of all test procedures and provided quantitatively accurate electrolyte resistance predictions. This talk will also include several updates to the model which alleviates the shortcomings observed in the published validation procedure.

1. Cornish, Michael, and Monica Marinescu. "Toward Rigorous Validation of Li-S Battery Models." *Journal of The Electrochemical Society* (2022).

Why diffusion coefficients in active materials are not constants – On the importance of state-of-charge dependent input parameters in battery simulation

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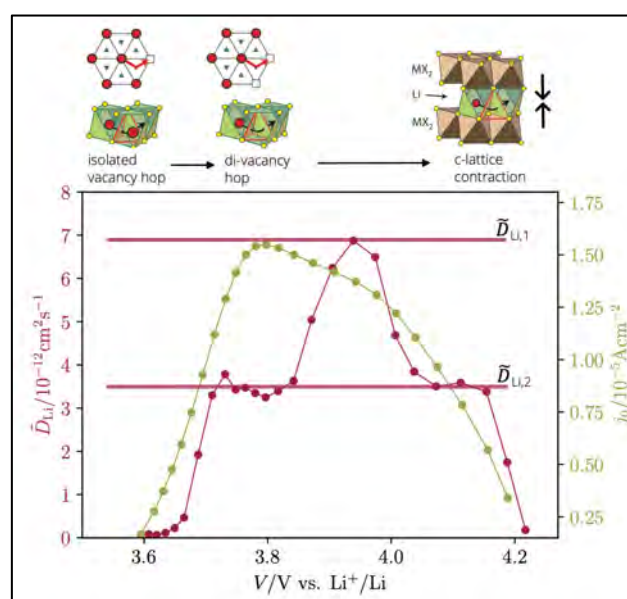
Anytime one sets up a (battery) simulation, input data is needed to feed the model. Therefore, deciding to rely on literature-known data, on rough estimates, measuring the required data oneself or extracting the "input" by fitting the simulation to experimentally obtained data, is one of the first hurdles to take. A reasonable choice of input parameters is crucial for the result and we therefore want to shed light on state-of-charge (SOC)-dependent input parameters in electrochemical battery simulations, namely the chemical diffusion coefficient of lithium in active materials and the exchange current density at the interface of the active material and the electrolyte.

With a case study on microstructure-resolved electrochemical modeling of a composite cathode for an all-solid-state battery, we will tackle the following questions:

- Which physicochemical meaning is behind these input parameters? Why do they depend on the SOC?
- Why do they matter and how do they influence the simulation results?
- How to obtain reliable input data?

The simulation relies on electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) data¹ for the SOC-dependent input parameters and focuses on NCM811 in combination with Li₆PS₅Cl as solid electrolyte².

Figure 1: Chemical lithium diffusion coefficient in NCM811 (red) and exchange current density at NCM811/Li₆PS₅Cl-interface (green) depending on the state-of-charge; data from Ruess et al.¹, schematics from Van der Ven et al.³, plot from Bielefeld et al.²



1. Ruess, R. et al. *J. Electrochem. Soc.*, **2020**, 167 (10), 100532. DOI: 10.1149/1945-7111/ab9a2c
2. Bielefeld, A. et al. *J. Electrochem. Soc.*, **2022**, 169 (2), 020539. DOI: 10.1149/1945-7111/ac50df
3. Van der Van, A. et al. *Acc. Chem. Res.*, **2013**, 46 (5), 1216-1225. DOI: 10.1021/ar200329r



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6. Battery fabrication II

6.1 Cell design on target – maximum performance at optimal cost in minimal time	51
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Cell Design on Target – Maximum Performance at Optimal Cost in Minimal Time

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Despite high efforts in digitalizing the design-process of Lithium-Ion batteries, it is still in crucial parts done by human beings with an outstanding expertise, which they had to acquire during many years of training and experience. The core problem of digitization lies in the fact, that by digitally designing a cell from the scratch, model uncertainties of each design step accumulate, which results in a model of very high prediction uncertainty. At the same time the knowledge of the true performance of a realized design and how well it actually turned out in reality is not fed back to the previously used cell design model.

In this talk we will present a digital cell design approach, which does not start the cell design process from the scratch, but from the physical model of an existing cell, where all electrochemical and geometrical properties and thus the complete thermal and current-voltage behavior is correctly digitally represented. From that point of very low model uncertainty but at the same time realistic level of complexity, cell design parameters can be systematically changed and their sensitivity on different cell performance indicators like capacity, peak power or fast-charging capability can be studied.

We will exemplify the approach by studying, which performance space can be spanned by variations of an exemplary basic design, meaning which energy and power densities can be reached by certain design changes and which changes in material cost would accompany those.

The talk will conclude with implications which this approach has for an industrial development process where now, due to the low prediction uncertainty, the cell design and its electrochemical and thermal properties can be “front-loaded” into the development process. Thereby, for example the development of the cooling system could start based on the digital cell design model and thus even before the actual cell has ever been built.

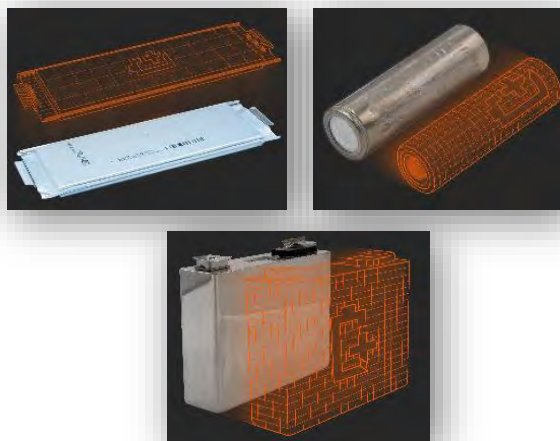


Figure 1: Physical modelling, parameterization and validation of various cell types is the basis

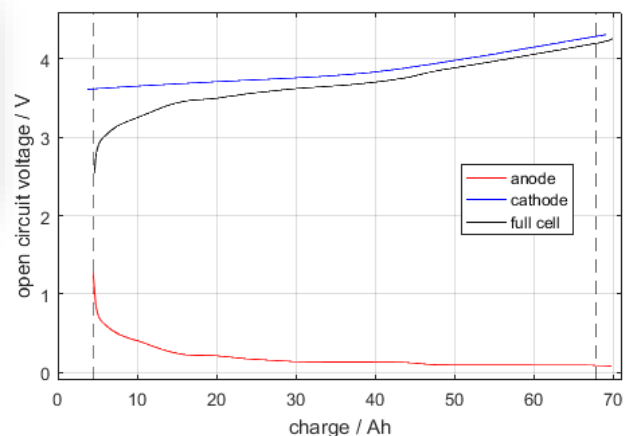


Figure 2: Cell balancing of a pouch cell for an automotive application

Coupled EIS-FIB/SEM Analysis of Wet Mixing Effects on Performance of Li-Ion Battery

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Wet mixing is one of the key production steps which mainly effects on structural behaviour and electrochemical performance of Lithium ion batteries (LIBs) electrodes [1]. Not only the mechanical stability of electrodes is enhanced, but also electronic connection of them is improved by mixing process [2]. The main role of wet mixing is combination of the dry components with the binder solution, which provides a homogeneous network between the binder matrix, the active materials and the additives [3]. Mixing time and intensity strongly determine the viscosity of the slurry, which is a crucial parameter regarding the coating step and rather an indication of the deagglomeration status of the conductive additives.

In this study, we combine microstructure characterization by FIB/SEM tomography with impedance measurement to investigate the influence of wet mixing time on electrochemical performance and morphology of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) cathodes. To analyse the impedance spectra on symmetrical cell setups, Transmission Line Model (TLM) has been employed in this work. The fitting result by TLM model shows the contact resistance between current collector and active material is reduced by increasing of wet mixing time. Meanwhile impedance data of electrodes by blocking electrode configuration which is achieved by using a non-intercalating electrolyte, demonstrates low electrical resistance for cathode with high mixing time. Moreover, quantitative FIB/SEM tomography obtained from cathode material with high mixing time reveals a homogeneous conductive/binder network which can explain improved performance observed by impedance measurement.

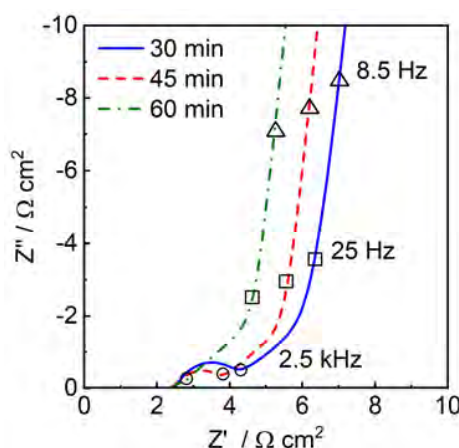


Figure 1: Impedance spectra of cathode symmetric cell with different mixing time under blocking condition.

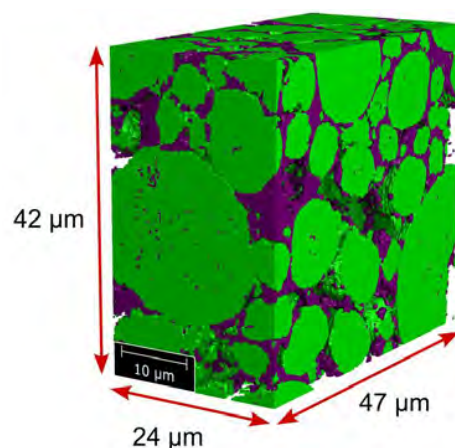


Figure 2: Quantitative FIB/SEM tomography obtained from cathode material with 60 minutes mixing time.

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- Bauer, W.; Nötzel, D. et al. *J. Power Sources* **2015**, *288*, 359-367. DOI: 10.1016/j.jpowsour.2015.04.081

DEM-Simulation of Drying and Calendering of Lithium-Ion Battery Electrodes

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With the help of the discrete element method (DEM) software LIGGGHTS an approach was developed that enables the generation and characterization of particulate electrode structures with defined target properties such as porosity or coating thickness. In the first step, the drying process of the wet electrode film is simulated by mapping the active material and conductive carbon black particles. On this basis the resulting electrode structure is compacted in the calendering process, whereby the carbon black particles are transferred together with the binder into a solid bridge model.

The presentation explains how particulate electrode suspensions can be modeled via DEM and how a simulation set up for the structure generating film drying process can be built. It is also presented how it was possible to avoid coupling with a CFD simulation and still adequately represent the relevant fluid effects by using appropriate substitute models in order to depict the formation of the electrode structure from the wet film. In this way, both the required computing time and computing power can be greatly reduced. Furthermore, all relevant interparticle interactions were identified and implemented in the DEM code as contact models. Also, the influence of the preceding dry mixing and dispersing step on the carbon black structure can be taken into account. The drying model was validated using a model suspension and different wet film thicknesses.

The electrode structure generated by the drying simulation is transferred to the calendering simulation. After a one-time calibration of the stiffness and damping behaviour of the inactive binder-carbon black network, the model is able to reproduce the experimentally achieved mechanical stresses and elastic strains of the particulate electrode for different calendering degrees and initial coating thicknesses.

The structures generated in this way can be used for further virtual analyses such as thermal or electrical conductivity.

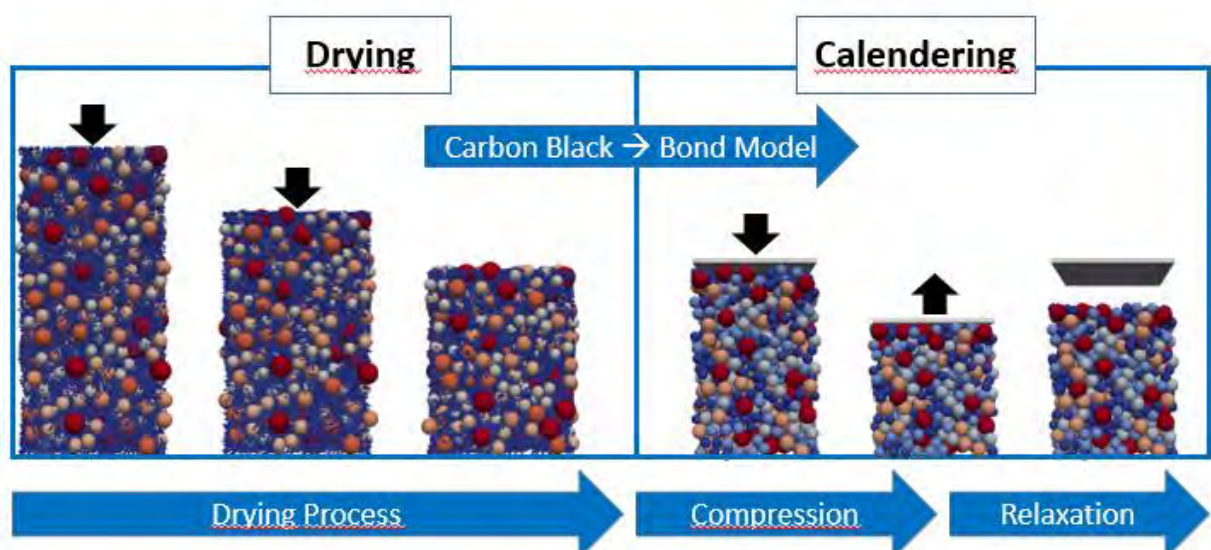


Figure 1: Simulation Workflow

Identification of SEI growth models during Li-ion battery cell formation

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The final process step in Li-ion cell manufacturing is the cell formation. It has decisive influence on the quality and cost of the battery cell (1). The formation includes several charge and discharge cycles. During these cycles, most of the Solid-Electrolyte-Interphase (SEI) is built. Despite its importance, the formation process is not well understood and therefore difficult to optimize. Due to multiple influencing factors and the fragility of the layer, which is only nanometers thick, high experimental effort is required to characterize the build-up of the layer. Model-based approaches can be used to elucidate the growth mechanisms involved and to extrapolate the influencing factors and their effects on the long-term aging behavior. This can significantly reduce the experimental effort and enable knowledge-based process design.

Here, first a method to identify and parametrize SEI growth models with low experimental effort is presented. Shifts of distinct peaks, i.e., feature, within the anode potential curve during a slow formation and a reference measurement are utilized to determine the capacity loss during the first cycle. This data is used to identify appropriate SEI growth models and their parameters (2). Then, the growth model is coupled with a pseudo-2-dimensional (P2D) model to simulate the impact of different formation protocols on the SEI growth during the first cycles. Simulation results for different formation protocols show good agreement with experimentally determined capacity losses, if time-delayed deposition is considered. These results confirm the "near-shore aggregation mechanism" described by Ushirogata et al. (3). Moreover, the simulation results show that the final effective film thickness is mainly determined by the formation time and the anode potential. Higher currents have a negative effect on the homogeneity of the SEI along the electrode.

In summary, a novel method for parameterizing the SEI growth models is presented. The SEI growth model is combined with a P2D-Model to investigate factors affecting SEI build-up during the formation process and to test their prediction capability.

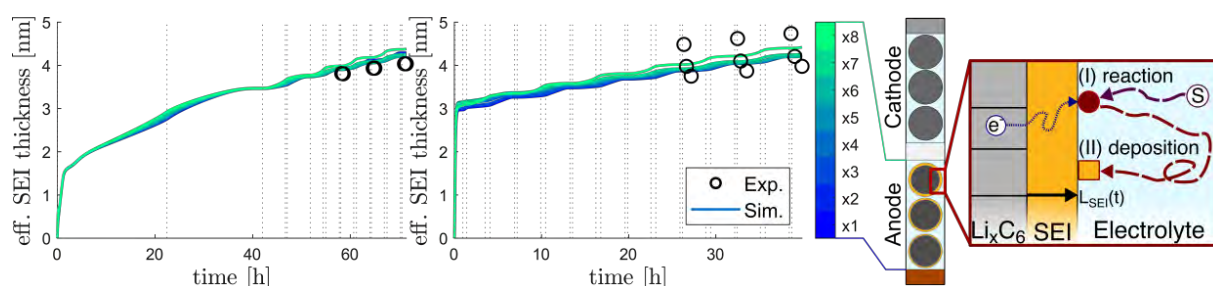


Figure 1: SEI thickness along the anode thickness as simulated by the combined P2D and SEI growth model for a slow formation protocol (left) and fast formation protocol (right).

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SESSION ABSTRACTS

7. SOFC / SOEC / Methods

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Simulation of Electrode Diffusion Models for Solid Oxide Fuel Cells

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The mass transport in porous electrodes is important since it determines the performance of solid oxide fuel cells (SOFCs). The Knudsen number Kn is defined as the mean free path (λ) of a gas molecule divided by the pore diameter (L).¹ Molecular interaction dominates if $Kn < 0.1$, and Knudsen diffusion dominates if $Kn > 10$. While when $0.1 < Kn < 10$, both interactions are contributing. The effect of pore structure, tortuosity (τ), and porosity (ε) must be considered to relate the effective diffusion coefficient (D_{eff}) to the bulk diffusion coefficient (D). There is Fick Model (FM), the Mixture-averaged model (MAM), the Maxwell Stefan model (MSM), and the Dusty Gas model (DGM).² In our work, these models are implemented and compared based on a 3D button SOFC multiphysics model. The models also are compared with and without Knudsen diffusion.

Figure 1 (a) shows the geometry of the button SOFC (Ni-YSZ|YSZ|LSM-YSZ). The thickness of the electrode is $15\ \mu\text{m}$, with a diameter of 1 cm, while the thickness of the electrolyte is $150\ \mu\text{m}$ with a diameter of 2 cm. The diffusion models determine the species concentration in the porous electrode, which reflects the concentration polarization. The concentration polarization is implicitly included in thermodynamic loss, i.e., the Nernst equation. Besides, it is also included in electrode kinetic models, i.e., Butler-Volmer equation and exchange current density (i_0). Figure 1 (b) and (c) shows the exchange current density and concentration polarization at the interface of the cathode/electrolyte (ICE), while applying the MSM model. One can see that the current density and concentration polarization are distributed concentrically. The exchange current density is larger at the rim of the electrode than at the center, where the concentration polarization is also larger.

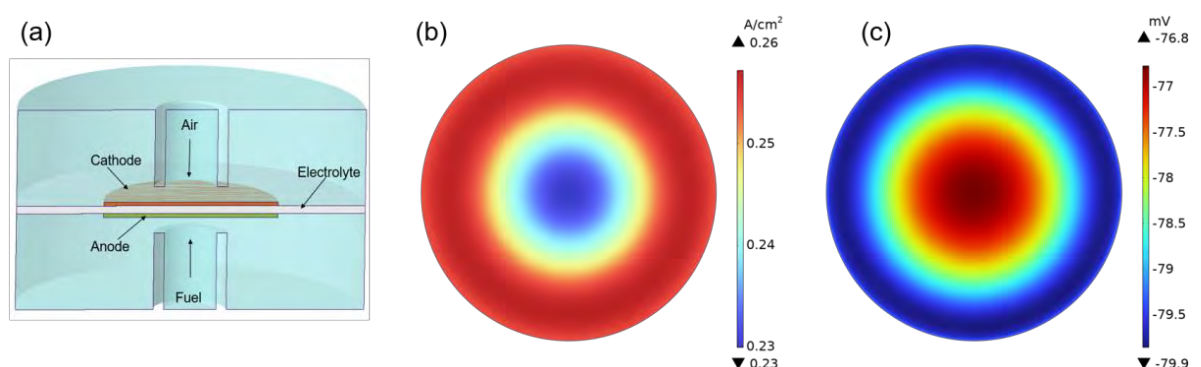


Figure 1 (a) Geometry of the button SOFC ; (b) Exchange current density at the cathode/electrolyte interface ; (c) concentration polarization at the cathode/electrolyte interface.

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3. Hajimolana, S. A.; Hussain, M. A.; Daud, W. M. A. W.; Soroush, M.; Shamiri, A. Mathematical modeling of solid oxide fuel cells: A review. *Renew Sust Energy Rev* **2011**, 15 (4), 1893-1917. DOI: 10.1016/j.rser.2010.12.011.

Predicting the SOFC anode performance from microstructure using convolutional neural networks

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A key challenge in the development of solid oxide fuel cells (SOFC) is to reduce the gradual performance loss caused by degradation of the electrode microstructure. Especially the anode contributes significantly to the cell performance loss [1]. Therefore, a lot of effort is put into understanding the relation between the material microstructure and anode performance, which is characterized by the polarization resistance R_{pol} .

A promising approach is to use microstructural parameters determined from serial sectioning tomography combining focused ion beam and scanning electron microscopy (3D-FIB/SEM) to parametrize a transmission line model [2]. The computationally most expensive part of this process is the numerical simulation of effective transport parameters (e.g., ionic conductivity) through the anode, for example using the fast Fourier transform (FFT) method.

Recently, there is an increasing interest in replacing such simulations by data-driven surrogate models [3]. Therefore, we propose a deep learning model based on convolutional neural networks (CNNs) that predicts R_{pol} directly from the SOFC anode microstructure. The model learns the structure-property correlations in a supervised manner from the physical simulation and can predict results for novel microstructures much faster than the reference method.

We compare different 2D and 3D CNN architectures and show that the recently published ConvNeXt [4] model achieves the best result. Furthermore, we demonstrate that a few 2D cross-section images are already sufficient for achieving a high prediction accuracy.

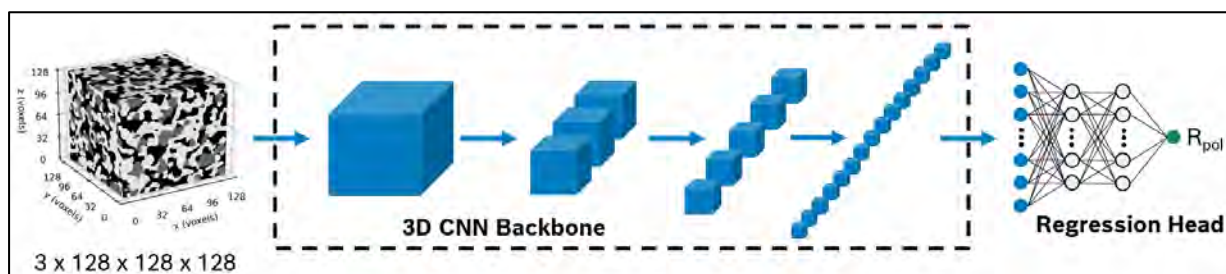


Figure 1: 3D CNN for the prediction of the SOFC anode performance from microstructure data.

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2. Dierickx, S. et al. *Electrochim. Acta* **2018**, *265*, 736-750. DOI: 10.1016/j.electacta.2017.12.029
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Multiscale and Multiphysics Modeling of an SOC Stack

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Electrolysers and fuel cells represent typical electrochemical devices that locates within the scope of clean and renewable energy. The high-temperature applications based on solid oxide electrolytes, solid oxide electrolysis cell (SOEC) or solid oxide fuel cell (SOFC), can often outperform the alkaline and proton exchange membrane (PEM) system. The SOC technology offers a promising option for the production of green hydrogen as SOEC as well as electricity and heat in the combined heat and power plants as SOFC. Scientific research on the predictive understanding of the transport phenomena in SOC stack and system is still needed to promote the commercialization.

In addition to experimental studies, which usually require large efforts in time and data analysis, numerical approaches are attracting attention and have shown the possibility to predict the performance in an easy and fast manner. This work employs two three-dimensional multiscale and multiphysics computational fluid dynamics (CFD) models, one detailed model and one homogenized model. These approaches consider the major physical phenomena, including fluid flow, heat and mass transfer, species transfer, thermal radiation, charge transfer, and electrochemical reactions. The detailed CFD model ¹ resolves the macroscopic geometry, while the homogenized CFD model ² simplifies the geometry and employs a volume-averaged approach.

The homogenized model is used to simulate the Mark-F10 stack in Forschungszentrum Jülich GmbH (FZJ). It includes 4 repeating units, each with an active area of $\sim 81 \text{ cm}^2$. According to the experimental conditions, the simulations were conducted at 700°C . The detailed model is used to simulate a single repeating unit at the same operating condition. Figures 1 and 2 show the comparison of two numerical approaches and the experimental data. The results agree quite well in the prescribed operating condition. More investigations will be conducted in different operating conditions.

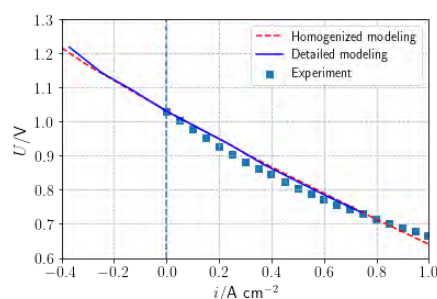


Figure 1: UI curve of the Mark-F10 design

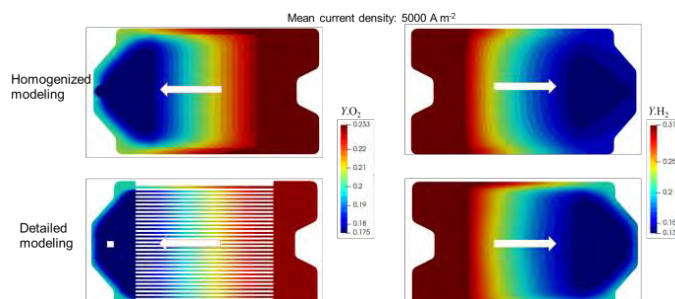


Figure 2: Comparison of mass fractions between two models

- (1) Zhang, S.; Hess, S.; Marschall, H.; Reimer, U.; Beale, S. B.; Lehnert, W. OpenFuelCell2: A New Computational Tool for Fuel Cells, Electrolysers, and Other Electrochemical Devices and Processes. *Computer Physics Communications*, to be submitted.
- (2) Zhang, S.; Peters, R.; Varghese, B.; Deja, R.; Kruse, N.; Beale, S. B.; Blum, L.; Peters, R.; Eichel, R.-A. Modeling of Reversible Solid Oxide Cell Stacks with an Open-Source Library. *J. Electrochem. Soc.* **2022**. <https://doi.org/10.1149/1945-7111/ac9c32>.

Modeling and simulation of an anion-exchange membrane electrolyzer using an unified open source platform for electrochemical systems

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At the cell level, the modelling equations for standard electrochemical systems, including battery, electrolyzer and fuel cell share a common structure determined by the laws of classical nonequilibrium thermodynamics. For each component of those devices, the governing equations consist of conservation laws where the fluxes are obtained as linear combination of the gradient of the potentials. The coupling between the components is typically represented as source terms in the equations. These similarities open the possibility for a unified platform which can promote rapid transfer of expertise between these different fields. This is one of the ambitions of the work we have initiated with the open-source platform BattMo. The complexity of the device grows with its number of components, each of them bringing new variables into the mathematical model of the system. The multi-component design implemented in BattMo enables us to keep track of this complexity. The use of a generic grid structure and discretization operators gives us easily access to 3D models. In this talk, we present the implementation of a model for AEM electrolyzer in BattMo and will use it to illustrate some of the general ideas behind the design of the code that we just mentioned. In addition, we will present results on the impact of degradation mechanisms such as electrochemical catalyst dissolution on the performance of the electrolyzer.

Ontology-based graph data model for scalable data management in catalyst layer fabrication

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Cost-effective and highly performing materials are of key importance to advance the commercial prospects of polymer electrolyte fuel cells and water electrolyzers. These systems span a high-dimensional parameter space encompassing categorical attributes (e.g., type of ionomer, solvent, catalyst), numerical attributes (e.g., solvent and ionomer content) and physical properties (e.g., density, viscosity, rheology, faradaic catalytic efficiency, stability). However, there exists a lack of infrastructures in the hydrogen community that provide access to machine-readable experimental and modeling data to enable a more complete exploitation of extensive data assets from experimental characterization, simulation, and modeling. Currently realized research practices generate scattered and poorly connected data that are all too often incompatible with FAIR data principles (findable, Accessible, Interoperable, Reproducible)^[1]. Inefficient data management and analytics, resulting from this situation, reduce the value and restrain the utility of research and development in the energy technology domain. FAIR data management is pivotal for developing data-driven methods. Highly curated fabrication data allow pretrained models for optimization or screening tasks in materials discovery and optimization workflows to be established. Here, we present a native graph database to store experimental and simulation data on catalyst layer fabrication. Our data model follows the EMMO (European Materials Modelling Ontology) blueprint as shown in Fig. 1. Unlike relational databases, our ontology-based data model is flexible, allowing for smooth parameter changes in multi-dimensional fabrication processes. The database is embedded in the Django framework, enabling its integration into python-based platforms. The graph data model can represent the whole bandwidth of data types, from fabrication to simulation data. Databases are being implemented into the cloud-based Virtual Materials Intelligence (ViMI) platform^[2] allowing members of the hydrogen research community to pool their resources and speed up their investigations by using rich and well curated data or pretrained models.

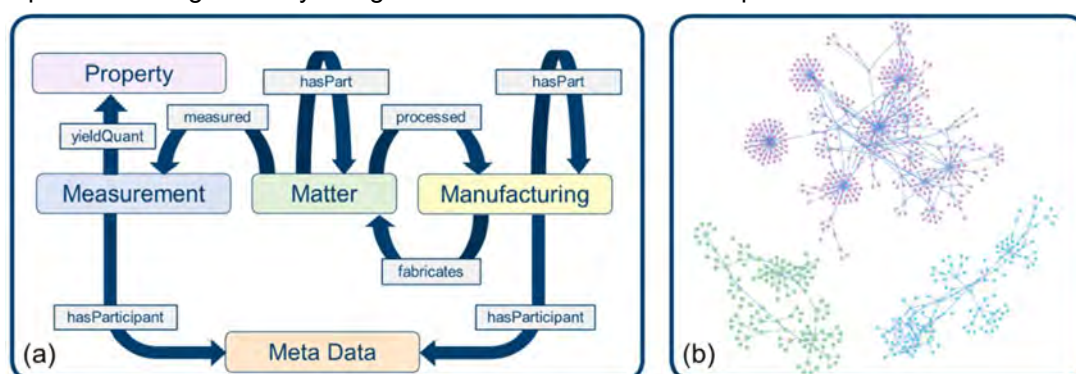


Figure 1: Schematic overview of the ontology-based data model for measurements, fabrications, and matter (a). The domain specific classes (e.g., specific quantities, materials, or processes) are represented as graphs within the database to which the items within the database can be mapped.

1. Scheffler M, Aeschlimann M, Albrecht M, Bereau T, Bungartz H-J, et al. FAIR data enabling new horizons for materials research. *Nature* 2022;604:635-42.
2. Malek A, Eslamibidgoli MJ, Mokhtari M, Wang Q, Eikerling MH, et al. Virtual materials intelligence for design and discovery of advanced electrocatalysts. *ChemPhysChem* 2019;20:2946-55.

SESSION ABSTRACTS

8. Redox flow batteries

8.1 Starting from the bottom: Coupling a genetic algorithm and a pore network model for redox flow battery porous electrode optimization	63
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Starting from the bottom: Coupling a genetic algorithm and a pore network model for redox flow battery porous electrode optimization

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Porous electrodes are performance- and cost-defining components in modern electrochemical systems as they facilitate mass transport, conduct electrons and heat, determine the hydraulic resistance, and provide surfaces for electrochemical reactions [1]. Combining microstructure-informed multiphysics simulations with evolutionary algorithms can accelerate progress in the optimization of porous electrodes as a pathway to system cost reduction. In this work, we deploy pore network modeling in combination with a genetic algorithm for the bottom-up design of porous electrodes for redox flow batteries.

In the first part, the coupling of an experimentally validated microstructure-informed, electrolyte-agnostic pore network modeling framework [2] with an evolutionary algorithm [3] is described. This genetic algorithm is used to optimize electrode microstructures by evolving the structure driven by a fitness function that maximizes electrochemical power output and minimizes pumping power requirements. The analyzed proof-of-concept flow-through cubic lattice structure with fixed pore positions shows significant improvement in the networks' fitness over 1000 generations. The fitness improved by 75% driven by a reduction in the pumping requirements by 73% and an enhanced electrochemical performance of 42%, resulting in a bimodal pore size distribution with large-pore longitudinal electrolyte flow pathways.

In the second part, I will discuss our latest progress on the genetic algorithm by implementing commercial fibrous electrodes as offspring networks, integrated flow field geometries, and extended evolutionary freedom during the optimization (i.e., merging and splitting of pores outside fixed coordinates). Coupling the genetic optimization to the desired flow field geometry affects the evolution of the fitness function, shifting the balance between hydraulic and electrochemical performance. By including more evolutionary freedom, existing electrodes can be enhanced. This algorithm offers great potential for the predictive design of electrode microstructures for specific electrochemical systems. Hence, this framework will accelerate and broaden the design and fabrication of advanced electrode structures.

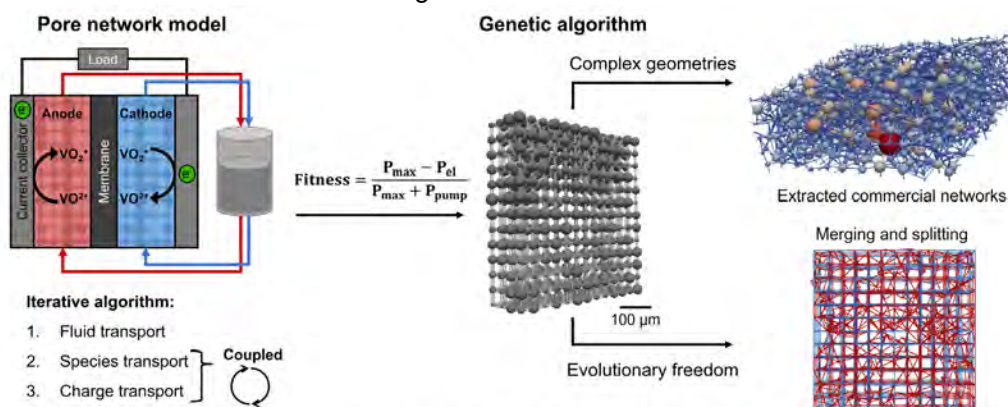


Figure 1: Schematic representation of the pore network model and genetic algorithm framework. The pore network model is coupled to a genetic algorithm that evolves the porous electrode microstructure driven by a fitness function. By implementing complex geometries and evolutionary freedom, the genetic algorithm offers great potential for the predictive design of electrode microstructures tailored for specific reactor architectures and redox chemistries.

[1] M. van der Heijden, A. Forner-Cuenca, *Encyclopedia of Energy Storage*, 480-499 (2022)

[2] M. van der Heijden & R. van Gorp *et al.*, *J. Electrochem. Soc.*, **169** 040505 (2022)

[3] R. van Gorp & M. van der Heijden *et al.*, *Chem. Eng. J.*, 139947 (2022)

Optimizing Electrode Geometry for Improved Mass Transfer in Redox Flow Batteries: A CFD Simulation and Experimental Study

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In recent years there has been a growing need for efficient energy storage systems as the share of renewable energy sources continues to increase. Redox flow batteries (RFBs) have emerged as a promising solution, offering advantages such as high capacity and long cycle life, as well as being eco-friendly. However, RFBs rely on electrochemical surface reactions, which require efficient transport of reagents towards the electrode surface. Mass transfer limitations, unfortunately, often result in a decreased efficiency and a lower yield of the RFB. While the academic community has focused on developing more active electrocatalysts, electrode configuration to increase mass transfer towards the electrode surface remains elusive.

Recent advances in additive manufacturing technologies such as CNC-milling and 3D printing have enabled the creation of structured 3D electrodes on micro scale, which have been shown to result in significant improvements in efficiency compared to felt electrodes shown in fig.1^{1,2}. In this work, we present computational fluid dynamics (CFD) simulations coupled to an experimental study aimed at improving mass transfer in RFBs using COMSOL Multiphysics®. We simulated, as visualised in figure 2, the stationary laminar flow and the concentration profile for different pillar electrode designs, yielding an understanding of the geometric parameters. Our simulations revealed that the mass transfer coefficient varies strongly with pillar shape, interpillar distance, and pillar size, while keeping pressure drops low. We found that diamond-shaped pillars result in a two-fold increase in mass transfer compared to cylindrical pillars, and that decreasing the interpillar distance can result in a 50-fold increase without an increased pressure drop. Our study provides insight into the impact of electrode geometry on mass transfer in RFBs and demonstrates the potential of CFD simulations to optimize electrode design and improve efficiency of RFBs³.

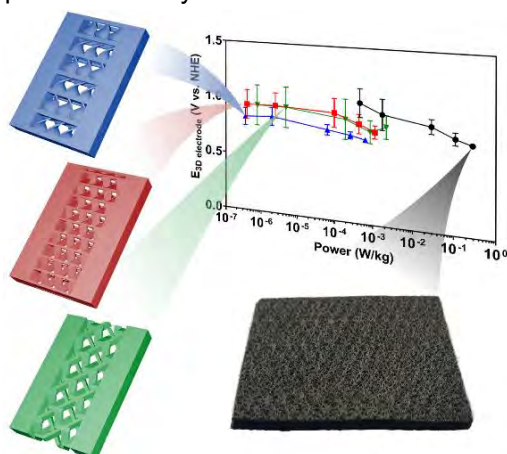


Figure 1: structured 3D electrode show an improved overall battery performance compared to felt electrodes¹.

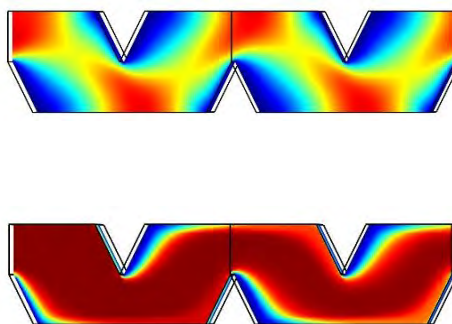


Figure 2: visualisation of the velocity profile on top and the concentration profile below in a structured pillar electrode.

1. De Wolf R., De Rop M., Hereijgers J. Effects of Structured 3D Electrodes on the Performance of Redox Flow Batteries. *ChemElectroChem* 2022, DOI: 10.1002/celc.202200640.
2. Hereijgers, J., Schalck, J., Lolsberg, J., Wessling, M. & Breugelmans, T. Indirect 3D Printed Electrode Mixers. *ChemElectroChem* 2019, 378–382 DOI: 10.1002/celc.201801436 .
3. Hereijgers J., Schalck J., Breugelmans T., Mass transfer and hydrodynamic characterization of structured 3D electrodes for electrochemistry. *Chem. Eng.* 2020 DOI: 10.1016/J.CEJ.2019.123283

Combining electrochemical and imaging analyses to understand the effect of electrode microstructure and electrolyte properties on redox flow batteries

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Reducing the cost of redox flow batteries (RFBs) is critical to achieving broad commercial deployment of large-scale energy storage. Different approaches have been proposed to lower costs and enhance performance, including improving the electrodes' design to increase power density. This work aims to better understand the relationship between electrode microstructure and performance by studying four different commercially available carbon electrodes (two cloths and two papers) using a non-aqueous organic RFB.[1] A comprehensive study of pore-scale and mass-transport processes within these electrodes is presented to elucidate their effect on the cell performance. We combined electrochemical tests at incremental flow rates and two supporting solvents; electrode images analysis using X-ray CT and a customised segmentation technique to extract microstructural parameters; a pore network model to calculate the electrodes' permeabilities and a 1D model to obtain mass transfer coefficients. With many parameters relevant to the cell performance, it can be difficult to confidently assert causal relationships. A combination of microstructural and transport properties along with the operating conditions, such as electrode compression, will ultimately lead to the resulting performance. We observed that permeability was directly correlated with performance, while other microstructural properties were not good indicators. When using an electrolyte with higher viscosity a reduced performance was observed, possibly due to regions in the electrodes being starved or not replenished fast enough. In agreement with previous authors,[2,3] we found that the best performances are observed when using cloths demonstrated both by their higher permeability and mass-transfer coefficients. Their favourable microstructural properties are a result of the relatively large pore size and the periodic fibre alignment, which promote a more uniform distribution of electrolyte across the electrode. These woven materials have potential to be tailored to enhance inter- and intra-pore mass transport while maintaining high specific surface areas for fixed flow configurations and output requirements.

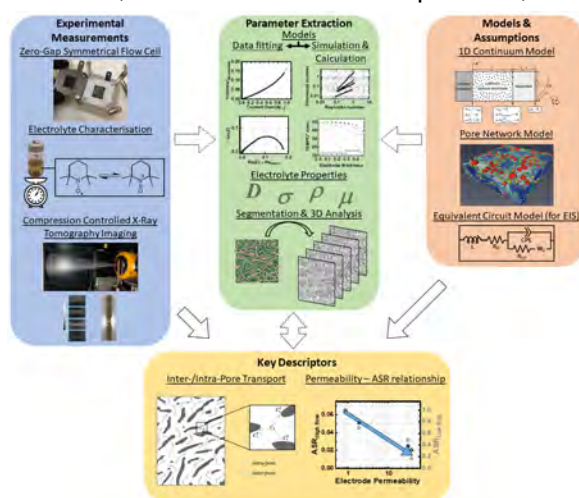


Figure 1: Schematic of different experimental and modelling tools and key performance descriptors.[1]

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2. Forner-Cuenca A.; Penn E.E. et al. *J. Electrochem. Soc.* **2019**, 166, 2230-2241.
3. Sadeghi M.A.; Aganou M. et al. *J. Electrochem. Soc.* **2019**, 166, A2121-A2130.

System-level performance modelling of regenerative fuel cells

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The redox flow battery (RFB), as an electrical energy storage (EES), could promote integration of renewable energy. Compared with the other EES, the RFB has advantages of superior lifetime, modularity, and the ability to decouple power and energy capacity¹. The all-vanadium redox flow battery (VRFB) is the most developed RFB, but it suffers from the volatile and high prices of the vanadium¹. Hydrogen regenerative fuel cells (RFC), such as the hydrogen/vanadium RFC (RHVFC) and the H₂/organic RFC, could offer pathways of cost reduction but the performances, such as energy efficiency and power density, need to be further improved to become competitive to the VRFB². A system-level performance model, consisting of a semi-empirical electrochemical physic model (integrated with a shunt current model), a hydraulic model and a steady-state thermal model, was built to analyse the RFC system-level power losses and round-trip energy efficiency, which is useful for system optimization. A 500-kW hydrogen/vanadium RFC multiple-stack system was chosen as a case study due to its relatively simple chemistry and data set availability. Later, the models could be applied to study other RFCs.

From the performance model, current distribution, flow rate distribution and temperature distribution throughout the cells in the system were obtained. It was found that the current was maximized at the middle cell and the flow rate decreased from the first cell to the last cell with a small inhomogeneity ratio (i.e., ratio of maximum flow rate to minimum flow rate) of 1.003. The temperature distribution was uniform among cells owing to the relatively large heat transfer coefficients between cells. Different energy losses, including the overpotential loss, shunt current loss, pumping loss and thermal management loss were assessed as well. Based on the result, the RHVFC case study could reach a round-trip energy efficiency of 71% with a constant current density of 0.072 A/cm² during both charging and discharging. The overpotential loss and the thermal management loss occupied the largest proportion of the total system energy loss during discharging and charging, respectively (Figure 1). A sensitivity analysis was carried out to analyse the relative importance of different factors, including design factors (e.g., cell active area) and operating conditions (e.g., temperature) on the RFC overall energy efficiency, which would give some insight into the possible pathways for performance enhancement.

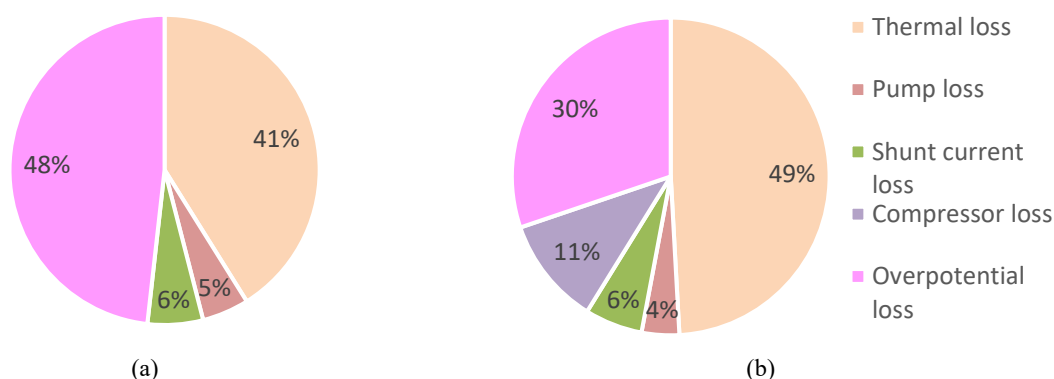


Figure 1- 500 kW RHVFC system energy loss distribution during (a) discharging (b) charging

1. Ponce de León, C.; Frías-Ferrer, A.; González-García, J.; Szánto, D. A.; Walsh, F. C., Redox flow cells for energy conversion. *Journal of Power Sources* 2006, 160 (1), 716-732.

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SESSION ABSTRACTS

9. PEM-Systems / Degradation

9.1 Modeling of Carbon Corrosion in PEM Fuel Cells applied to 3D Simulation	69
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Modeling of Carbon Corrosion in PEM Fuel Cells applied to 3D Simulation

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The catalyst support in PEM fuel cell catalyst layers is prone to corrosion due to the presence of water. Carbon support corrosion is strongly affected by the absolute value and the dynamics of the applied voltage. The strongest corrosion rates can be observed under PEMFC start-up conditions where the voltage can reach maximum peaks of 1.5 V or even higher. However, also below 1 V, during the normal fuel cell operating conditions, carbon corrosion takes place, although in a smaller magnitude.

The carbon corrosion model presented in this work is based on the formation of unstable carbon surface oxides and platinum hydroxyl groups [1]. It is implemented in a commercial CFD code [2] and applied to a 3D simulation of a four-serpentine channel PEM fuel cell with an active area of 50 cm² [3]. The obtained results are compared to measurements of steady-state and dynamic carbon corrosion rates. After a calibration of the reaction rates via reaction parameters (exchange current densities, equilibrium potentials, charge transfer coefficients) a good comparison between simulation and experiment in the whole investigated voltage range can be achieved. Figure 1 shows calculated vs. measured carbon corrosion rate for a voltage jump from 0.95 V to 0.5 V and back. Figure 2 shows the carbon corrosion rate distribution in the cathode catalyst layer at the highest peak (30 s). At the channel inlet (bottom) the rate maxima can be found below the ribs (higher humidity) whereas at the channel outlet (top) the rate maxima are located below the channels (larger local potential). Close to the channel inlet at the locations where the serpentes meet, gas crossover between the channel groups leads to local humidity drops, and consequently, to strong local carbon corrosion rate minima.

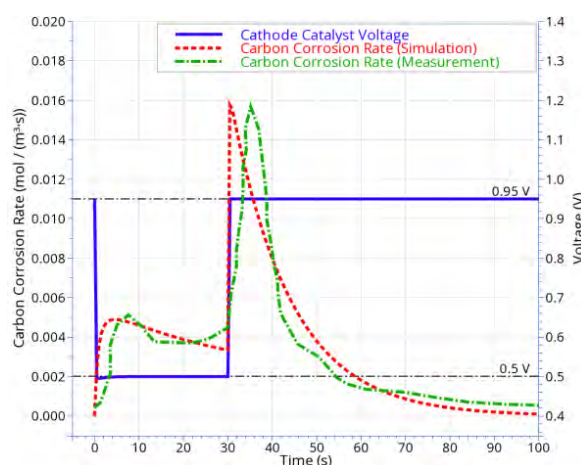


Figure 1: Calculated and measured [3] carbon corrosion rate for a voltage jump 0.95 V / 0.5 V and back.

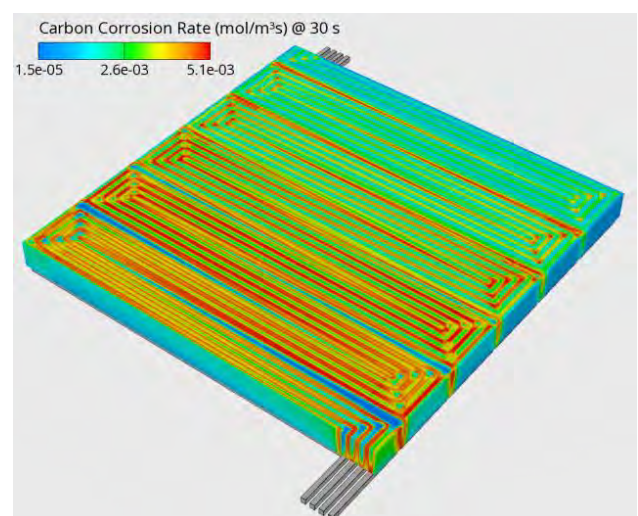


Figure 2: Carbon corrosion rate in the cathode catalyst layer at 30 s; CL thickness scaled by a factor of 200.

1. A. Kregar et al., *Appl. Energy* **263**, 114547, 2020.
2. AVL List GmbH, *FIRE™ M User Manual 2022 R2*, 2022.
3. N. Macauley et al., *J. Electrochem. Soc.* **165** (6), F3148, 2018.

Simulating Cathode Catalyst Morphology and Degradation on Porous Carbon Supports

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On the way to optimizing fuel cell performance and cost, it is vital to design the cathode catalyst layer (CCL) such that maximum catalyst utilization and lifetime can be obtained. In this context, highly porous carbon supports have come to play an important role as their composition of carbon primary particles with internal nanopores strongly increases the surface area on which catalyst particles can be dispersed. The ionomer distribution on these supports is still a matter of discussion, with some authors stating that catalyst particles inside nanopores are not contacted by ionomer while others provide evidence that the ionomer does penetrate the nanopores to a certain extent. At the same time, the local morphology such as the size and location of catalyst particles inside pores and on the support surface as well as their connection to the protonic network by water or ionomer is expected to have significant influence on the degradation behavior of the CCL in accelerated stress tests. In order to accurately capture the degradation of CCLs with variously porous supports, a model should therefore be sensitive to the local morphology determined by the given material composition and reproduce measured changes in morphology when degrading conditions are imposed.

To this end, we propose a distribution-based model framework composed of two sub-models. The first part is a morphology model which simulates catalyst and ionomer distribution on the support depending on the material composition and different support types from low to high surface area [1]. Input parameters for the model can be obtained from ex-situ experiments and include the primary pore size distribution of the support, particle size distributions for catalyst particles located within the support nanopores and on the support surface and the applied ionomer content. Depending on the encountered pore size, nanopores can be either blocked or impregnated by ionomer with according consequences for the protonic connection of the particles within. Further, protonic activation of particles inside pores due to capillary condensed water is taken into account. The model allows for the calculation of a variety of parameters which can be checked against measurements, for instance, the pore volume distribution of the support before and after Pt deposition and the protonically active catalyst surface area at different applied humidities. In this way, the begin of test morphology for different material combinations and conditions is validated and subsequently supplied to the second model part, a catalyst degradation model.

The degradation model simulates the impact of accelerated stress test conditions on the given CCL morphology, taking into account processes such as Pt dissolution into the ionomer and re-deposition onto the support (Ostwald ripening), Pt oxide and sub-surface oxide formation and Pt ion diffusion toward the membrane [2]. Next to the applied potential, these ageing processes are strongly dependent on catalyst particle size. The extent of degradation hence varies in different domains, e.g. on the support surface where comparatively larger catalyst particles can be found versus small primary pores which can only hold small Pt particles [3]. Consequently, the simulation results are sensitive to each unique Pt/C/ionomer system and exhibit good correspondence to measurement data. From the input material composition to the resulting degradation predictions, the model framework offers access to a large variety of parameters for validation against measured data as well as the possibility to analyse the impact of specific material properties on CCL ageing.

1. Scherzer, A.-C.; Schneider, P. et al. *Journal of The Electrochemical Society* **2022**, 169 (3), 034509. DOI: 10.1149/1945-7111/ac58c2
2. Schneider, P.; Sadeler, C. et al. *Journal of The Electrochemical Society* **2019**, 166 (4), F322. DOI: 10.1149/2.0881904jes
3. Padgett, E.; Andrejevic, N. et al. *Journal of The Electrochemical Society* **2018**, 165 (3), F173. DOI: 10.1149/2.0541803jes

Numerical Modelling and Simulation of Metal Interconnect Oxidation of SOC Stacks

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Solid oxide cells (SOCs) are particularly suited to convert energy between chemical and electrical energy, providing several advantages such as high efficiencies, the high temperature level unlocking sector coupling on the heat side, the capability of being reversibly operated, and the tolerance to various fuels. To accelerate commercialization, the degradation behaviours need to be alleviated. In addition to experimental investigations, numerical modelling can be a helpful assistance in studying degradation as it requires less time, effort and costs and can visualize the distribution of physical variables. Moreover, the electrochemical performance (e.g., IV-curves and U-t curves) can be predicted by the simulation.

In this work, a three-dimensional multiphysics model of a single repeating unit (one channel) of a SOC stack is built via the open-source software OpenFOAM based on the code of openFuelCell2 [1] in order to study performance and degradation phenomena. Main governing equations include the Darcy-Forchheimer equation for momentum transfer, Fick's law for species transfer and linear Chang-Jaffe kinetics for electrochemical reactions. Geometrical data and material properties are chosen based on the F10 stack design by Forschungszentrum Jülich [2]. Measurements derived from experiments with a stack of four layers (stack ID: F1004-115) were used for validating the model based on IV-curves in fuel cell mode and electrolysis mode (Figure 1). Thereby, operating temperatures of 700°C and 800°C, a fuel to water vapor ratio of 50/50 and an oxygen to nitrogen ratio of 21/79 were considered. The model accurately predicts the IV-curves in the range of current density from -0.5 to +0.5 A cm⁻². The open-source model is also compared with a similar model developed with the commercial software COMSOL Multiphysics (Figure 1). Again, a good agreement is found which supports the reliability of openFuelCell2. In addition, a time-dependent simulation considering the degradation of the metal interconnect (MIC) via oxidation is developed by using the ultra-thin-film resistance model. It is found (Figure 2) that this oxidation only contributes ca. 40 mV (around 10%) to the total degradation after ~100 kh operation (stack ID: F1002-97). Spatial distribution of overpotential and molar fractions of chemical species are present and their influence on degradation is discussed.

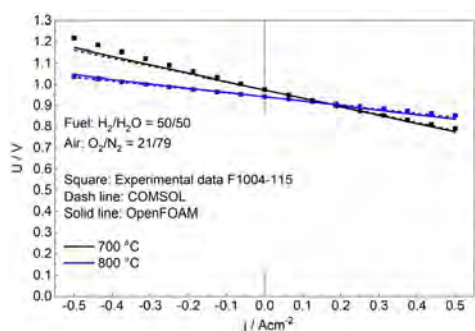


Figure 1: Comparisons between experimentally measured I-V curves, OpenFOAM simulation and COMSOL simulation.

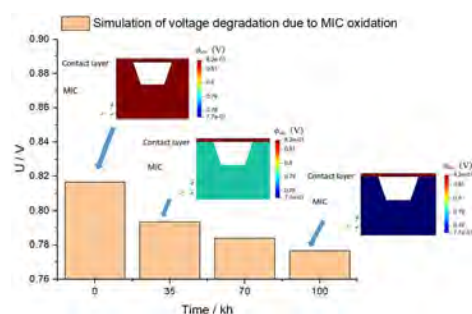


Figure 2: Simulation of the stack voltage evolution with time. The MIC oxidation is the only degradation. The inserted figures are the distribution of the electronic potential (ϕ_{ele}) across the contact layer and the MIC.

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Investigation of scaled-down fuel cell system components by means of the IPEK X-in-the-loop approach

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The design of the PEM fuel cell stack and the fuel cell system components are strongly dependent on each other. If changes are made to the choice of material or to the geometric parameters, the operation of the fuel cell and the fuel cell system can change tremendously. Currently, PEM fuel cell systems are developed for different transport solutions such as trucks, ships or air planes [1]. For each application, different power and load profiles lead to a different optimum in design for the fuel cell stack and the system components. Furthermore, the deep investigation of the interactions between the system components and the design parameters of the fuel cell stack are still not completely understood. A deep investigation of all relevant parameters is rather complex and requires a huge effort with respect to time and costs. In order to reduce this effort, one typical solution for developing PEM fuel cell stacks is to reduce the number of cells to investigate a representative repeating unit as a short stack. A further reduction to a single cell is usually challenging, as the boundary conditions such as thermal and mechanical parameters are difficult to set properly.

In this study, a possible solution will be presented on how the correct boundary conditions can be measured and applied to a single cell setup. Furthermore, this concept can be transferred to fuel cell system components, such as an air compressor or a hydrogen recirculation unit. It is shown how investigations of scaled-down components can be conducted by using a model-based testing tool based on the IPEK X-in-the-loop approach [2, 3].

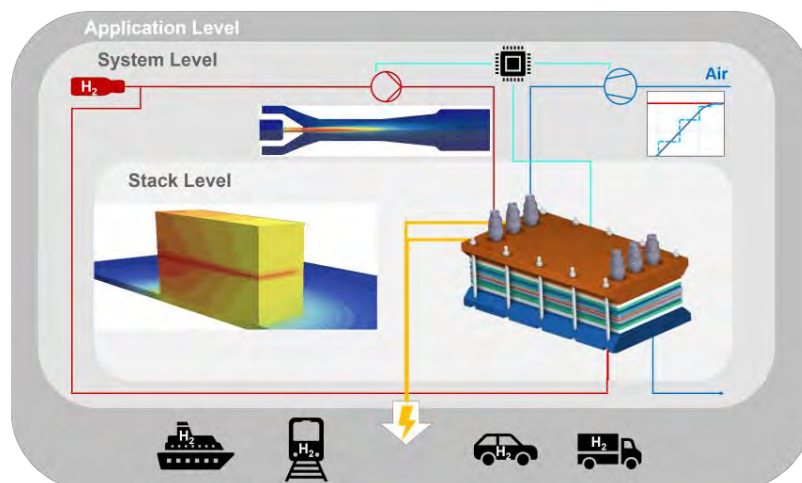


Figure 1: Testing of fuel cell systems with scaled-down components

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Studies on Operational and Failure Dynamics of a Phase-Change Cooled Aviation PEM Fuel Cell System using Flownex®

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Aviation is experiencing a clean, sustainable and electric transition. Among it, hydrogen-electric propulsion using Proton Exchange Membrane (PEM) fuel cells is being taken as the most competitive solution. A PEM fuel cell system mainly consists of the fuel cell stack, thermal management sub-system, power electric sub-system, air supply line and hydrogen supply line. Of them, thermal management has profound effects from components up to the system level and from microscopic, mesoscopic, to macroscopic phenomena, structures and performances.

For PEM fuel cells, our previous simulation work has secured their viability for aviation via a novel phase-change+heat-pump (PCHP) cooling design, by 1) an approximate 25% gain in their system power-to-weight ratio, as well as 2) plenty of heat exchanging surface area on an airframe is now guaranteed.

This current work is bridging between the above previous work on feasibility and building an experimental demo system planned as the next step, by detailing the cooling design parameters and proposing more refined alternative cooling loop arrangements, e.g., single-loop, double-loop, referring to cooling efficiency, system dynamics, fault tolerance among other core performance indices identified.

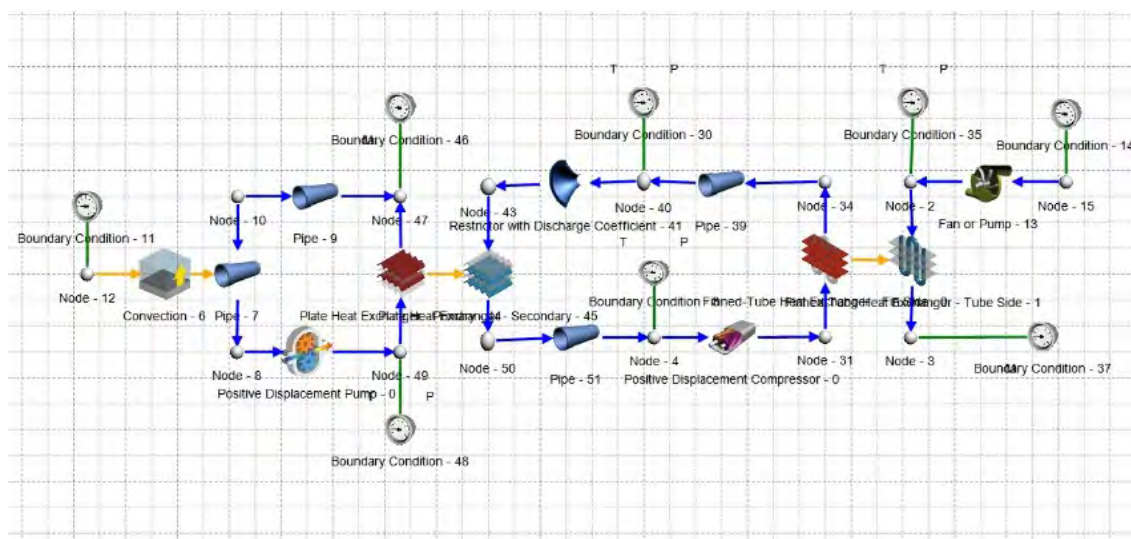


Figure 1: LC-PCHP cooling system modeling by Flownex®.

SESSION ABSTRACTS

10. AEM, PEM and Alkaline Electrolysis

10.1 Multiphase zero-gap electrode simulations for alkaline water electrolysis	75
10.2 CFD modeling of a PEM water electrolyzer: relationship between flow regime and performance	76
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10.5 Membrane electrode assembly simulation of anion exchange membrane water electrolyser	79

Multiphase Zero-gap Electrode Simulations for Alkaline Water Electrolysis

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Modern alkaline water electrolyzers for the production of green hydrogen often use electrodes that are directly pressed onto the diaphragm in a zero-gap configuration. Millimetre-sized holes allow gas bubbles to escape to the back-side, where they do not influence the ohmic resistance. Very few studies exist into what the hole size, shape, and open-area fraction of such electrodes should ideally be to maximize the energy efficiency [1].

Here we report electrode simulations that self-consistently take into account gas distribution and its interaction with the current distribution. A mixture model is used with hydrodynamic bubble dispersion that increases near an imposed maximum gas fraction. A secondary current distribution model with a Bruggemans relation for the effect of gas fraction on the conductivity is coupled to Butler-Volmer kinetics for the oxygen and hydrogen evolution reactions. Figure 1 shows the 2D development of the gas fraction profile and Figure 2 a close-up of the potential and current distributions around a simplified zero-gap electrode geometry. Using these simulations, we can for example understand the anomalously high resistance observed in many zero-gap electrolyzers [2, 3], study the effect of misalignment of the anode and cathode, and provide detailed understanding of the interesting interaction between gas fraction and current distribution.

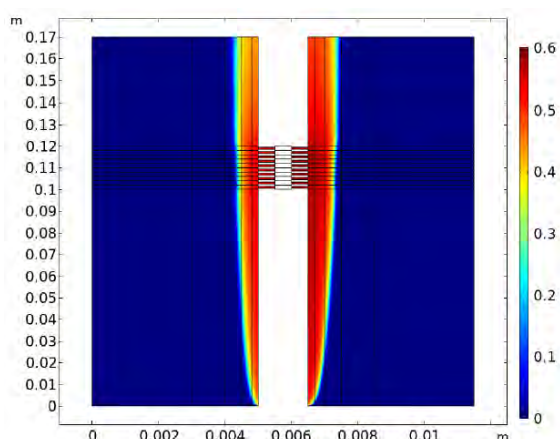


Figure 1: A 2D full cell simulation (stretched view) result for the gas fraction at 6 kA/m². The electrode structure is only resolved between 10-12 cm of height.

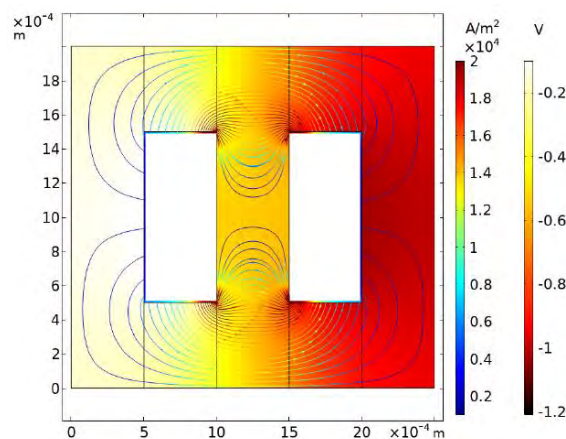


Figure 2: A close-up of the potential (coloured background) and the current density (coloured lines) in a simplified zero-gap electrode geometry.

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CFD modeling of a PEM water electrolyzer: relationship between flow regime and performance

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The relationships between operating conditions, two-phase flow regime in the anode channel, and performance of a polymer electrolyte membrane water electrolyzer (PEMWE) is not well understood. These relationships are important for optimizing cell operation in view of power consumption and stability. To address this issue, a model for the interplay of the relative velocity between the two phases and the bubble diameter in the anode channel is developed. It accounts for the effect of current density on the bubble diameter using fitting to experimental data as input [1]. This model is coupled with the electrochemical kinetics in catalyst layers to perform 3-D computational fluid dynamics (CFD) simulations of a PEMWE (Fig. 1) in the open-source platform OpenFOAM. The operating point is defined by the average area current density i , and the water stoichiometry λ . The two-phase flow regime is quantified by the normalized flow regime number, frn^* , and the cell performance is characterized by the cell voltage, U . The model is compared to the experimental data of two-phase flow reported in Ref. [2]. Results show that the frn^* provides a criterion to distinguish the three main flow regimes (bubbly, plug, and slug). Simulation results help furnish relationships between operating point, flow regime and cell performance. The best cell performance (lowest cell voltage) is found to occur at the highest water stoichiometry, $\lambda = 1000$, in simulations, where the bubbly flow regime prevails for current densities from 0.1 A/cm² to 2.0 A/cm². Slug flow with the highest value of frn^* appears at 0.8 A/cm² with the lowest water stoichiometry 100 (Fig. 2) due to the high oxygen volume fraction. Among other findings, it demonstrates that the water stoichiometry should be increased to decrease cell voltage and oxygen bubble sizes in the anode channel. This work provides important basic trends and limiting values for cell operation.

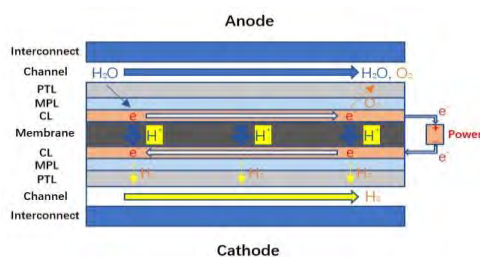


Figure 1: Principle and physical structure of the PEM electrolyzer model (dead end of cathode inlet)

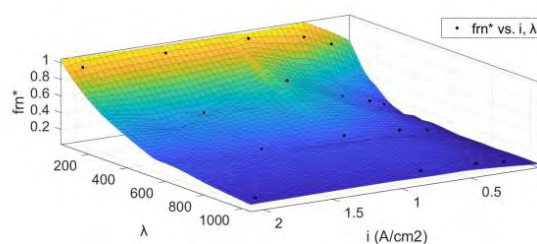


Figure 2: Relationship between operating point and normalized flow regime number

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Transient hydrogen crossover in dynamically operated PEM water electrolysis cells - a model-based analysis

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Hydrogen crossover in polymer electrolyte membrane electrolysis cells is important concerning faradaic efficiency, flammability hazards, and degradation phenomena. Steady-state measurements have shown that the hydrogen crossover increases with current density, due to mass transport limitations in the cathode catalyst layer. This work, however, is the first to investigate hydrogen crossover during dynamic operation, using a comprehensive dynamic 1-D model. The model includes the distributed dynamic mass and charge balances along the sandwich coordinate, including the channels, with a focus on the detailed description of the reaction and mass transport dynamics of hydrogen in the membrane electrode assembly. Simulated down steps in current density, lead to transient overshoots in the H₂-in-O₂ content at the anode side. The membrane acts as short-term mass storage for the dissolved hydrogen, and mass transport lags the instant response of the current density. This phenomenon is influenced by the current density step size, pressure, temperature, membrane thickness, cathode catalyst hydrogen mass transport resistance, anode water flow rate and the flow-channel height. Under specific conditions with high cathode mass transport limitations, the lower explosion limit of H₂-in-O₂ can be transiently exceeded. This work provides for the first-time insights into transient hydrogen crossover phenomena and is a further step into dynamic model-based analysis of polymer electrolyte water electrolysis cells.

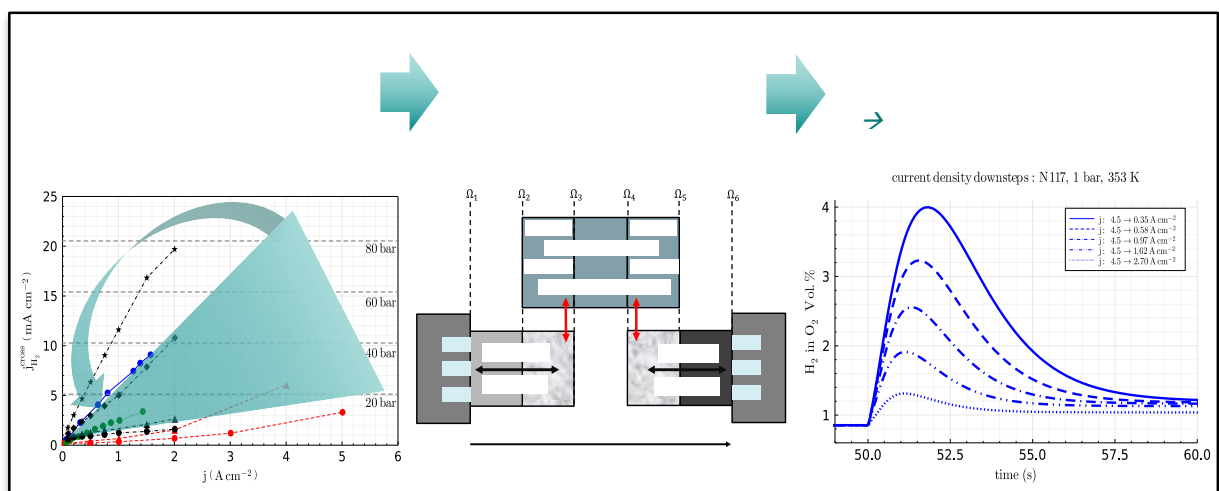


Figure 1. Transient hydrogen crossover from steady-state measurements to the modeling and simulation of current density down steps.

Structure-Performance Relationship of IrO₂ Nanoparticles during Oxygen Evolution: Investigation by Dynamic Microkinetic Modeling

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PEM water electrolysis promises high conversion rates of electrical energy into the chemical energy carrier hydrogen. High overpotentials, however, need to be overcome to achieve sufficient conversion, caused by the slow kinetics of the anodic oxygen evolution reaction.^[1] Highly active electrocatalysts, e.g. IrO₂, are used to enhance the performance. Yet, they frequently suffer from degradation. In order to improve activity and stability, an inherent understanding of the reactions at the electrocatalyst is required. Model-based analysis and optimization is a suitable tool to provide insights into the thermodynamics and kinetics of reaction processes and states, which cannot be determined experimentally, and thus, enables us to provide solutions for catalyst and electrode optimization.^[2]

In this work, differently structured IrO₂ catalysts were investigated by a dynamic microkinetic model. All catalysts were prepared by flame spray pyrolysis and afterwards calcined at different temperatures, which resulted in different crystallographic structure, crystallinity, and morphology.^[3,4] By modeling and validating cyclic voltammograms (CV) with experimental data, we can show the influence of calcination temperature on the reaction kinetics, surface coverages of the adsorbed species as well as detailed thermodynamics.

Our work shows that increasing calcination temperature does not change the limiting processes, and trends in the reaction free energies (G_r^0) of the elementary steps. Nevertheless, the value of ΔG_r^0 for the oxygen desorption in step 7 is lower for the less calcined IrO₂ catalyst. This refers to a faster oxygen evolution and thus leads to a higher performance. All in all, the method provides important insights into the effects of synthesis conditions and catalyst structure on performance, as well as valuable insights for optimization.

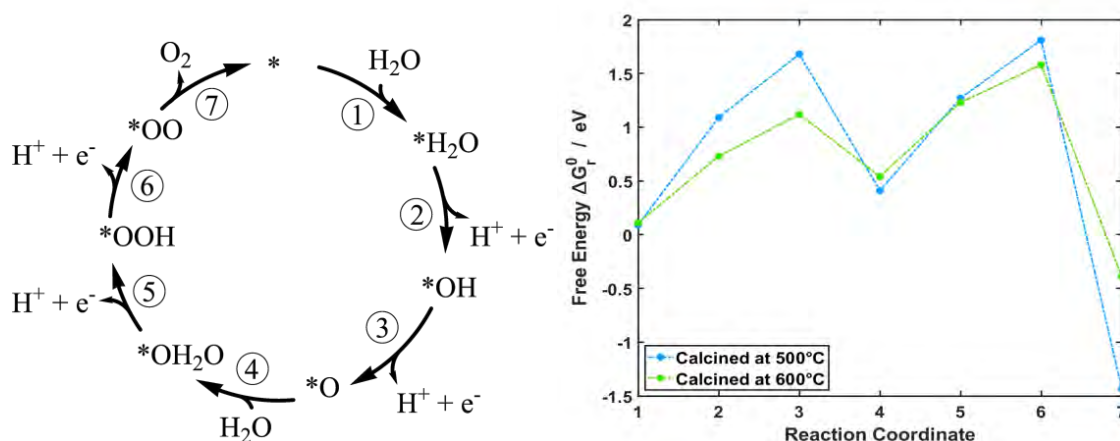


Figure 1: OER mechanism of the IrO₂ catalyst (left), identified reaction free-energy parameters for the reaction steps 1–7 at electrochemical standard conditions of $\alpha = 1$ and $T = 25^\circ\text{C}$. (right).

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Membrane Electrode Assembly Simulation of Anion Exchange Membrane Water Electrolyser

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Anion exchange membrane water Electrolysers (AEMWE) have gained prominence recently with their ability to replace platinum group materials (PGM) with non-PGM catalysts, which are Ni, Fe, and Mo based. However, more mathematical models must be explored involving membrane electrode assemblies of AEMWE. Currently, the Sustainion X-37 50 membrane series have been vastly explored for water electrolysis with a proven durability study¹. In this study, SS316L Fibre felt, and moulded graphite layer (MGL370) are used as anodic and cathode substrates, respectively, to develop a numerical model using COMSOL[®] 6.0 fuel cell and electrolyser module. The membrane electrode assembly (MEA) architecture consists of MGL370-NiFeCo || X37-60RT || NiFe₂O₄-SS316L as layers.

Stationary and time-dependent two-phase studies have been performed for the 1D, 2D, 3D and 3D MEAs with and without flow channels. A base case for the model is established, where the cell is operated at 60°C, 1 M KOH and atmospheric pressure. Polarisation curves and electrochemical impedance spectroscopy have been simulated based Butler-Volmer equations and a standard AEMWE equivalent circuit model², respectively. An attempt is made to verify the simulation with experimental measurements. The exchange current densities of the catalysts in aqueous KOH were calculated based on rotating disk electrode (RDE) measurements and adapted to the model.

A model-sensitivity analysis on i) Membrane Thickness, ii) Temperature, iii) KOH Concentration, iv) applied Current Density iv) Wet and Dry Cathode feeds have been performed. Finally, the sensitivity parameters have been ranked based on changes in the HHV Efficiencies.

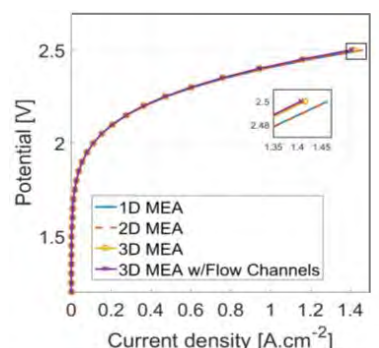


Fig 1: Simulated JV Curve

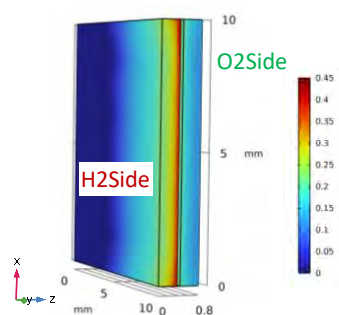


Fig 2: 3D MEA Gas Fraction

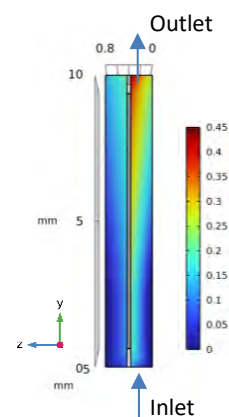


Fig3: 2D Gas Fraction

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SESSION ABSTRACTS

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Noninvasive Local Impedance Determination in Polymer Electrolyte Fuel Cells Stacks

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Water management in polymer electrolyte fuel cells (PEFC) needs to ensure a homogeneous membrane humidification without local dryout or flooding from inlet to outlet of cell with active areas of some hundreds of square centimeters. Existing measurement methods that are able to provide spatial resolved information on the current density, membrane conductivity or water content distributions of PEFCs are usually invasive and therefore difficult to use in actual applications. Based on the learnings of the development of electrical impedance tomography (EIT) for PEFCs [1], a new method is presented that is capable to determine 1D humidity profiles between the gas inlet and outlet in a 6-cell commercial stack [2,3]. Local AC current injections and voltage measurements are performed using electrodes positioned all around the fuel cell attached to the flow field plates (see Figure 1a). Each electrode combination characterizes a specific area of the cell as the current crosses the membrane electrode assembly (MEA) very locally.

The presentation will discuss the calibration of the local impedance values, the sensitivity of the approach to relative humidity (rH) gradients in the cell (see Figure 1b) and present use cases of measurements during fuel cell operation. Finally, we will present results on multiply frequency AC stimulation that allows local electrochemical impedance measurements and thereby insights beyond membrane conductivity, i.e. into mass transport limitations due to water accumulations in the cell.

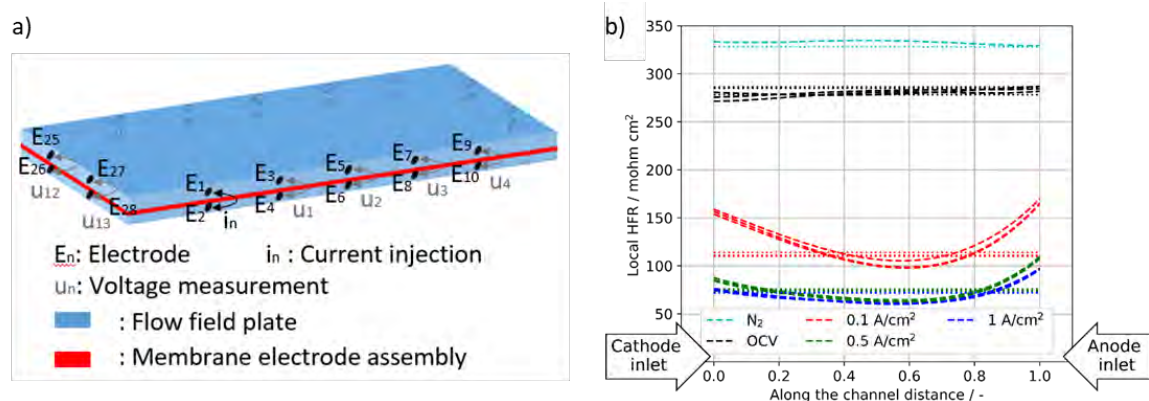


Figure 1: a) Scheme of simplified PEFC geometry with electrodes locations at the flow field's outer surface that are used for current injection (black arrows) and potential measurements (gray arrows) in varying combinations during data acquisition; b) Determined distribution of the cells high frequency resistance for different stack operating conditions (temperature 70°C, RH inlet & outlet 50%).

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Experimental and modelling analysis of liquid water and current density distribution in a PEMFC stack.

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In this work, a broad experimental and modelling analysis of an in-operando PEMFC stack for automotive application is proposed. Neutron imaging is used to quantify liquid water distribution for several operating conditions. Current density and temperature distribution in the stack are probed using specific segmented high surface sensors. A pseudo 3D two-phase flow model coupling all the electrochemical and transport phenomena supports the understanding of the relationship between all these parameters. The model is able to predict qualitatively the quantity of liquid water at anode and cathode side. Moreover, fluid flow directions of the stack have a major influence on liquid water distribution. As a general trend, it is observed that the average total water thickness always decreases when current density increases, in all tested stack flow configurations. Furthermore, a clear relationship is noticed between flooding, cathode pressure drop and cathode liquid water content. Finally, a detailed analysis is proposed to explain the flooding phenomena, in order to improve the fuel cell stack control.

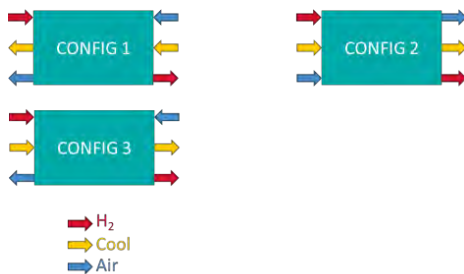


Figure 1: Stack flow configurations

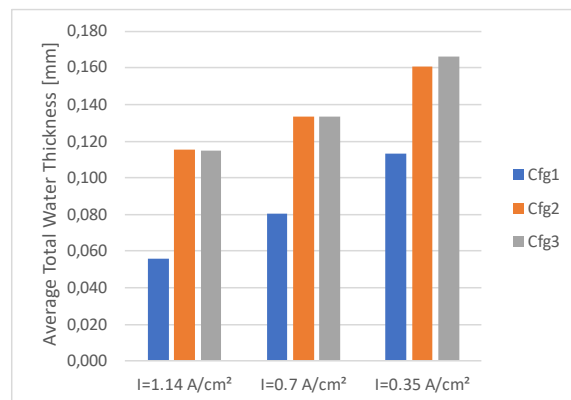


Figure 2: Average total water thickness vs current density

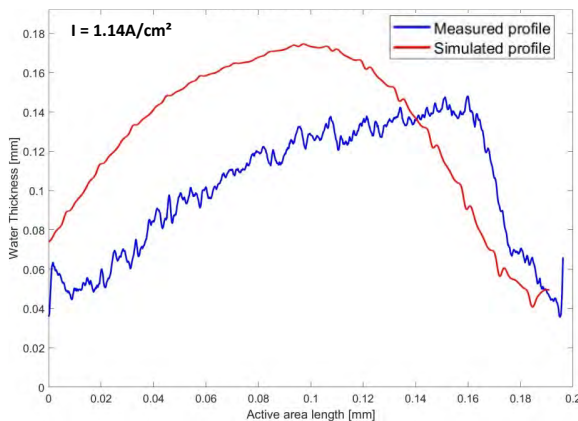


Figure 3 : Water profile @ I = 1.14 A/cm² (Cfg3)

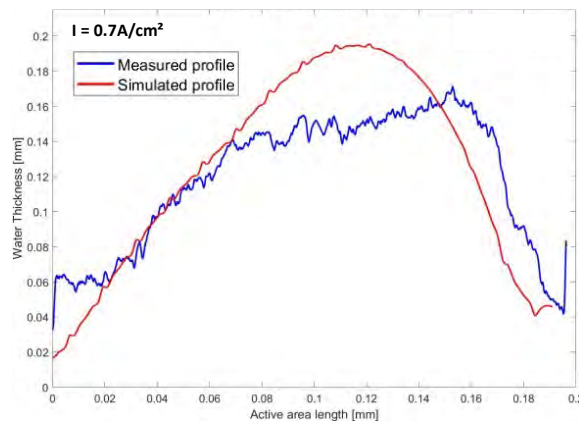


Figure 4 : Water profile @ I = 0.7 A/cm² (Cfg3)

Spatial Distribution of Loss Processes in PEMFC

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The operation of large-scale polymer electrolyte membrane fuel cells (PEMFC) inevitably leads to significant spatial gradients in operating conditions along the gas channels. Depending on the local operating conditions, the physico-chemical processes and the related resistances, determine the local performance. The identification of performance-determining and degradation-accelerating cell states enables specific conclusions on the optimization of components design and operating strategy. A profound understanding of the spatial distribution of resistance and their dependencies is essential. Integral measurement and analysis methods reveal only information about the overall cell behaviour averaged over the entire cell area. Considering impedance spectroscopy the individual loss processes are broadened and it is hardly possible to deconvolute them in detail.

We address this challenge by an impedance-based methodology that enables a spatially resolved deconvolution of resistance contributions along the channel. This is realized by electrochemical impedance spectroscopy (EIS) and an impedance data analysis by the distribution of relaxation times (DRT) [1,2], on a segmented cell. By fitting the measurement data to a physically motivated transmission line model, the loss process-related resistances can be determined as a function of the operating conditions [3].

In this contribution an experimental analysis of ohmic, charge transfer and ionic resistance will be presented. The impact of operating conditions such as relative humidity and current density on resistances and their distribution along the gas channels will be discussed. Furthermore, it is shown how an impedance-based, multi-physical DC-performance-model [4] can benefit from these results.

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Electrochemical pressure impedance spectroscopy for PEM fuel cells: Model-based signal interpretation

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Electrochemical Pressure Impedance Spectroscopy (EPIS) is currently being investigated as a promising method to study mass transport processes in PEM fuel cells [1]. It describes the cell voltage response to a harmonic excitation of the gas phase pressure in the frequency domain, which creates distinct signal features in the frequency range between 1 mHz – 1 Hz [2-5]. Experiments showed that the signal changes with operating conditions and structural changes of the fuel cell and thus contains information about mass transport processes. However, so far there is only limited qualitative and no quantitative understanding of the origin of the observed EPIS features. Yet, this is necessary to draw further conclusions from measured spectra.

In order to assess the origin of EPIS features and improve interpretation, we used a pseudo-2D model of a polymer electrolyte membrane fuel cell (PEMFC). We extended state-of-the-art modeling by additionally considering the effect of the gas volume inside the humidifier. With this approach we were able to reproduce published EPIS experiments at moderate current densities [6]. Based on a detailed analysis of the pressure dynamics, we could trace the main features of the signal back to the oscillation of the inlet flow rate. Furthermore, we simulated the separate influence of time-dependent fuel cell processes on EPIS by appropriate model configurations. As main conclusion, EPIS features of transport processes within the cell are largely masked by the EPIS response of the humidifier.

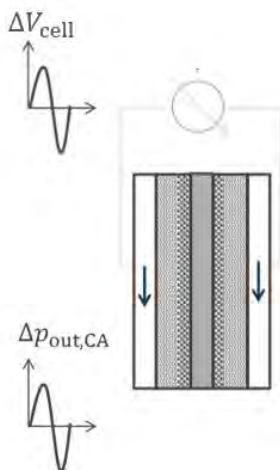


Figure 1: EPIS scheme

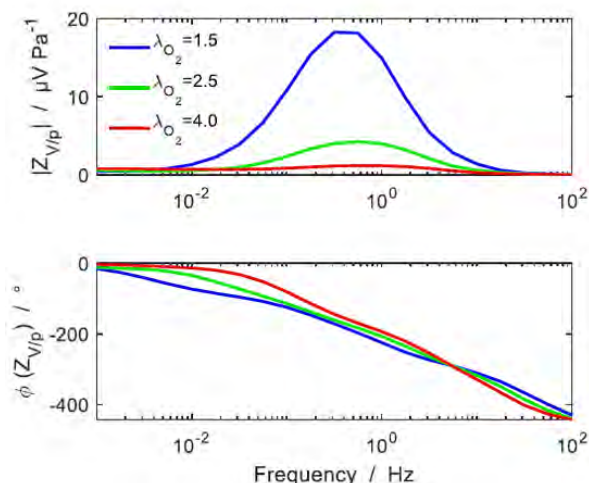
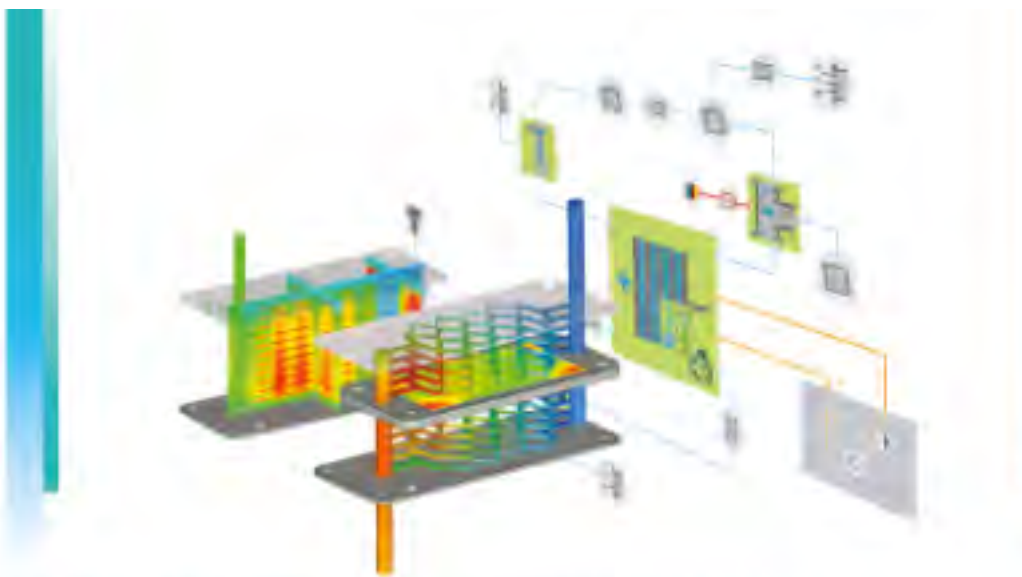


Figure 2: EPIS signal in Bode representation

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- Develop safer, more efficient operating strategies under all conditions



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Machine Learning for the Characterization of Fibrous Gas Diffusion Layers

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The permeability of gas diffusion layers (GDLs) depends on their micro-structure, and is relevant for transport simulations at higher scales, e.g., fuel cells and stacks. Given the micro-structure's qualities, the permeability can be obtained using transport simulations [1], which typically require large computing resources.

Drawing on previous published simulations [1] of the gas flow through fibrous GDLs, a convolutional neural network (CNN) was trained [2, 3]. The underlying data were based on a stochastic geometry model that also featured different binder models and compression levels. A small number of micro-structures – 541 – was sufficient not only for achieving good accuracy of the predicted permeability but also for reproducing the binder type as a hidden feature that was not explicitly trained.

The calculation of the permeability of the micro-structures required high-performance computers (HPCs), with the training of the CNN also requiring significant computational resources, preferably GPU-based ones. With a trained CNN, the permeability prediction can be run on a standard computer.

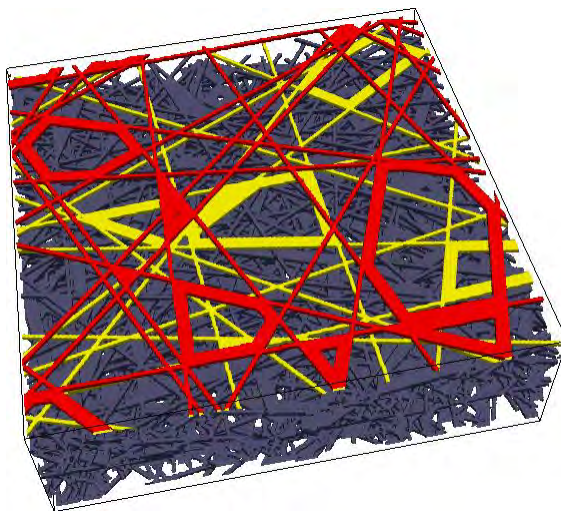


Figure 1. One of the stochastic micro-structures from [1], with two fiber layers highlighted.

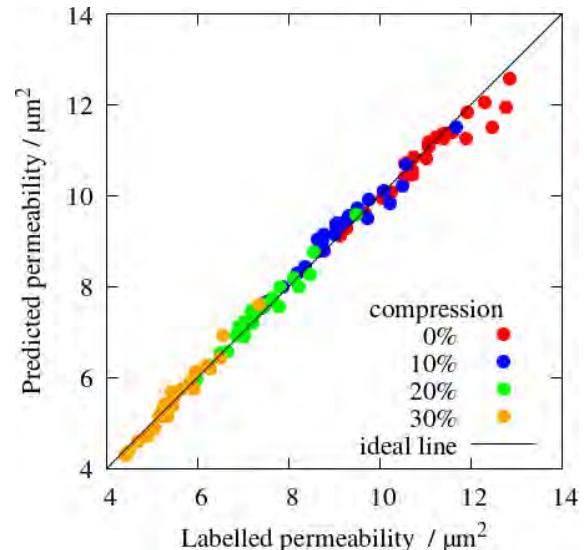


Figure 2. Permeability calculated by transport simulations [1] and predicted by a neural network [3].

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Multiscale simulation of nanostructured electrocatalytic systems by coupling neural network surrogates and continuum models

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The kinetic Monte Carlo method (kMC) is a physically well-justified approach for addressing the kinetic interplay of elementary processes at electrocatalytic surfaces but also comes at high computational costs. Therefore, computationally efficient surrogate models are highly desirable which allows the utilization of kMC simulation results at the much coarser scale of electrochemical devices.

Using the oxygen reduction reaction on Pt(111) as a prototypical example, we investigate regression neural networks as surrogates to reproduce the stationary TOF as a function of all reaction conditions, i.e. electrostatic potential, concentrations, and temperature (Fig. 1). We found that a relatively shallow network implemented using the Julia package Flux.jl serves as an appropriate choice. This surrogate is then coupled to a conservative and thermodynamically consistent Finite Volume discretization of a nano-fluidic model implemented on top of the Julia package VoronoiFVM.jl. The resulting hybrid meso-scale model will be employed to discuss the interplay of the nanostructure, transport, and kinetics.

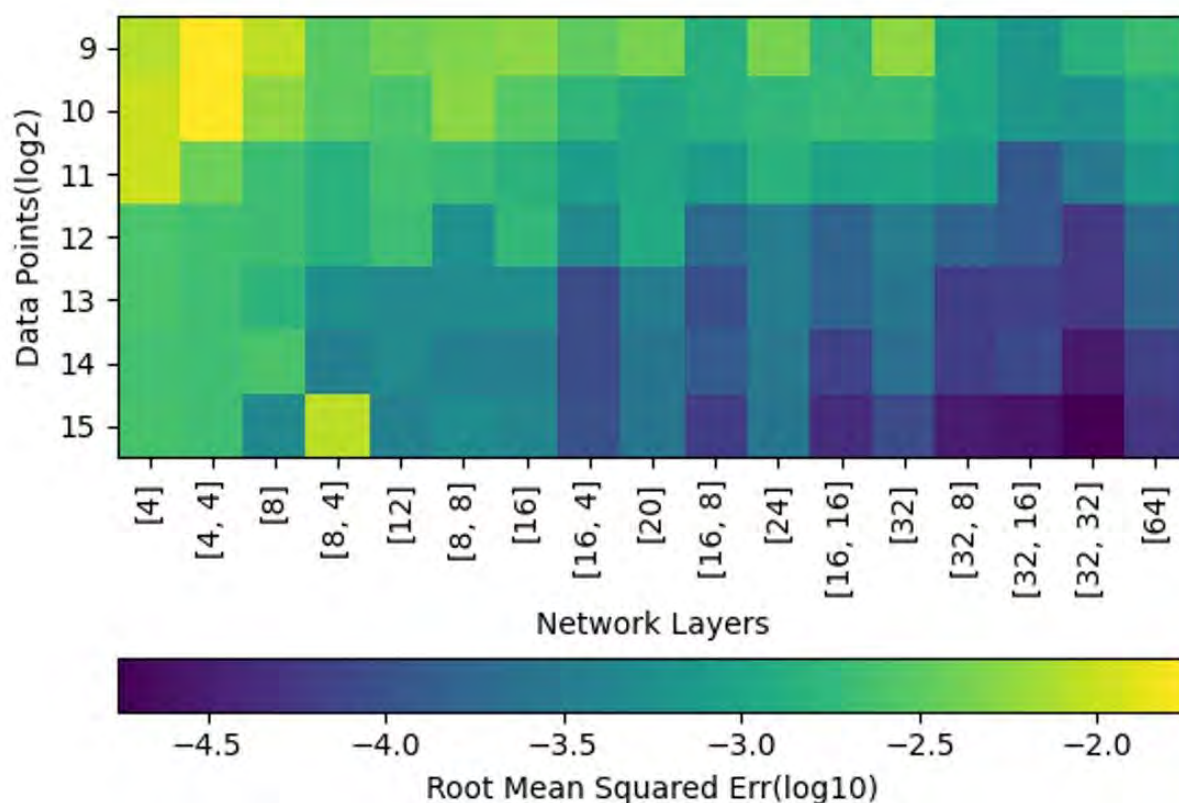


Fig. 1: Root Mean Squared Error obtained for different network structures and varying number of training data points provided by kMC simulation of oxygen reduction reaction on Pt(111). The network output is scaled in [0,1]. The activation function used for neurons is Sigmoid Linear Units(SiLU).

A coupled diffusion-mechanics model to investigate the interfacial mechanical damage at the microscale in block copolymer-based solid-state battery cathodes

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All-solid-state batteries (ASSBs) present safety advantages over more traditional Li-ion batteries with liquid electrolytes. However, ASSBs usually exhibit insufficient cycling performance due to the mechanical damage. Interfacial mechanical damage at the microscale between different ASSBs' material components can lead to the fading of battery performance during the charge/discharge process. Hence, minimizing the interfacial damage in ASSBs is a vital issue. Polymers are one of the most commonly used materials in ASSBs electrolytes. Use of block copolymers (BCPs) in ASSBs is an alternative way to improve both mechanical and conductivity properties. In this approach, the polymer comprises of a soft component enhancing the ionic conductivity and a hard component improving the structural integrity.

In this study, a computational diffusion-mechanical model is developed to investigate the effect of BCP (soft to hard component ratio) and interfacial strength on the interfacial debonding between the cathode's NMC particles and surrounding matrix at the microscale. In this model, a pressure dependent Fick's law is introduced to consider the diffusion-deformation interaction in the bulk. Moreover, a phenomenological diffusion-deformation coupling at the interface takes into account the interactions between interfacial gap and diffusivity. The model is implemented in the ABAQUS implicit solver and its user subroutines (UINTER, UMATHT, UMAT and UXTERNALDB).

The simulation results show that both the polymer's elasto-visco-plastic behaviour and the interfacial strength have a significant impact on the interfacial damage. Hence, both material characteristics must be taken into account when designing future ASSB cathodes based on polymeric materials components.

Advancement and validation of OpenFOAM PEMFC toolbox on automotive PEMFC design

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In the meantime, Computational Fluid Dynamic (CFD) methods are standard application within the development process of fuel cell stacks. Design variations can be implemented in short time, which leads to a significant reduction of development costs. Moreover, advanced models including the relevant physico-chemical processes can contribute to a deeper understanding of fundamental mechanism within fuel cells. Commercial CFD codes like ANSYS FLUENT® offer such special modules including electrochemical (Butler-Vollmer equation), membrane and liquid water transport models. But also some PEMFC models for open source CFD software OpenFOAM® are available, e.g. openFuelCell project [1]. The advantage of these models are the free availability based on the GNU General Public License and the possibility of user defined code implementations.

In this work the OpenFOAM® PEMFC toolbox of Kone et al. [2] is analyzed and further developed. This toolbox is a 3-D, non-isothermal and single-phase flow model of a complete cell including bipolar plates (BPP), GDL and CCM. The electrochemical processes are modeled at the cathode catalyst (CL) layer membrane interface. Further improvements are the implementation of MPL and coolant channel, improved modelling of membrane humidity plus modification of cathode and anode activation overpotential. A schematic structure of the model is illustrated in figure 1.

Simulations are performed on an automotive PEMFC Design. Simulation results are compared to similar simulation using PEMFC module of commercial CFD Software FLUENT®. Validation are done by experimental results (polarization curve, S++ device) of automotive short stacks. The improved OpenFOAM PEMFC toolbox shows good agreement to experimental data and similar results to ANSYS Fluent PEMFC module.

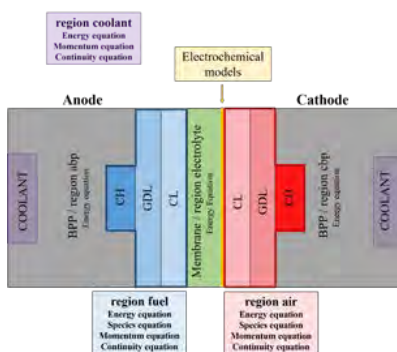


Figure 1: schematic structure of OpenFoam PMFC toolbox

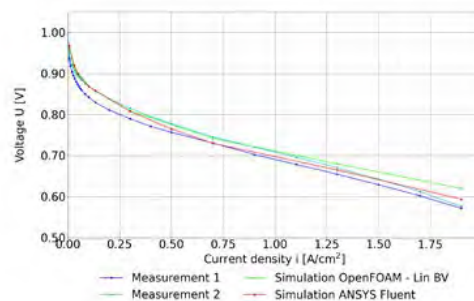


Figure 2: U-I-curve comparison of simulation and experimental results

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Particle based computation of mechanics in granular multiphase electrodes including different material behavior

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To be able to improve the cell performance of a lithium-ion battery, the interaction of individual particles of the granular cathode, which make up its overall material behavior, must be investigated. These include the elastic active material, which defines the main part of the granular structure and the viscoelastic binder, which is localized in their pore space. Discrete element method can be used to simulate the calendaring step of the electrode production. It realizes a mechanical compression by numerical simulations with which the packing state and the stress state of the structure can be calculated. In the DEM scheme, each particle is identified as a discrete element. Random packing algorithms can build an initial model with periodicity in all spatial directions and an overlap free particle system. Rheological models are used to describe the real contact behavior of the individual particles. The interaction between elastic active material particles is described by the Hertzian law [1], which represents the behavior of a nonlinear spring. The viscoelastic mechanical behavior of the binder with a special focus on the rate-dependence is realized by the Maxwell-Zener model, a combination of two nonlinear Hertzian springs and a linear dashpot [1,2].

A contact model which contains the elastic and viscoelastic behavior is realized by two core-shell particles (Fig.1). One single particle is defined as an overall spherical particle with an inner elastic sphere as the active material and a viscoelastic shell representing the binder. Due to the time-dependence of the binder, a dynamic DEM-routine is used [2]. We present the idea of splitting the contact force of two core-shell particles into a part which describes the influence of the elastic core and a second term which has the information of the shell. We use modifications of the known rheological models [2]. These investigations are compared to a finite element reference model implemented in AbaqusCAE [3].

Keywords: lithium-ion battery, discrete element method, electrode structure, material behavior, core-shell particle.

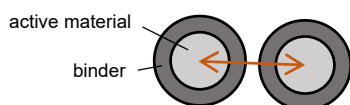


Fig. 1: idea of an interparticle core-shell contact models

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Post Mortem Analysis of the Same/Different Degradation Mode Cells Identified by Modified Degradation Mode Identification Technique

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In a previous article, a modified degradation mode (DM) identification technique (by employing incremental capacity curve) was proposed [1]. Later, the results of the technique were verified by other techniques, such as electrochemical impedance spectroscopy (EIS) and differential voltage analysis (DVA) [2]. However, EIS and DVA could not validate the modified DM identification technique directly as EIS and DVA do not provide sharp peaks as incremental capacity (IC) curves. Thus, further investigation (by postmortem analysis) was done on the cells classified as similar (or different) DM cells using a modified DM identification technique. The most pertinent DM of the cells were identified by matching their IC curves at the end of first life. It is believed that the IC curves of the cells are identical when their degradation is identical [3]. If degradation is identical, then their physical changes inside the battery are expected to be identical. Therefore, it is anticipated that when a set of the same DM cells is opened, their physical conditions might be the same. To observe the electrodes of identical (or different) DM cells, Cell i - viii are opened.

DM of the Cell i-viii was identified by employing the modified DM identification technique [1]. Initial visual inspection suggests that degradation marks are highly visible in the negative electrode, and no remarkable sign of degradation is observed in the positive electrode. To match the electrode images, several visual criteria were selected. The visual criteria were selected based on the colour and shape changes of the degradation mark among the negative electrodes. When the visual criteria of the whole electrodes are similar, the electrodes are considered visually similar. Visual criteria and electrode images of the cells suggest that though the DM of Cell i, ii & v and iii & vi are similar, their visual criteria are not similar. In contrast, the visual criteria of Cell vi & vii are similar. The dissimilar visual criteria of Cell i, ii & v and iii & vi and the similar visual criteria of Cell vi & vii may be due to the ageing history of the cells. The ageing history of Cell i, ii & v and iii & vi was different, whereas the ageing history of Cell vi & vii is similar. Thus, electrode images of the cells suggest that physical changes of the electrodes is also dependent on the ageing history of the cells along with the SoH and DM of the cells.

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The “square plot”: a graphical heuristic to visualise Li-ion cell stoichiometry and aging

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Li-ion cell state depends on the extent of lithiation (stoichiometry) at the two electrodes; in turn, the extents of lithiation for each electrode in the limits SOC = 0% and SOC = 100% evolve during aging. As a result, electrode balancing and degradation mechanisms can be interrogated by differential analysis of galvanostatic charge–discharge data (dQ/dV and dV/dQ plots), wherein peaks and troughs reveal characteristic lithiation processes attributable to the two (or more) active materials in a cell [1–4].

A novel graphical heuristic is introduced – the “square plot” [5]. In this plot, the extent of lithiation of the negative electrode is plotted against that of the positive electrode. Possible states of a cell in a given aging condition form a straight ‘charging line’. Voltage and differential analysis data are then overlaid.

The purpose of the square plot is to aid qualitative reconstruction and interpretation of dQ/dV and dV/dQ data, using single-material properties obtained either from half-cell measurements or from a literature database. Direct visual analysis of the square plot reveals the expected evolution of differential analysis signatures due to different degradation mechanisms, such as loss of accessible active material (LAM) from either electrode, or loss of cyclable lithium inventory (LLI) due to parasitic reactions. Various different rules and nomenclature conventions introduced in prior literature are rationalised.

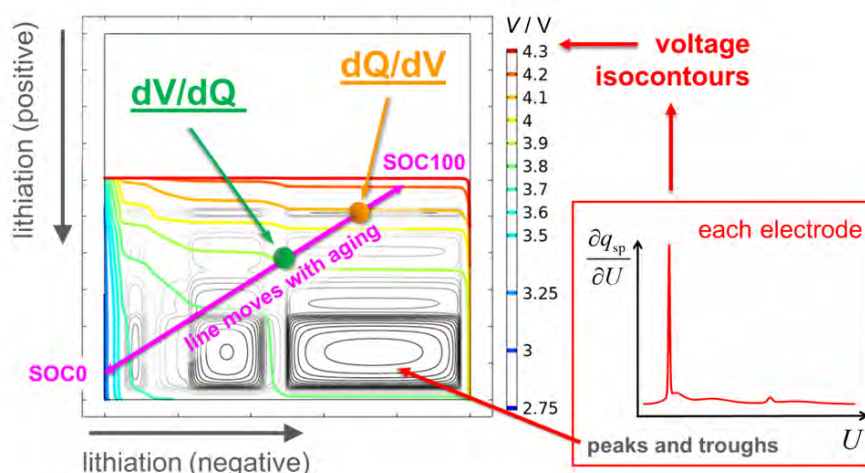


Figure 1: Schematic of the square plot (data for an LCO|graphite cell) [5]. The charging line (pink) is the locus of possible cell states for a given aging condition. Superimposed greyscale data indicates dQ/dV intensity, derived from single-material data for each electrode. Charging line intersections with a greyscale peak indicate dQ/dV peaks (orange dot); charging line intersections with a greyscale trough indicate dV/dQ peaks (green dot).

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Applying Experimental and Numerical Thermal Runaway Results on Thermal Propagation Processes

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Due to the rising importance of energy storage, lithium ion batteries have recently been in the focus of researchers around the world. Advances in battery active materials, especially cathode materials with high nickel content, have led to higher energy densities, which is beneficial for mobile application [1]. However, this comes at the cost of lower thermal stability, making further investigations on thermal runaway risks and mechanisms necessary.

This work is located in the project Agilobat. Main goal of this project is the build-up of a highly flexible battery cell production for cells of various types, sizes and shapes [2]. This requires a quick evaluation of a battery's safety risk due to thermal runaway. Therefore, a numerical tool for safety assessment of lithium ion batteries is developed.

In order to achieve this a chemical model was built. A list of 9 reactions represents the decomposition of battery components such as SEI, anode and cathode active materials, conducting salt and electrolyte solvent. Coupled with a thermal simulation this allows to obtain detailed data on thermal runaway onset and peak temperatures of the cells under testing. In addition, the chemical model provides amount and composition of liberated gases.

For validation, battery cells with different capacities but same cell chemistry were tested under thermal abuse conditions. The cells were heated with a constant heat rate until the thermal runaway event. The used test rig is equipped with temperature and pressure sensors and gas analysis.

The numerical and experimental results of these studies are used to predict thermal runaway and propagation behaviour of cell assemblies and modules. These predictions can be used to dimension safety measures such as heat shields for the battery packs designed in the project.

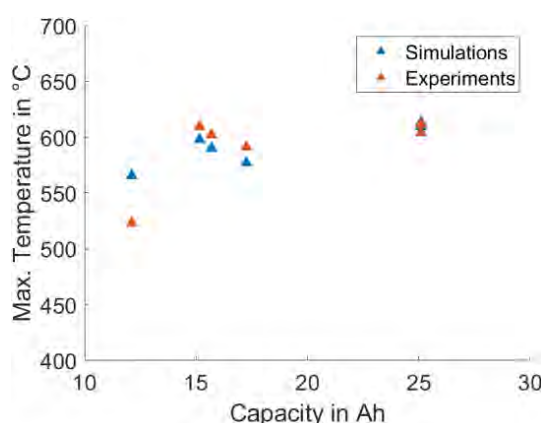


Figure 1: Comparison of experimental and numerical peak temperatures of cells with different capacities

Keywords: lithium ion battery, thermal runaway, chemical modelling.

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Validated Simulation of Strain-induced Battery Aging

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Volumetric changes of the active material during cycling causes stress in the electrode material in a battery. These stresses on the micro- and macro-scale lead to cracks, delamination, and deformation of inactive layers and the battery casing. Direct observation of this volumetric change on the microstructure needs operando measurements and thus is only possible to a very limited extent due to the high time and cost investment.

For this reason, we have developed a simulation tool to determine and assess the structural changes at the microstructure level in real or artificially generated 3D electrode structures. In this way, a rapid understanding of the effects of material selection, electrode structure, and cell design is possible, and origins of mechanical cell aging can be identified. The tool we present was validated with an exemplary application. For this purpose, the microstructural evolution of a schematic battery consisting of a graphite anode and a $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$ cathode was simulated during cycling, and the results were compared with X-ray tomography data sets of those electrodes taken during the electrochemical cycling. Simulatively, we investigated the effect of different volumetric expansion behaviors of the cathode material on the strain in the cell stack.

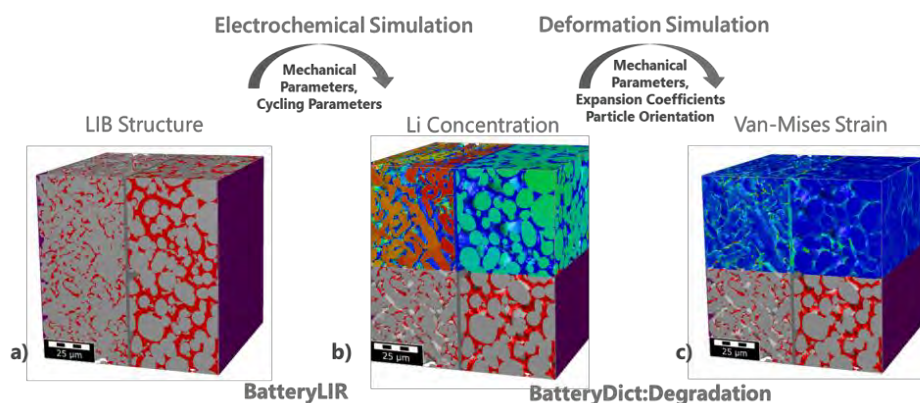


Figure 1. Functionality of the 3D electrochemical-mechanical battery simulation tool. The developed tool combines 3D electrochemical and mechanical modelling and allows simulation of full-cell stacks with microstructural resolution. a) The battery structure is digitally assembled from the measured or artificial electrode volumes. b) After parametrization of the materials and specification of the cycling protocol, the electrochemical behavior of the entire cell is simulated. c) Based on the resulting local lithium concentration within the cell, the lithium concentration expansion coefficient is used to compute the stress and strain. Using the deformed structure subsequent (dis-) charge cycles can be simulated.

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Ionic Transport Paths in hierarchically structured Electrodes depend on Calendering and Discharge Rate

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Hierarchically structured battery electrodes achieve a good specific capacity under fast discharge due to short diffusion paths in the active material [1]. The active material particles have an open porosity (intragranular porosity) filled with electrolyte. Therefore, ionic transport within the electrolyte takes place both in pores between particles (intergranular porosity) and in intragranular pores. However, there is little knowledge about specific ionic transport paths in hierarchically structured electrodes.

Here, we employ a modelling framework [2] to study ionic transport paths in hierarchically structured electrodes. The continuum cell model based on the porous electrode theory [3] separates three distinctive scales, namely electrode scale, active material particle scale, and solid diffusion scale. With this model, we investigate to what extent the intragranular porosity contributes to the ionic transport across the hierarchically structured electrode. For this purpose, we test two assumptions for the ionic transport at electrode level. First, we assume the ionic transport through the intergranular pores to be much faster than the ionic transport through the intragranular pores. We model this by applying a single phase transport law through the intergranular pores. Second, we assume that the intragranular porosity significantly contributes to the ionic transport across the electrode. We idealize the effective ionic transport path as a parallel arrangement of intergranular and intragranular porosity. The acquired values of the effective ionic transport properties correspond closely to the Hashin-Shtrikman upper bound for material properties of multiphase media [4].

Our results show that the contribution of intragranular porosity to the ionic transport across the electrode depends on the degree of calendering and on the applied current density. Calendering hierarchically structured electrodes mainly reduces the intergranular porosity of the hierarchically structured electrode [5]. In slightly calendered electrodes with a high intergranular porosity the main ionic transport path leads through the intergranular pores. The intragranular porosity only enables ionic transport from intergranular pores into the porous particle. In contrast, highly calendered electrodes experience a significant contribution of the intragranular pores to the ionic transport across the electrode during fast discharge. Under these conditions, the intragranular porosity has to be considered at the electrode scale to accurately model the ionic transport through hierarchically structured electrodes.

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Efficient Chemo-Mechanical Simulation of Coupled Anode Particles and SEI

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Next-generation lithium-ion batteries with anode materials such as silicon feature the forming and growth of the solid-electrolyte interphase (SEI). The SEI serves as a protection shield for the anode particles, but further results in an increase of capacity fade due to continued SEI growth. Using efficient numerical simulations, the prediction of the mechanical behavior and growth of the SEI on active particles is possible for multi-dimensional studies.

As model approach we build on the recently developed thermodynamically consistent continuum model: an anode active particle is surrounded by a SEI layer as in [5]. Chemical and mechanical effects are treated for the particle and coupled to the SEI for its deformation and growth. For the SEI, mechanical and plastic behavior is focused and for the SEI growth we assume electron diffusion [4].

Since accurate one-dimensional simulations already need high computational costs, higher-dimensional geometrical setups and long-term considerations for few years of charging and discharging cycles are not feasible with reasonable effort. With an efficient finite element approach and an adaptive solution algorithm from [1, 2, 3, 6], we are able to overcome this limitation. The usage of parallel programming capacities for a further simulation speedup enables the study on the effect of SEI growth and long-term cyclings in different multi-dimensional examples and computationally demanding parameter regimes within a reasonable simulation time.

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

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Simulating Interface Impedances for Solid Electrolytes

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All-solid-state batteries (ASSBs) are candidates for the next-generation of battery electric vehicles. They potentially enable the use of lithium metal as an anode material thereby highly improving the energy density of the battery. Among the most promising candidates for solid electrolytes are polycrystalline materials such as LLZO, due to their high ionic conductivity and chemical stability. Lithium dendrites form above a critical current density (CDC) of as low as 0.6 mA/cm² [1], however. While some explanations were suggested, the underlying mechanisms are not yet understood. In a recent paper a more viable CDC of 5 mA/cm² was reported, which was achieved by protonating the interfaces and grain boundaries [2], this shows that understanding both external and internal interfaces is crucial for the successful development of ASSBs.

One often used tool in battery analysis is Electrochemical Impedance Spectroscopy (EIS). We developed a continuum scale model [3] in order to compare experimental impedance data with simulated impedances for a range of possible interface configurations. Space charge layers and their effects are included in the model and material properties are informed by atomistic simulations.

In our contribution we simulate impedances at ASSB interfaces using continuum scale modelling. The comparison to experiment helps us validate the model while better understanding the relevant interfaces including the effect that different interface configurations have on the resistance. The gained understanding can inform the development and manufacturing of future ASSBs.

Acknowledgements

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe). The authors thank the German Ministry of Education and Research (BMBF) for funding of the project CatSE under grant number 03XP0223E.

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CFD-DEM simulation of structure formation during battery electrode drying

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During the manufacturing of Li-ion battery electrodes, the drying process plays a major role in the formation of the final particulate microstructure, therefore strongly determining the later performance of the cell. The mechanisms of structure formation have not sufficiently been revealed yet, as experiments are expensive, time consuming and lack insight into the ongoing processes on the microstructure level. Simulation methods can help to investigate the influence of formulation and process parameters on the microstructure and the mechanisms involved more deeply. Therefore, in this study CFD-DEM coupling is used to simulate the evolution of structure formation during the drying process. For simulating a two phase fluid flow by means of CFD, the volume of fluid method is used, which was expanded by a negative source term in the phase fraction transport equation to reflect the evaporating liquid during drying. Coupling of CFD and DEM then enables the consideration of fluid-particle interactions within the simulation. This can be done either via a computationally expensive resolved method, or with a faster unresolved method. For both approaches, models that represent the action of surface tension on the particles by means of a capillary force are used [1, 2]. Apart from that, structure forming particle-particle interactions are taken into account on the DEM side, such as cohesion, lubrication and contact forces. The simulation output allows the examination of the structure formation process over time as well as the characterization and prediction of the final electrode microstructures. Using this simulation tool, the impact of different parameters such as mass loading and solids content on the later microstructure can be assessed and explained. This is of great use when developing processes for new materials, especially if defined microstructural characteristics are to be realized.

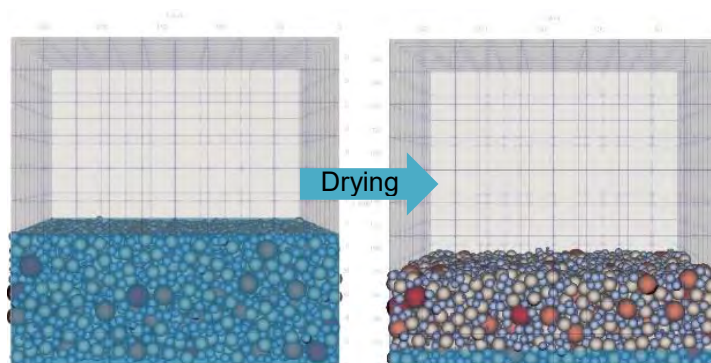


Figure 1: Representation of a CFD-DEM simulation of the electrode drying process

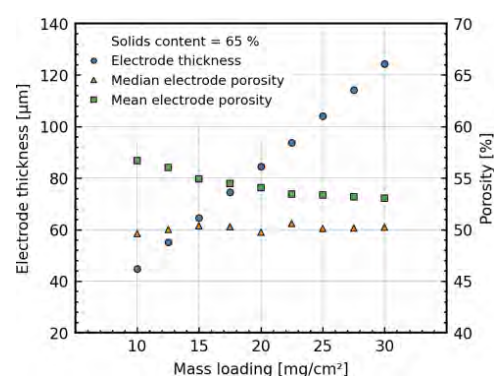


Figure 2: Impact of mass loading/film thickness variations on final coating thickness and porosity

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Analysis of OCV and Quasi-OCV measurements for silicon anodes

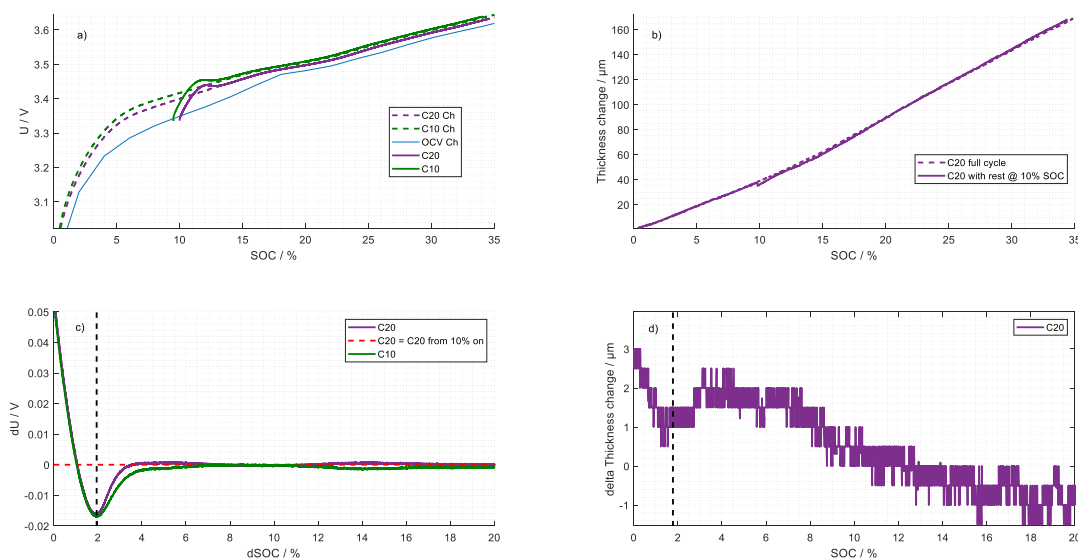
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As energy density is one of the most important factors for the usage of electrochemical storage systems, manufactures steadily optimize this figure. On anode side, silicon is one of the most prominent prospects for the usage as anode active material, as the theoretical gravimetric capacities would be increased by a factor of ten compared to standard graphite anodes. However, silicon also brings negative aspects with it. While alloying, silicon undergoes a volume change of over 300% and shows a volume hysteresis as well as a voltage hysteresis. This can lead to particle cracking and accelerated ageing. The voltage hysteresis as well lowers the energy efficiency. We conducted a comparison of GITT (open-circuit voltage) and Quasi-OCV measurement. The results show significant differences between state-of-the-art graphite and silicon as the Quasi-OCV measurements (e.g. C20-C100) still show a significant overpotential. Our analysis indicates that parts of this overpotential is not time but rather charge-throughput dependent. A certain amount of charge needs to be charged or discharged to build up an additional constant overpotential. This overpotential is independent on current. Therefore, it seems like an offset to the OCV measurement. This results in a deviation between OCV and Quasi-OCV of around 40 mV at room temperature, which further lowers the energy efficiency. Remarkably, the overpotential declines over time to the OCV curve. This effect can also be observed in silicon-graphite composite anodes, but only in the region where silicon is active (i.e. mainly lower SOC ranges). Further evaluations of thickness measurements of silicon-graphite anode cells show a correlation to the shown overpotentials, which suggests a significant influence of mechanical effects on the measured potential of silicon.



- a) OCV and Quasi-OCV curves of a silicon-graphite/NMC811 62Ah pouch cell
- b) Thickness change of the pouch cell at C20 full cycle vs. with a relaxation of 12h @ 10% SOC
- c) Voltage difference between C20 full cycle and C20 charge after relaxation @ 10% SOC
- d) Thickness change difference between C20 full cycle and C20 charge after relaxation @ 10% SOC

Fast uncertainty prediction in digital twins of lithium-ion batteries via Bayesian quadrature

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Digital twins are promising tools for accelerating battery development and designing control systems—however, they can never give exactly the same response as the actual device. There are always uncertainties in parameter estimation, model selection, and training data. Dismissing these uncertainties leads to overconfidence when designing safety and degradation-aware limits of a battery control system. As such, we require uncertainty quantification for creating reliable digital twins. The Bayesian approach quantifies predictive uncertainty by considering all processes to be probability distributions—uncertainties in parameter estimation, model selection, and prediction are quantified, respectively, via the parameter posterior distribution, marginal likelihood, and predictive posterior distribution. However, a Bayesian approach requires sampling. Existing sampling methods, such as Markov chain Monte Carlo (MCMC), have poor sampling efficiency, often requiring over 100,000 samples for convergence [1]. Furthermore, this expensive procedure must be repeated for each uncertainty quantification task, including prediction.

In this work, a Bayesian quadrature (BQ) approach is adopted to accelerate uncertainty prediction of a lithium-ion battery model, the single particle model with electrolyte dynamics (SPMe) [2]. BQ is a model-based numerical integration technique designed to minimise the number of required samples [3]. This method can infer posterior distribution and marginal likelihood in one go by adopting a surrogate model for the intractable SPM likelihood function—usually a Gaussian Process (GP) surrogate is used. Previous work demonstrated that BQ could accelerate parameter estimation [3] and model selection [4]. This work tackles accelerating the predictive posterior inference from a model with probabilistic parameters. The computation of the predictive posterior in simulation-based inference is not trivial, requiring drawing tens of thousands of random samples from the parameter posterior distribution. Namely, prediction with uncertainty requires running the SPM countless times at each given operational condition. BQ can minimise the number of samples required for predictive variance inference via approximating Monte Carlo integration by weighted summation of carefully chosen sparse samples. Such weights and sparse samples can be automatically selected via kernel recombination [5] as a post-process of parameter estimation with negligible computational overhead. The weights and samples can be recycled to any operational conditions because they share the signed measure. Our current research shows that BQ can then infer the predictive variance with tens of weighted samples with equivalent accuracy to tens of thousands of random samples. This has significant implications for its further application in batteries and elsewhere, such as evaluating the reliability of digital twin models and control systems based on them.

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A grey-box model for lithium-ion batteries including long-timescale dynamics with neural ordinary differential equations

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Lithium-ion batteries exhibit slow dynamics on the minute scale. For example, they show complicated behaviour during dynamic profiles such as driving cycles or pulse tests, and slow relaxation times when trying to measure the true open-circuit voltage. These dynamics can also be seen in the low-frequency behaviour of electrochemical impedance spectra. Modelling the slow dynamics is challenging because they have multiple potential causes, including transport processes on the microscale (diffusion inside active materials particles), on the mesoscale (diffusion of lithium ions), and on the macroscale (thermal gradients). Moreover, pure Fickian diffusion results in a fractional order differential equation in the time domain which is numerically hard to solve¹.

In this work, we introduce a grey-box approach to model the long-timescale dynamics of lithium-ion batteries. The model is inspired by a combination of Fickian diffusion in a spherical particle and the Nernst equation. Fickian diffusion can be described by a partial differential equation. We used the finite volume discretization along the radius of the sphere to derive a system of ordinary differential equations². We chose five discretisation volumes to keep the computation time short. The distribution of these volumes along the radius was treated as a degree of freedom and was approximated by one learnable parameter per equation. The diffusion coefficient and its dependency on the concentration are represented by a neural network. We used a linearized Nernst equation to describe the dependency of transport-induced voltage drop and surface concentration.

Training data were generated using equivalent circuit models including either a Warburg element or an RC element for the slow dynamics. The current served as the model input, the state of charge of the battery and the voltage drop across the Warburg or RC elements were the outputs. The Warburg voltage was calculated using fractional integration of the current. We used different input current signals for training: six time series representing charging and discharging according to a constant current constant voltage protocol with different C-rates and two time series representing charging and discharging of a battery with a pulsed current. The resulting grey-box model can reproduce the simulated voltage during constant and dynamic current operations for both the Warburg-type dynamics and the RC-type dynamics, thus showing the flexibility of the approach.

We finally applied the grey-box model to experimental data of a 180 Ah large-format lithium-ion battery cell with lithium iron phosphate (LFP) chemistry. The model can reproduce the dynamics during experimental pulse tests.

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Effect of geometry upscaling on accuracy and computational performance of electrochemical-thermal model for Li-ion pouch cell

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As part of the European Green Deal, the EU has set itself a binding target to achieve climate neutrality by 2050. This requires a significant reduction of the current greenhouse gas emission. As an intermediate step towards climate neutrality, the EU has raised its 2030 climate ambition, committing to cutting emissions by at least 55% by 2030 [1]. From now, in order to reduce air pollution, electric vehicles are in the center of the energy transition.

In the framework of lithium-ion battery research, multiphysics modelling can be helpful to unravel complex phenomena, such as ionic diffusion mechanisms, heat generation and transport through multi-layered structures during cell cycling, electrodes utilization and current distribution, aging and so forth.

In this work, three different electrochemical-thermal models of LiFePO₄ pouch cell were developed with COMSOL Multiphysics and compared to evaluate the accuracy and the computational performance of the models.

A simplified electrochemical P2D model of an LFP-graphite single cell was developed and coupled with a 3D thermal model of a real dimension pouch cell. Additionally, Joule Heating Multiphysics is added to account for the heat produced by electrical current flowing through the tabs. Following the same approach, a second model with an enhanced P3D electrochemical physics was derived. Finally, a fully 3D electrochemical and thermal model of the pouch cell was developed.

Electrochemical and thermal results of the proposed models will be compared and validated with experimental data [2].

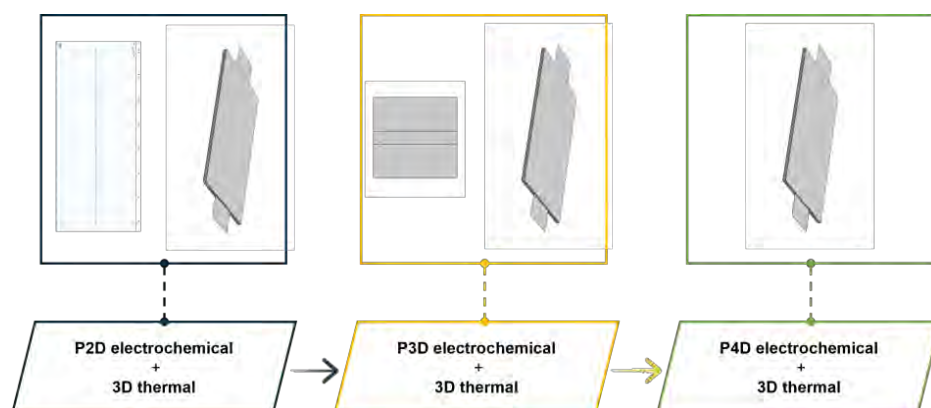


Figure 1: Electrochemical-thermal models geometry upscaling

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Calibration of a Density-Potential Functional Theory Model of the Ag(111)-KPF₆ Interface

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The density-potential functional theory (DPFT) of electrochemical double layer (EDL) is upgraded by adopting (generalized) gradient approximations for kinetic, exchange and correlation functionals of metal electrons.[1] A new numerical scheme that is more stable and converges faster is proposed to solve the DPFT model. The DPFT model is calibrated with existing differential double layer capacitance (C_{dl}) data of the EDL at Ag(111)-KPF₆ aqueous interface at five concentrations.[2] Metal electronic effects are essential to explain why the two peaks of the camel-shaped C_{dl} curves are almost symmetric despite of the size difference of hydrated cations and anions. A systematic parametric analysis is then conducted in terms of key EDL properties, including the potential of zero charge and the differential capacitance. The parametric analysis, on the one hand, elucidates how quantum mechanical behaviors of metal electrons as well as interactions between metal electrons and the electrolyte solution impact the EDL properties, on the other hand, identifies key parameters of the DPFT model which should be calibrated using first-principles calculations and/or advanced experiments in the future.

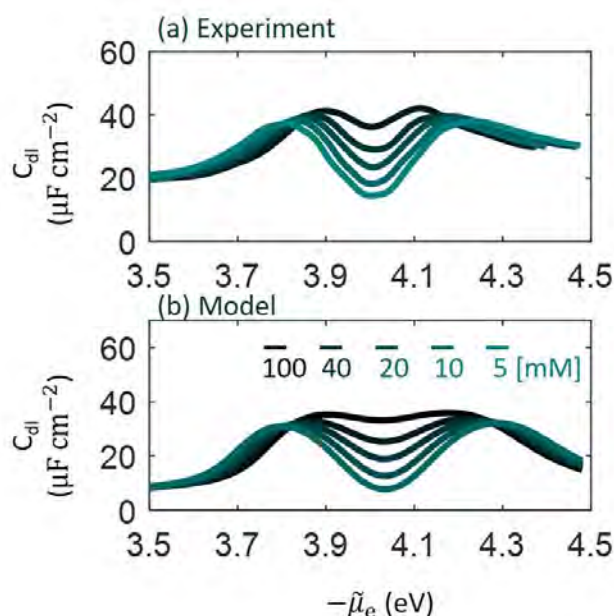


Figure 1. Comparison between model and experimental results of the differential double layer capacitance (C_{dl}) of Ag(111)-KPF₆ aqueous interface at five concentrations indicated in the figure. Experimental data were reported by Valette in the third part of his fundamental measurements on silver single crystals. Experimental data are corrected using the roughness factor of 1.08 determined by Valette. The model is parameterized according to the experiments. The model results at five concentrations are calculated using a single set of model parameters.

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Model-assisted scalability approach for single-layer lithium-ion battery cells

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In the academic environment, battery material studies often choose small laboratory cell systems due to their simplicity and reliability, e.g. setups with a 3-electrode system such as the patented PAT-cell design of the company EL-Cell® [1]. However, transferability to larger systems is not guaranteed because of local differences along the electrode surface [2]. Therefore, a Doyle-Fulle-Newman (DFN) model specific to the selected cell chemistry is first parameterized using the modular battery toolbox PyBaMM [3]. This model is extended by a 2-dimensional consideration of the electrode area to account for local effects. During the development of the additional spatial model, the critical parameters for transferability are determined based on experimental data from tests of PAT-cells and single-layer pouch cells. In this way, quantitative statements can be made about the limited aspects of the smaller cell format and the requirements the model must fulfil to guarantee transferability for larger-area cells. In the future, the dimensional extension of the DFN model will allow a better estimation of the results from laboratory cells to multilayer cells.

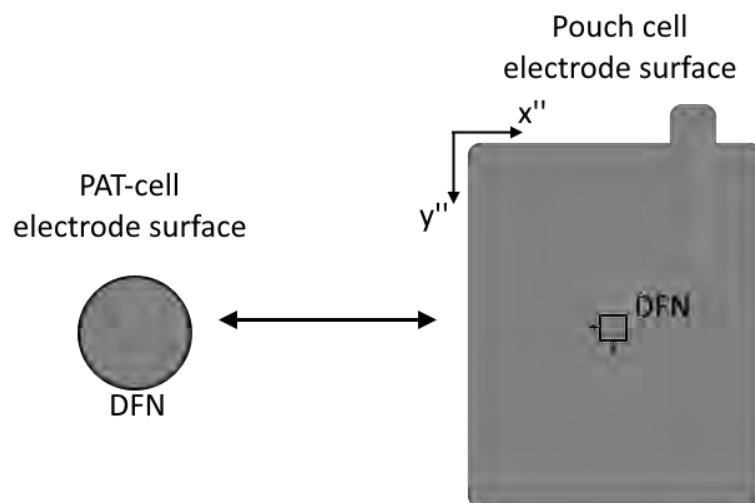


Figure 1: Model-assisted scaling from laboratory cell to single-layer pouch cell by addition of 2D spatial model for overlapping electrode surface area.

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Determining kinetic parameters of large format commercial lithium-ion battery cells

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Parameterization is essential for the successful application of physicochemical models of lithium-ion batteries. The solid-state diffusion coefficient and the exchange current density are key kinetic parameters for these models. Often these parameters are taken from various literature sources, varying over a wide range [1], or they are adjusted, in a generic manner, to minimize the deviation to measured full-cell voltages. The prediction capability of models using such parameterization approaches is limited. Therefore, it is important to develop methods to reliably identify parameters.

In this work, we investigate different methods to determine the solid-state diffusion coefficient and the exchange current density of the electrodes of a large-format pouch cell. The values are determined at three operating temperatures (0°C, 20°C, 50°C) and different states of charge (SOC) in steps of 10%. For this purpose, a commercial pouch cell with a capacity of 56 Ah from the automotive sector was disassembled, the positive and negative electrodes were extracted and used to construct small-format cells with a reference electrode (PAT-cells from EL-Cell GmbH). Galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) was performed on these cells. Various fitting methods based on electrical equivalent circuit and electrochemical models were used to determine the lithium diffusion coefficient and exchange current density in the active materials. Further, the open circuit voltages of the electrodes were measured with a half-cell configuration to determine the lithium concentration at the evaluated states. The determined diffusion coefficients show significant temperature and concentration dependence for both the positive and negative electrodes. It is observed that the diffusion coefficients, especially from the negative electrode, vary by several orders of magnitude as a function of lithium concentration. Therefore, it is concluded that the concentration dependence should not be neglected in electrochemical models. The exchange current densities of the electrodes are also affected by the operating temperature and lithium concentration. The results show that the temperature dependence can be well described by the Arrhenius equation for both investigated parameters.

In summary, a parameterization procedure for determining key parameters of large-scale battery cells is presented. It is further shown that these parameters exhibit significant concentration and temperature dependence, which should be considered in physicochemical models.

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Automated Battery Model Selection with Bayesian Quadrature and Bayesian Optimization

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In the process of constructing physics-based battery models, there are usually several candidate submodels for any mechanism of interest, as seen in the modular battery model software PyBaMM [1]. Parameterizing such varied model sets is a challenging task, since developing a specialized routine for each combination of submodels is unfeasible. Aitio et al. have shown that Metropolis-Hastings can directly fit a model to measured voltage [2]. Kuhn et al. have shown that Metropolis-Hastings scales poorly when the models or measurements get more involved [3]. Hence, they propose EP-BOLFI as an alternative, which can parameterize a wide variety of models reliably, and do it faster as well.

But, a well parameterized model does not imply that the data supports that model. Adachi, Kuhn et al. have shown that the closeness of the fitted model to the data is not a reliable measure [4]. Hence, EP-BOLFI does not help in selecting a model. Instead, they propose a Bayesian Quadrature approach for model selection, BASQ [5]. The caveat is that BASQ needs to perform a successful parameterization to then give good measures for model quality. And the result of BASQ depends on the randomly chosen model evaluations it is initialized with. In contrast, if the optimal parameter set is within the prior bounds, Metropolis-Hastings and EP-BOLFI have a much higher chance to eventually reach that optimum.

In this work, we investigate if the stability of EP-BOLFI can supplement BASQ. We showcase this on the example used in Ref. 4, the selection of the number of RC-pairs in a R-RC-RC-... equivalent circuit model. We find that preconditioning the prior probability distribution with EP-BOLFI before giving it to BASQ can improve the parameterization, and hence, the model selection success rate.

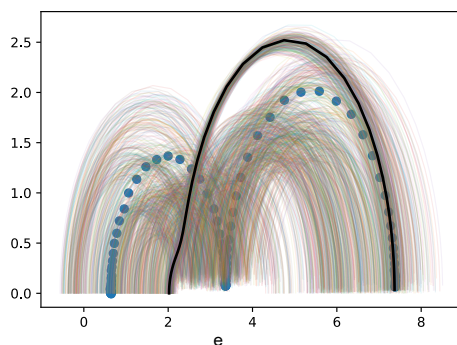


Figure 1: BASQ with poor initialization

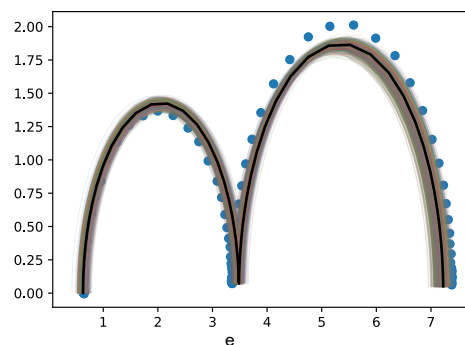


Figure 2: BASQ preconditioned with EP-BOLFI

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On the mechanical discrete approach of silicon/graphite-based anode breathing

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In the current researches intended to improve the Lithium-ion batteries capacity for automotive or electronic devices applications, enriching anode with silicon is one of the forehead solutions¹. However, silicon shows a tremendous volume change of +280% in the fully lithiated state², leading to a significant « *breathing* » of electrodes during cycling. When combined with more or less rigid casings, detrimental pressure or deformation levels can be reached and raise safety and performance issues. Hence, prediction of the volume changes related to applied pressure is key to design the cells. Irreversible volume changes are observed and conjectured to be related to microstructure changes², but current publications addressing the modelling aspects mostly use analytical or continuous models that can hardly capture the nonlinear changes of granular media microstructure. In that sense, *Discrete Elements Methods* (DEM) has proven to efficiently simulate granular medias³. Thus, this study aims to apply DEM on a silicon-based anode in order to take into account the discrete microstructure in the breathing behaviour.

The core of this work is to use the DEM software LIGGGHTS[®] on a sample of anode, modelled as a 3D distribution of spherical particles that can mechanically interact with each other. The breathing amount during charge and discharge cycles is evaluated via evolutions of thickness, void volume, porosity and coordination number. The global approach follows a progressive enrichment of contact laws, and successive sensitivity analysis of each upgraded parameter evaluate their capacity to reproduce more finely the observed behaviours. Besides, a systematic statistical analysis of initial random particles distribution is lead in order to avoid false interpretation of some evolutions.

In the parameters studied so far with the model, the coefficient of friction between particles, the confinement pressure applied on the anode and the adhesion are three major parameters that affect the breathing of the anode. Indeed, considering the change of anode thickness, the coefficient of friction analysed from 0.005 to 0.6 increases the breathing range with a factor of 1.5, the pressure analysed from 0.01 to 100 MPa decreases the breathing range with a factor of 1.7. Moreover, the adhesion analysed from 0 to 100 J/m² is able to create an irreversibility at first cycle of around 30% of breathing range which reproduce a characteristic experimental observation.

As a result, DEM showed its potential to introduce the granular properties in the anode model and explain some phenomena of irreversibility. It is a useful tool to determine the physical parameters to focus on, with a view to increase the reliability of the batteries. More parameters are planned to be explored, such as inter-particles bonds, plasticity and non-spherical particles. An experimental macroscopic measurements using a controlled-pressure test bench will be carried out to complete the available data².

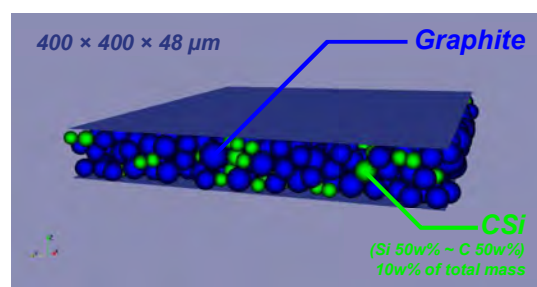


Figure 1 : DEM model of anode sample

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Towards a better understanding of lithium dendrite growth in solid electrolyte interphase using a Multi-Phase Field Model

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Lithium dendrites formation is an inherent drawback in the development of all solid-state lithium batteries technology. This issue remains unsolved due to the multiple and competing issues during lithium plating and stripping. The inhomogeneous mechanical and chemical properties of the solid electrolyte interphase^{1,2} (SEI), leads to uneven current distribution and unsmooth lithium plating and stripping³.

Several numerical model were proposed to link the lithium dendrite growth to the ion transport and electrochemical reaction at the lithium /electrolyte interphase. Phase-field model have been proposed^{4,5} to simulate the microstructure evolution of lithium in contact with different phases. However, these studies do not take into consideration explicitly the SEI. In this work, we developed a phase-field model that consider the SEI as a dynamic multi-domains object. Each region has its own chemical properties (ion transport, ion concentration ...). The multi-domains design leads to the appearance of preferential ion diffusional path that involves a local deformation of the SEI due to the lithium electrode growth.

First results showed two different growths mechanism (fig. 1). Under a large applied potential, the SEI is broken due to the strain imposed by the lithium growth, creating proto-dendrite. For smaller deformation (low current) (fig. 1 right), the plating leads to decrease the porous SEI thickness and to bend the passivation layer, therefore the electrodeposition does not imply the dendrite formation.

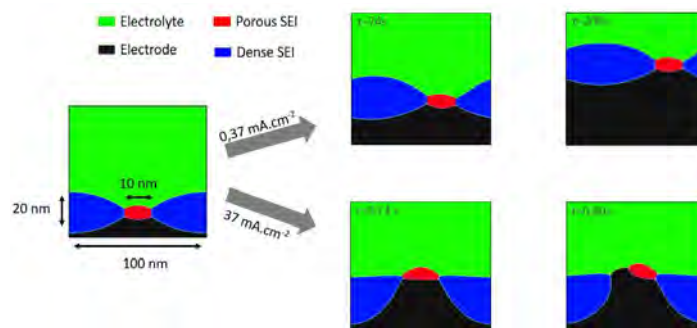


Figure 1: On the left, the lithium (in black color) is in contact with a solid electrolyte interphase constituted of a dense (blue) and porous (red) SEI, and polymer electrolyte (green). The dynamic evolution of lithium and SEI, under low current density 0.37 and 37 mA/cm² are reported on top and bottom figures respectively. Fast reaction with vertical growth of lithium dendrite is noticed at high current density, while slow reaction with lithium diffusion in the SEI is observed at lower current density. Due to the phase-field model, phases minimize the size of the interface (fluid behaviour), that leads to spherical conformation.

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Impact of solid precipitate on the morphology and performance of Lithium-Sulfur battery cathodes using the lattice Boltzmann method

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Lithium-sulfur batteries (LIB) are a promising technology for next-generation energy storage. However, LIB are affected by solid precipitate formation during cycling, which changes cathode morphology and passivates active surfaces, resulting in overall battery performance degradation.

Morphological changes in the microstructure, from surface reactions, dissolution, and precipitation are difficult to characterise due to their complex interactions. Traditional computational method approaches typically use simplified abstract modelling [1,2] or homogenization relying on representative volume elements [3]. However, accuracy and predictions of these approaches are limited. Nevertheless, understanding these elusive phenomena are important to mitigate them in future LIB developments. The driving dynamics and phenomena in LIB are mesoscopic in nature, where computational simulations can provide detailed insight.

In this work, a lattice Boltzmann method (LBM) model is presented that was specifically developed to simulate the relevant physicochemical phenomena. The LBM has shown to outperform many conventional methods at the pore scale due to its sound physical basis and efficient computational parallelization.

Our model was applied to simulate and study three-dimensional porous cathodes, fully resolved in sub-micron resolution. The resulting simulations capture precipitates growth successfully and were used to investigate pore clogging and surface passivation. This study sheds light on the pore-scale happenings of LIB microstructures and will help to optimize the design of LIB systems.

Acknowledgements: Funded by the Federal Ministry of Education and Research with grant 03XP0491A

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Modelling and simulation of electrodes for sodium-ion batteries on the continuum scale

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Sodium ion batteries (NIBs) are a promising and sustainable alternative to state-of-the-art Lithium ion technology [1]. Development of novel materials and improved cell designs are key to increase the energy density of NIBs making them competitive to Lithium ion batteries (LIBs). Modelling on the continuum scale has proven to be a powerful tool for cell design and provides a deeper understanding of the relevant physio-chemical processes. However, compared to the large amount of modelling publications on LIBs, only few studies investigate the modelling and simulation of sodium ion batteries.

A promising cathode active material for NIBs is NVP ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$) which provides a high diffusion coefficient of sodium ions in its NASICON crystal structure. However, its low intrinsic electric conductivity is a major hurdle for practical applications [2]. One approach to improve the intrinsic conductivity, is embedding carbon into NVP. Additionally, one can use conductive additives to further increase the electric conductivity on the electrode scale. The calendaring process during electrode manufacturing has a significant influence on the arrangement of the NVP particles in the microstructure of the electrode.

In this contribution we present our research on the modelling and simulation of NVP cathodes for NIBs using three-dimensional microstructure-resolved simulations. To understand the influence of calendaring on the effective conductivity, we performed a simulation study on 3D reconstructions of electrodes with different porosities. 3D image data of the NVP electrodes is obtained by synchrotron tomography. Moreover, we extended our computations to different bulk conductivities of the NVP to represent different embedding strategies of carbon into the crystal structure. Our simulations provide insights to limiting transport processes on cathodes of NIBs and are able to guide the development of improved electrode designs.

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Impedance fingerprints of couplings between interfacial electron transfer reaction and electrolyte-phase ion transport

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Electron transfer (ET), electric double layer (EDL) charging and ion transport (IT) are three elementary physicochemical processes in electrochemistry.¹ These processes are coupled with each other in the way that the local reaction environment for the ET is shaped by EDL charging that is nothing but IT in a nanoscale nonelectroneutral region. Herein, we investigate fingerprints of the coupling between these processes in electrochemical impedance spectroscopy (EIS). EDL charging and IT are described uniformly using the Poisson-Nernst-Planck theory, and interfacial ET is described using the Frumkin-corrected Butler-Volmer theory.² Different diffusion coefficients for cations and anions ($D_+ = D_-$) are considered. Exact analytical expressions are obtained when the potential of zero charge (E_{pzc}), the equilibrium potential of the reaction (E_{eq}), and electrode potential (E_M), are equal. The analytical solution shows that a decoupling treatment is valid only for the case of $D_+ = D_-$. Using a new scheme of calculating impedance response at any electrode potential, we observe an inductive loop in the low frequency range which is a clear impedance fingerprint of the coupling effects.

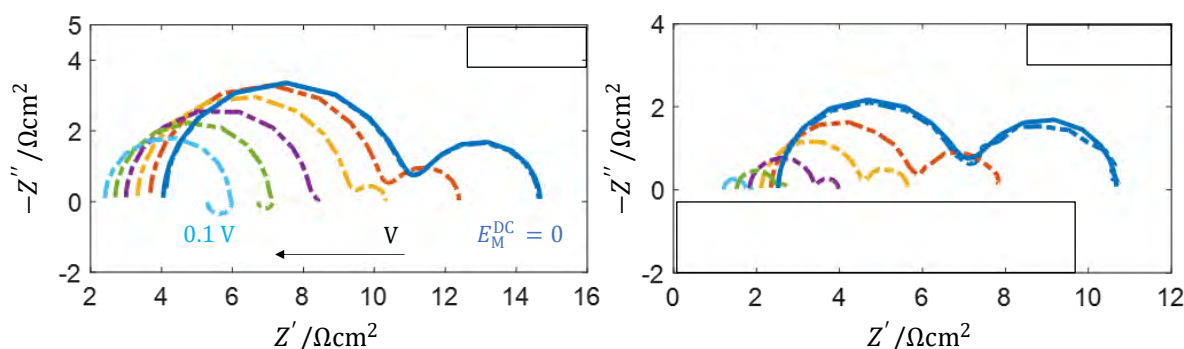


Figure 1 Numerical solution of EIS at $E_M \neq E_{eq}$ for (a) the coupling case, and (b) the decoupling case.

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A Finite Element Formulation to Resolve Space-Charge Layers in Solid Electrolytes

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All-solid-state lithium-ion batteries are seen as promising candidates to overcome drawbacks of conventional batteries with liquid electrolytes like high energy and power density, while maintaining high safety standards [1]. However, they are not yet feasible for many relevant applications and still require intensive research. Hereby, one challenge is the identification of physical effects inside all-solid-state batteries and their quantitative influence on the performance of the entire battery cell. Simulation models can contribute to answering the aforementioned challenge by systematic studies, e.g. enabling or disabling certain physical effects or by varying their parametrization. Especially the influence of space-charge layers on the performance of the entire battery cell is heavily discussed in the scientific community ranging from negligible to relevant [2]. The different length scales of space-charge layers on the one hand and of the microstructure of a battery cell on the other hand made a spatial discretization of realistic microstructures with resolved space-charge layers infeasible so far. However, thermodynamically consistent continuum models which are applied to simplified one-dimensional geometries are already established in the literature.

In this work [3], we propose a model that enables to predict the spatial development of space-charge layers within geometrically resolved microstructures by exploiting that effects in space-charge layers are predominantly one-dimensional. By a split of the geometric domain into regions where space-charge layers are expected and the remaining domain, discretizing the domains with different dimensions, and introducing a mathematically consistent coupling between the domains, we are able to resolve space-charge layers in three-dimensional microstructures of battery cells. The continuous equations are discretized using the finite element method and the nonlinear system is solved within one monolithic system to ensure robustness and efficiency of the solver. By using a tailored iterative solver, we can apply the model to realistic microstructures with more than 10 million unknowns [4].

With the proposed approach it is possible to quantify the geometric influence of realistic microstructures on the formation process of space-charge layers. In addition to what is already well known from results computed by one-dimensional models of SCL, this work is the first to show that the formation process of SCL is strongly influenced by the geometry of the microstructure: The dominating trend is an axial propagation of the temporal development of the space-charge layer through the composite electrode, i.e. from the separator to the current collector side of each electrode. Simultaneously, deviations in the lateral direction are observable originating from laterally different percolation paths as a consequence of the stochastic nature of the investigated microstructures and their geometric complexity.

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Modelling of Magnesium Intercalation into Chevrel Phase

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Regarding energy density, safety, cost, and sustainability rechargeable magnesium batteries are a very promising next-generation energy storage technology. However, for a successful commercialization of Mg batteries there are still some challenges to overcome. Generally, the high charge density of the bivalent cation causes strong coulomb interactions with anions and solvent molecules. Therefore, energetic barriers for desolvation and solid-state diffusion are usually very high, which can have a crucial impact on the battery performance. Former can significantly hinder the electron-transfer reaction,[1] whereas latter makes the choice of suitable cathode materials very challenging. For instance, it is well-known that the morphology of an intercalation material can strongly influence the battery performance and smaller particles as well as thinner electrodes are common strategies for avoiding adverse effects of transport limitations. Moreover, the presence of chlorides can influence the intercalation process.[2]

Up to date Chevrel phase (CP) Mo_6S_8 is considered as a benchmark intercalation cathode. In our contribution we carefully study this model system of a magnesium-ion battery to get a better understanding of how to overcome undesired limitations. Therefore, we present a newly-developed continuum model, which is able to describe the complex intercalation process of magnesium cations into a CP cathode (Fig. 1). The model considers not only the different thermodynamics and kinetics of the two intercalation sites of Mo_6S_8 and their interplay, but also the impact of the desolvation on the electrochemical reactions and possible ion agglomeration. The parameterization and validation of the model is based on DFT calculations and experimental data. The impact of different electrolytes as well as the role of electrolyte constituents, especially chlorides, on the battery performance are studied in detail. All in all, the combination of modelling with experimental measurements provides important insights into the operation of magnesium ion batteries and enables an optimization of the cell design.

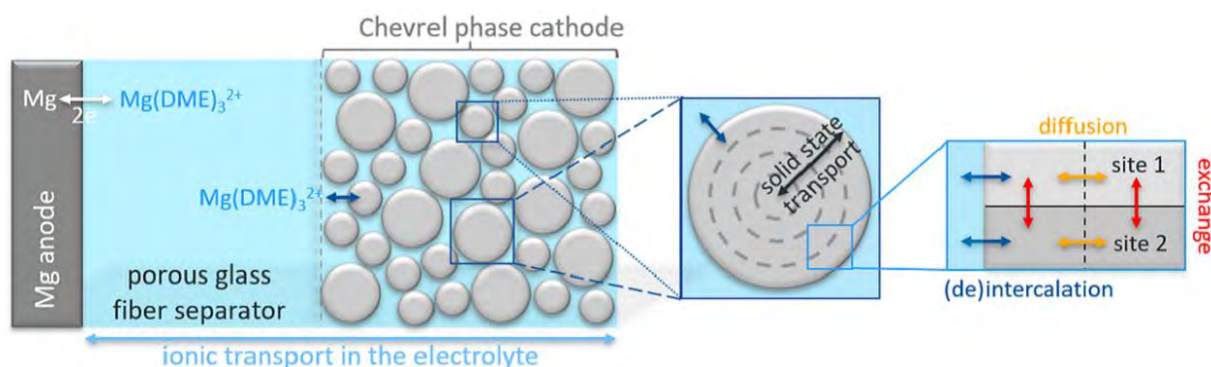


Figure 1: Schematic illustration of the 1+1D continuum model for a Mg / $\text{Mg}_2\text{Mo}_6\text{S}_8$ battery.

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Parameter identification in a Newman-type model by fitting of electrochemical impedance spectra

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A common choice for modelling and simulation of the electrochemical behaviour of Lithium-ion batteries is the well-known P2D-Newman-model. Parametrizing this model is still a challenging task and often based on additional supplementary models and specific assumptions. However, validation with experiments is often insufficient and requires additional parameter-fine-tuning. In this work, where the experimental data comes from a battery characterization of the electric vehicle VW ID.3 [1,2], we take another approach by extending the Newman-model with a capacitive double layer in order to simulate electrochemical impedance spectroscopy (EIS) measurements [3]. The impedance spectrum is efficiently obtained by applying a voltage step with subsequent Fourier transformation [4]. Qualitatively the influence of several parameters (including their Li-concentration and spatial dependence) on the impedance spectra has been analysed to choose a set of optimization variables. Both the real and imaginary part of the impedance spectrum as a function of frequency are used in the computation of the residual in a least-squares problem to fit unknown material parameters (see Fig. 1). The parameter identification problem is solved by applying a gradient-based optimization method. Uniqueness of the determined parameters is assessed by repeating the optimization procedure with varying start values. For the considered EIS-data we found that the slow solid-diffusion cannot be determined accurately. We attribute this observation to the limited lowest frequency in the measurement data. Therefore, we perform a hybrid optimization where the solid-diffusion is fitted to rate-test experiments.

As validation, the obtained parameter set is applied on power profiles of electric vehicle drive cycle experiments in an urban, interurban and highway environment where the cell potential of simulation and experimental data are compared (see Fig. 2). The dynamic overpotentials of simulation and experiment match very well, even in the case of strong acceleration or recuperation.

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4. Wolfgang G. Bessler **2007** *J. Electrochem. Soc.* 154 B1186. DOI: 10.1149/1.2772092

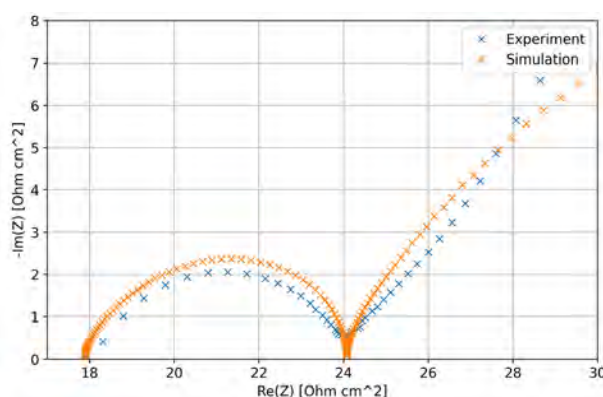


Fig 1: Parameter Fit on EIS-data

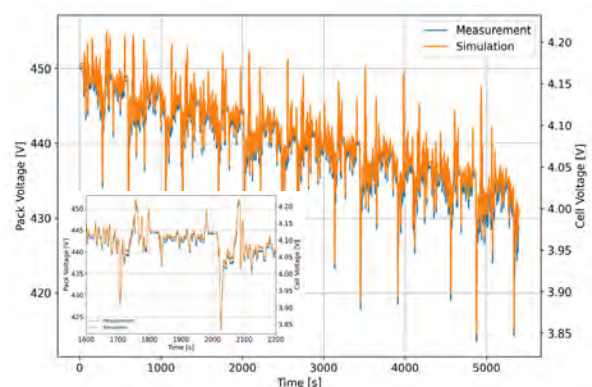


Fig 2: Validation on interurban drive cycle

Modelling inhomogeneous lithium plating with a distributed equivalent circuit network

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In lithium-ion batteries, lithium plating can form dendrites that cause a short-circuit, creating a safety hazard. Some of the plated lithium is permanently lost, reducing the capacity of the battery.

Many models of lithium plating exist. However, most models assume that plating can be prevented by keeping the graphite half-cell potential above 0 V, which experiments have shown to be incorrect. [1] Even models that calculate how much lithium is plated do not account for inhomogeneities in the cell, which is a problem because plating mostly occurs close to the edges of the graphite electrode.

Distributed equivalent circuit network (DECN) models have been used before to predict thermal gradients within a cell. [2] However, they are normally parameterized using experimental measurements that do not track the internal variables required to predict lithium plating.

In this work, we parameterize the same DECEN model with the predictions of a validated pseudo-2D model computed using PyBaMM [3]. This has been done before, [4] but inhomogeneities in the cell were not considered. The pseudo-2D model tracks the graphite half-cell potential and the changing stoichiometry of the graphite in addition to the full cell voltage and current. These two additional variables allow the DECEN model to predict inhomogeneous lithium plating.

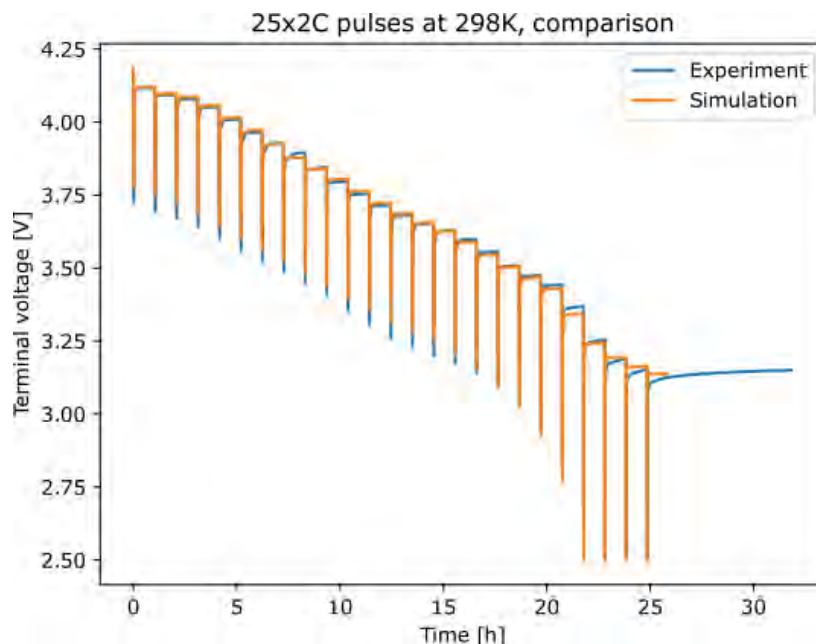


Figure 1: Validation of the PyBaMM pseudo-2D model

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Physics-informed equivalent circuit model of a lithium iron phosphate-based lithium-ion battery cell for state estimation

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State diagnosis of lithium-ion batteries is an up-to-date topic, because the state of charge (SOC) and state of health (SOH) are important parameters for the manufacturers and users of batteries. State diagnosis of lithium-ion cells with a positive electrode consisting of lithium iron phosphate (LFP) is particularly challenging due to the inherent thermodynamic hysteresis, the flat charge/discharge voltage characteristics and the asymmetry of internal resistance with respect to SOC and current. We have developed a new state estimation algorithm that is based on measured battery voltage [1]. This algorithm requires an equivalent circuit model (ECM) for the model-based state estimation.

We present the development, parameterization and experimental validation of an ECM of a commercially-available 180 Ah prismatic LFP/graphite cell. The structure of the model is shown in Figure 1. The model consists of an open-circuit voltage source (V^0), a hysteresis voltage source (η_{hys}), an ohmic resistance (R_s) and three resistor–capacitor elements (R_1, C_1 etc.). Open-circuit voltage is calculated as function of lithium stoichiometry in the active materials rather than as function of global charge throughput. This allows a physically-informed description of electrode resistances as function of stoichiometry. Asymmetric overpotentials of LFP are included in the model by using a current-dependent R element (R_2).

Charge/discharge experiments at different C-rates and temperatures [2] as well as electrochemical impedance spectroscopy and pulse test measurements were carried out as basis for model parameterization. Equivalent circuit fits are used for parameters identification. The parameterized model shows a good agreement with the original experimental data in the time domain (cf. in Figure 2). First results on model-based SOC and SOH diagnostics of a cyclic aging experiment are presented.

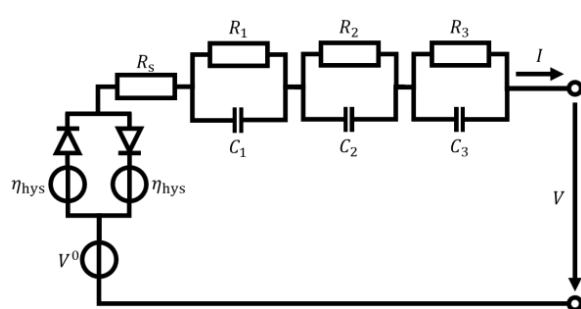


Figure 1: Structure of the physics-informed equivalent circuit model.

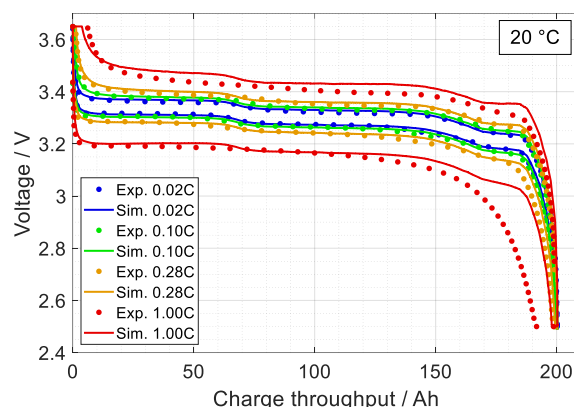


Figure 2: Validation of the model from Figure 1 with help of measured (points) and simulated (solid lines) charge/discharge curves at different C-rates and 20 °C.

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A Model Based Study of Path Dependency in Lithium-Ion Battery Aging

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Numerous studies have shown that battery aging depends not only on the type or magnitude of stressors, but also on the order in which they are applied to the battery [1]. This phenomenon is known as path dependence of battery aging. However, it is not always apparent in experiments, so the reason for the occurrence of this phenomenon during aging is an open question. There are suggestions that the cause of the path dependence is the positive/negative feedback between the degradation mechanisms in a lithium-ion battery [2]. However, it is unclear what type of aging test is appropriate to effectively trigger these interactions and understand the path dependence of battery aging.

In this study, these issues are addressed in a simulated environment. Here, PyBamm, a battery simulation library for Python [3] is used, where several battery models, degradation mechanisms and their interactions are already implemented [4]. We take a single particle model and couple it with the aging models for SEI growth and lithium deposition. We consider temperature as an operating condition and choose two values (45°C and -10°C) where one of the two mechanisms dominates the degradation in each case. Finally, we simulate aging experiments and analyse the change in capacity and performance of the cell over 1000 cycles.

Using this problem setup, we highlight three aspects of path dependence in battery aging. First, we show that the rate of change in cell capacity is affected by the magnitude of the applied stress factor, even when there is only a single active degradation mechanism. Second, we show that when the two operating conditions are applied in different orders, the cells exhibit a different degradation pathway only when the degradation mechanisms interact. Finally, we show that the characteristics of the applied sequences, such as the frequency at which the temperatures are switched, have an impact on the degradation pathway.

Using a model-based aging study, we show that interacting degradation mechanisms are an essential prerequisite for observing path dependence in battery aging. Furthermore, we see that testing cells with dynamic stress factors could be a way to characterize the interaction of aging mechanisms in lithium-ion batteries. Thus, this approach could be a promising step toward understanding the complex, path-dependent nature of degradation in lithium-ion batteries.

Keywords: Lithium-ion battery, aging mechanisms, path dependency

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Electrochemical impedance based simulative analysis of the behaviour of Li-Ion Cells

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The inner cell processes as well as outer influence factors like thermal boundary conditions affect the performance and the ageing behavior of lithium-ion batteries (LIB). Electrochemical impedance spectroscopy (EIS) as a well-established measurement method, can provide experimental data on impedance as a representation of the integral behavior of the cell. At the same time EIS allows to resolve the individual processes taking place inside the cell according to their time constants.

Behavior modelling with well-established equivalent circuit models (ECM) are a supportive tool for cell characterization and a valuable option to gain a better understanding of cell behavior. For a deeper understanding and more detailed insights into the processes taking place inside the cell, physically based models resolving the complex interaction of charge, heat and mass transfer as well as the electrochemical reaction by physical equations (such as Fick's law and Nernst-Einstein-Equation) are needed.

In this work a model consisting of the combination of an ECM and a physical pseudo-2D (p2D) model according to Doyle-Fuller-Newman was developed in COMSOL Multiphysics. With the help of this model, impedance spectra based on the multi-physical processes can be simulated and the underlying parameters can be systematically analyzed. The comparison of the simulated impedance spectra with experimental data provides a data set of the physical parameters by inverse-parameterization. By the addition of a least square optimization tool the simulated impedance spectra are fitted to an experimental data set by automatically optimizing the physical parameters thereby accelerating the inverse-parameterization significantly.

In this contribution a sensitivity analysis of the individual physical parameters and their impact on the impedance spectra are shown. With profound variation studies complex interactions among the parameters were identified and physical parameter sets representing the cell behavior at the Begin-of-Life (BoL) derived and discussed. Additionally to impedance spectra of commercial pouch cells, also spectra of full- and half-cell configurations from experimental cell set-ups are used in this work to gain a deeper understanding of the individual sub processes of each electrode.

Based on the gained insight the developed simulation tool can be used in future works to analyze the impedance data of different End-of-Life (EoL) cells and reveal changes in the physical parameters with cell degradation.

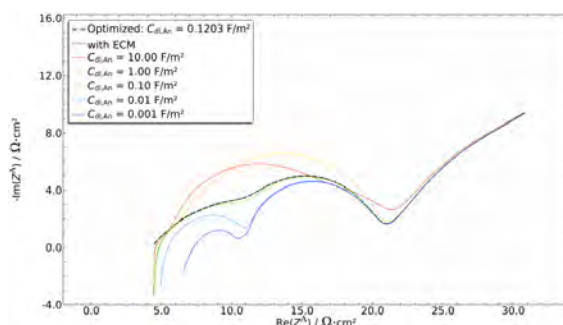


Figure 1: Sensitivity of the Anode Double Layer Capacity shown in Nyquist-Plot

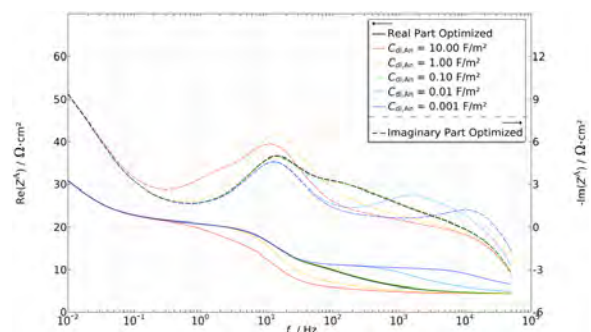


Figure 2: Sensitivity of the Anode Double Layer Capacity shown in Bode-Plot

Physical Modelling of Impedance Response of Nanoscale Solid Electrolytes

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Understanding nanoscale ion transport in solid electrolytes is of great significance for many energy storage and conversion technologies. Electrochemical impedance spectroscopy (EIS) is commonly used to characterize ion transport in such systems. Interpretation of EIS data requires an appropriate model, and equivalent circuit models are difficult to assign the physical meanings of model parameters. In this work, we develop a physical model for ion transport in the nanoscale solid electrolyte that is sandwiched between two blocking electrodes, which is described using the Poisson-Nernst-Planck theory. The EIS response at the potential of zero charge is solved analytically and that at other potentials is solved numerically using the finite difference method¹. Depending on the calculation of EDL charge, two definitions of EIS are compared. When the EDL charge refers to the total ionic charge in the diffuse layer, the EIS shows a nearly vertical line. When the EDL charge refers to the electrode surface charge, the EIS shows a semicircle in high-frequency range, followed by a tilted line in mediate frequency range and a vertical line in low frequency range, Figure 1 (a). The high-frequency semicircle is attributed to the electrolyte resistance in parallel with the electrolyte geometric capacitance. The mediate-frequency tilted line is attributed to finite-rate ion transport in the diffuse layer, leading to frequency dispersion of the double-layer capacitance. The low-frequency vertical line is associated with the equilibrium EDL capacitance. The model is then employed to analyze experimental data, from which fundamental parameters of ion transport are extracted, Figure 1 (b).

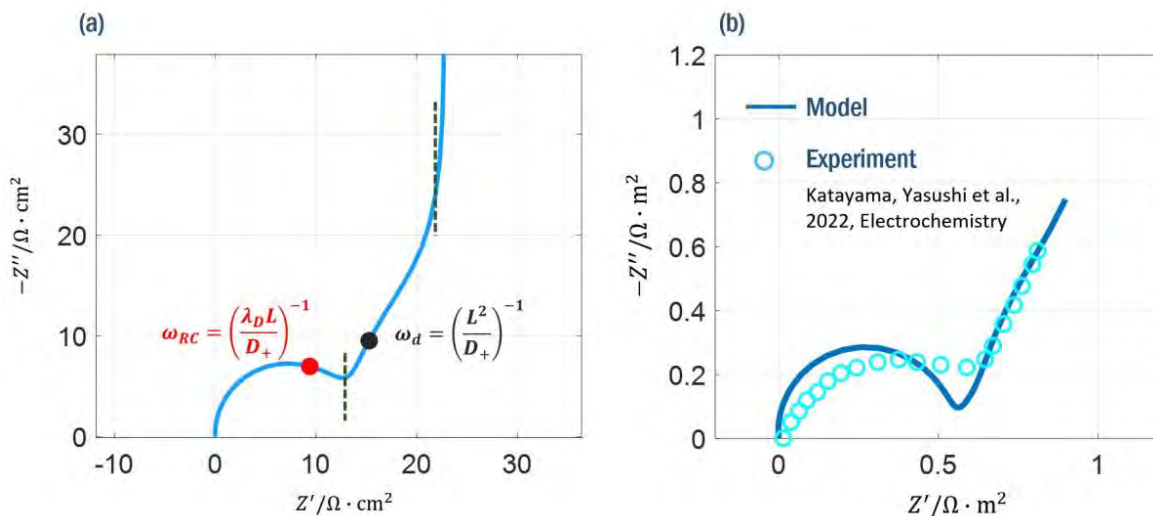


Figure 1: (a) Numerical solution of EIS at potential $U_M^{dc} = -5 (e/k_B T)$; (b) Comparison between model and experimental results of EIS. Experimental data were reported by Katayama on a Ni/LiPON/Ni symmetric blocking cell².

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Modeling the Nonlinear Frequency Response of plated Lithium-Ion Batteries

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Current studies [1, 2] have shown, that plating of metallic lithium on a standard graphite anode significantly lowers the impedance response of lithium-ion batteries (LiBs). This is caused by the faster kinetics of the plating/stripping reaction, compared to intercalation. When both reactions are present in parallel, the impedance drops. This behavior could be used in future applications to detect the safety-critical formation of lithium dendrites during fast charging. Beside the impedance, Nonlinear Frequency Response (NFR) is sensitive to plating [3].

For a better understanding of the observed behavior, a physics-based model for lithium plating is inevitable. Common models [4, 5] for plating were implemented in a standard P2D model. However, both show only two possible states for the impedance. If plating occurs, the impedance of the electrode drops and stays constant afterwards. This is contradictory to the experiment, where the impedance is decreasing monotonously with the amount of plating. The dissent can be ascribed to the assumption, that the metallic lithium is forming a homogeneous film, covering the whole electrode. Intrinsically, only a part of the electrode is covered with metallic lithium, which allows simultaneous plating and intercalation reactions depending on the surface coverage of the plated lithium.

Consequently, an additional state variable is introduced into the second [5] model, which is the proportion of electrode surface covered by metallic lithium. For the growth rate of the coverage a simple, empirical model is proposed. Thus, the film can either grow fast in thickness or surface coverage, leading to different model response, both in time-domain and frequency-domain.

It is shown that the model can reproduce nucleation behavior during a charge simulation. Furthermore, the impedance response, as well as the Nonlinear Frequency Response is now monotonously dependent on the surface coverage with metallic lithium. In future studies, this could lead to an approximation of the plating amount, solely relying on the dynamic NFR measurement.

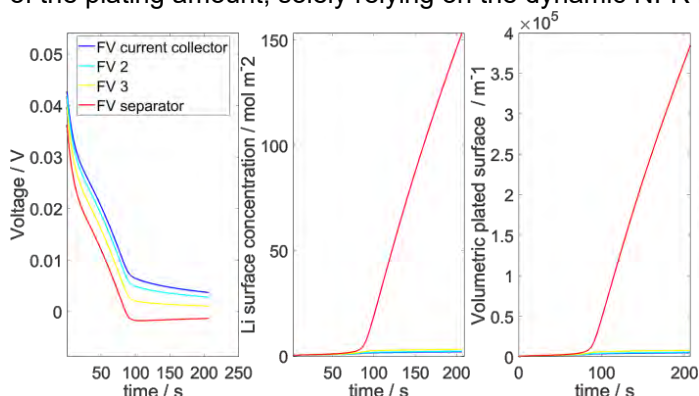


Figure 1: Fast charge simulation, anode potential of finite volumes (left), Li surface concentration (middle) and plated Surface (right)

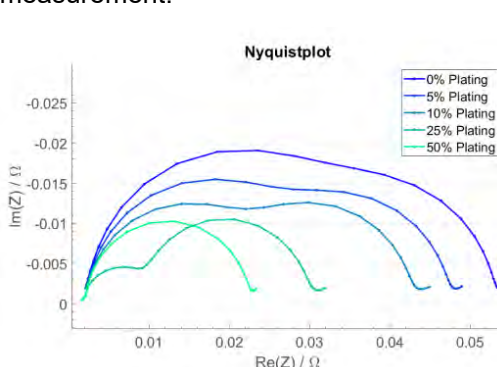


Figure 2: Dependence of impedance on the proportion of covered surface

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0-dimensional Performance Modelling of Solid Oxide Cells under pressurized Conditions

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The current-voltage behaviour of a solid oxide cell can be described with an OCV minus losses model. A zero-dimensional impedance-based dc performance model developed and validated for the operation under atmospheric conditions is available for an anode-supported cell (ASC) with a nickel / yttria-stabilized zirconia (Ni/YSZ) fuel electrode as well as for an electrolyte-supported cell (ESC) with a nickel / gadolinium-doped ceria (Ni/CGO) fuel electrode. The model contains loss mechanisms in the cell such as ohmic, charge transfer and gas diffusion, which are described by physical model equations. The model parameters are determined experimentally by electrochemical impedance spectroscopy and the subsequent analysis of the distribution of relaxation times. [1,2]

Based on this, the cell behaviour under elevated pressures will be analysed in this contribution [3,4]. The impact of pressure towards the loss mechanisms and resulting cell performance will be discussed and compared between anode and electrolyte supported cells as shown in figure 1.

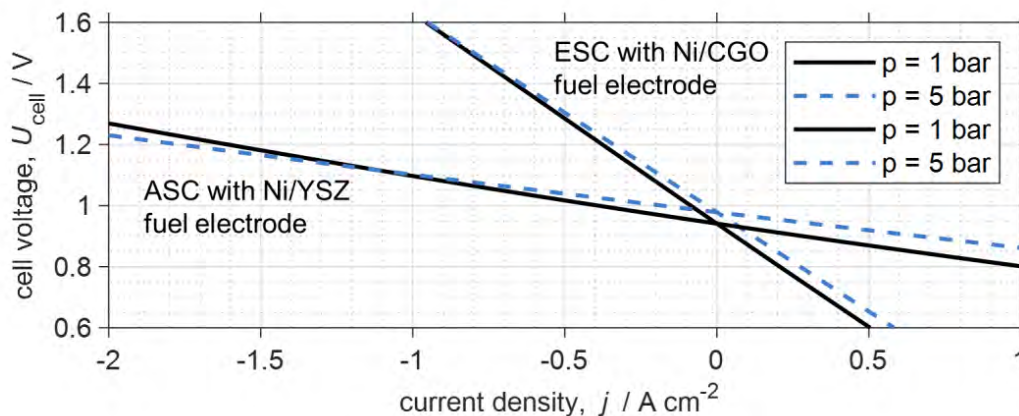


Figure 1: Comparison of the modelled current-voltage characteristics of an ASC with Ni/YSZ fuel electrode and ESC with Ni/CGO fuel electrode between 1 bar and 5 bar at 800 °C with a fuel gas mixture of 50 % H₂ (balance H₂O) and air at the air side.

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2D transient electro-chemical model of steam electrolysis with Ni/Gd-Doped Ceria (CGO) fuel electrode

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The advantages of solid oxide electrolysis cells (SOECs), such as high electrical efficiency and long-term stability, make them a promising candidate for conversion of electrical energy into chemical compounds. The presence of the active double phase boundary (DPB) [1] between CGO surface and gas phase in Ni/Gadolinium doped ceria (CGO) electrodes improves the performance compared to other types of Ni/cermet electrodes, where the active area is limited to the triple phase boundary (TPB) between nickel, oxygen ion conducting ceramics and gas phase. Detailed understanding of underlying physical processes within SOEC in general and within the Ni-CGO fuel electrode in particular is crucial for cell optimisation and understanding of cell degradation.

In the current study a 2D dynamic multiphase model of a commercial electrolyser cell is presented. The model spatially resolves cell composite layers as well as the gas channels. The following aspects are included: detailed surface kinetics, charge transport, as well as gas transport/conversion in the channels and porous electrodes. The main accent is made on understanding of electro-chemical processes in the fuel electrode. The model is parametrised and validated by electrochemical impedance measurements of an incremental 1 cm² electrolyte-supported symmetrical cell with Ni-CGO electrodes fueled with different compositions of H₂, H₂O and N₂ [2]. A spatial extension of the model and subsequent validation is successfully done for 16 cm² full cells exhibiting lateral temperature and gas concentration gradients. Furthermore, using this cell model as a building block, the development of a transient 2D model of a SOEC short stack will be discussed in this contribution.

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2. C. Grosselindemann et al., J. Electrochem. Soc., 168, 124506 (2021).

Transmission line modelling of ceria-based fuel electrodes

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For investigation of the performance limiting processes in a solid oxide fuel cell the electrochemical impedance spectroscopy is a powerful tool and the method of choice. The distribution of relaxation times analysis enables the separation of individual polarization processes in the measured spectra [1]. By using a complex nonlinear least square fit to approximate an equivalent circuit model to the measured data, a quantification of these processes is feasible [2].

The model cells which are used in this study are electrolyte supported cells with a 200 µm thick 8YSZ electrolyte. A ceria-based fuel electrode is applied by screen printing in a symmetrical setup followed by a NiO layer for an appropriate electronic contact between the nickel contact mesh and the fuel electrode.

In this study a physical meaningful modelling approach based on a two-channel transmission line model was developed. This model enables the quantification of the loss processes which occur during the operation as ionic and electronic conductivity losses of ceria and losses attributed to the charge transfer reaction. For parametrization different techniques such as the electrochemical impedance spectroscopy, 4-point dc measurements and FIB-tomography are used.

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Tools for Nonlinear Frequency Response and Time Series Analysis

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An established method for characterizing galvanic cells is electrochemical impedance spectroscopy (EIS). The cell or stack is perturbed by a sinusoidal voltage or current excitation, and the response is measured. For online monitoring in applications, cell voltage measurement (CVM) is the most common method. To increase the lifetime and reliability, non-invasive in-situ methods and tools are needed to detect the formation of local issues within the stack and reveal the cause of degradation to promote optimization of operation. Both approaches have weaknesses. EIS does not provide insight into local problems within the stack, and most of the available EIS hardware devices are designed for cell or short stack characterization and do not provide access to time series data. CVM is prone to measurement error due to fragile cell probe connections and cannot explain the cause of problems.

The publication presents an adaptable tool chain for characterization and monitoring of full-size electrochemical stacks (battery, electrolysis and fuel cells) and some approaches for new interdisciplinary methods for characterization and monitoring.

The core of the methodological approach is a proprietary customizable software that controls the perturbation via an arbitrary wavelet generator (AWG) and synchronizes the data acquisition via a multichannel digitizer (AVL X-ion™). A perturbation unit is controlled via the analogue AWG output signal, and the hardware may vary depending on the stack size. The setup depicted below can be fully integrated with test bench control software via a TCP/IP socket connection. The freedom of arbitrary perturbation and access to the unfiltered time series data with sampling rates up to 2 MHz and vertical resolution up to 24bit allow the use of methods besides classical EIS. Examples are Nonlinear Frequency Response Analysis (NFRA) or Pseudo Random Binary Signal (PRBS) excitation which are also discussed in the publication.

Initial experimental measurements and EIS characterizations using this methodology and measurement setup have already been performed on polymer electrolyte water electrolysis (PEMWE) stacks. The measurements also include a comparative benchmark study with a commercial system (GAMRY Reference 3000). The data quality without smoothing is equivalent or even better. Compared to the commercial system, the excitation current can be lower by a factor of 0.2.

A future research focus based on this methodology is on PEMFC in combination with interdisciplinary algorithms (e.g., speech recognition combined with artificial intelligence) to reduce or completely remove CVM. This improved diagnostic system will contribute to reduced degradation and hence to increased efficiency.

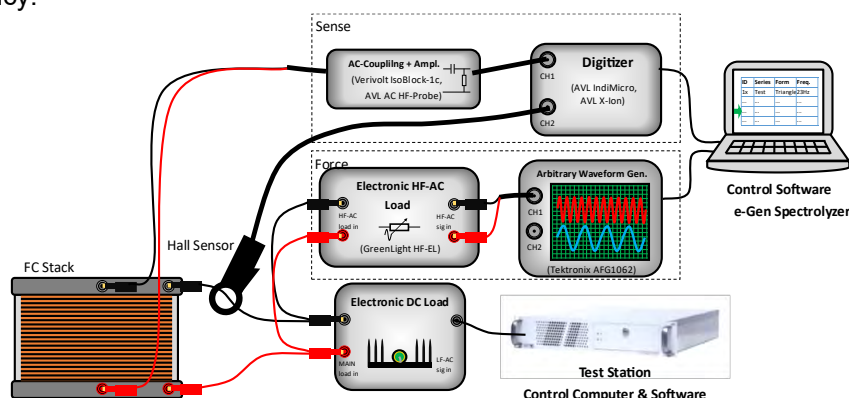


Figure 1: Flexible setup for Nonlinear Frequency Response and Time Series Analysis of galvanic cells and stacks.

Implementation of constraint-adaptation based real time optimization on a solid oxide fuel cell stack: impact of filters

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Solid oxide fuel cell (SOFC) technology is of great potential for efficient power production with low overall emissions. Control and optimization of SOFC system performance with proper methodologies are vital during the operation. This is normally achieved by standard model-based optimization. However, mismatch or disturbances always exist between a model and a 'plant' (real system), making the use of detailed models impractical for online implementation. In this case, a constraint-adaptation (CA)-based real time optimization (RTO) algorithm is proposed to drive the system to optimal electrical efficiency, while enforcing the satisfaction of operational constraints, regardless of the plant-model mismatch and disturbances.

Input or constraint filters are the main tuning parameters of the CA algorithm. They enable to control the amplitude of input changes between consecutive iterations. Thus, a proper filter value will keep the system inside the safe region during iterations, avoiding severe degradation or stack failure. Here, a comparison between input and constraint filtering with values ranging from 0.01 to 1 is performed to determine the most suitable filter for the (SOFC) stack. Based on a lumped SOFC stack model [1], the impact of different filters is investigated statically and dynamically.

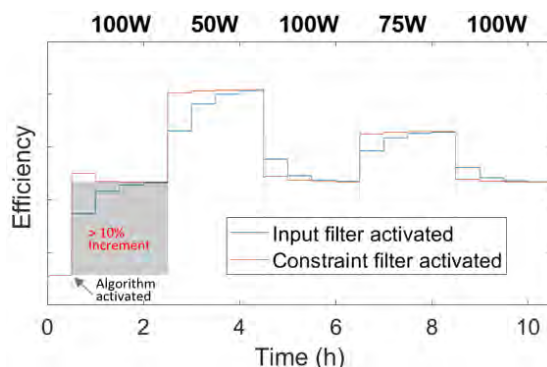


Figure 1: Impact of different filters on efficiency.

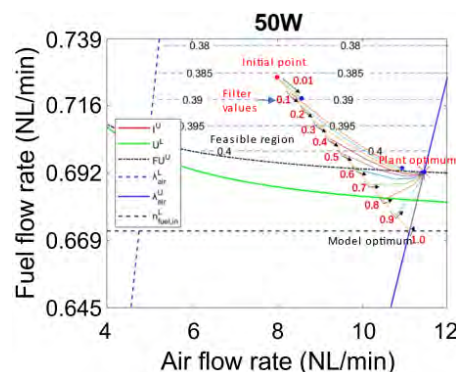


Figure 2: Impact of input filter values.

Figure 1 indicates that a CA-based RTO algorithm drives the system to its maximum efficiency in a few iterations, and that good reversibility is observed when the power output target is switched regularly, regardless of the type of filters. Note that the first RTO iteration after activation of the algorithm in Figure 1 shows a higher efficiency with constraint filtering, but this iteration is indeed infeasible since several constraints are violated. This reveals the potential danger of operating in undesired region when applying constraint filter. According to Figure 2, it can be concluded that without filtering (filter value equals to 1), the optimization process will happen outside the safe region. On the other hand, the plant optimum is not reached in 20 iterations when the filter value is too small. With a proper input filter value (e.g., 0.5), RTO iterations stay in the feasible region and the plant optimality can be reached in ≤ 20 iterations. For the constraint filter scheme, the optimization process happens in an undesirable operating region due to optimum predicted by the model falling outside the feasible region of the plant. In conclusion, a CA-based RTO algorithm with input filter can make a SOFC system hit its optimum quickly and safely.

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An analytical gas fraction and velocity profile model for gas-evolving electrodes

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Gas-evolving electrodes are present in various electrochemical processes, including the chlor-alkali process and water electrolysis. Gas bubbles rise due to buoyancy, which sets the electrolyte into motion resulting in a natural convection flow. Because visual access into dense bubbly flows is severely restricted, very few measurements of the gas fraction and velocity profile near gas-evolving electrodes exist. Knowledge of these profiles as a function of height and current density is useful for various purposes: for example as a boundary condition for reduced simulations, or to determine the convective heat transfer rate; the wall shear rate plays a role in bubble release and mass transfer as well.

In analogy with heat transport [1], the boundary layer equations can be solved analytically. This predicts that an increase in current density leads to a decrease in gas plume thickness, contrary to what is seen in most experiments. One of the reasons is that, contrary to the analogous temperature, the gas fraction is limited by the space that bubbles take up. We assume additional hydrodynamic diffusion of bubbles arises as the maximum gas fraction is approached, resulting in a broader plume. COMSOL simulations in a simplified geometry, see Figure 1, show that the gas fraction approximately follows a step-function profile, see Figure 2. We use this profile in the integral method to approximately solve the mixture model boundary layer equations [2]. This allows reasonably accurate formulas for the gas fraction and velocity profiles as a function of height over a wide range of current densities and bubble sizes.

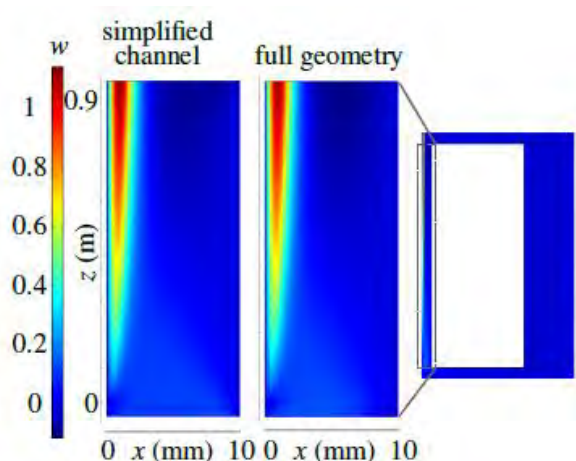


Figure 1: The vertical electrolyte velocity w is modelled accurately in a simplified geometry using Bernoulli boundary conditions [3].

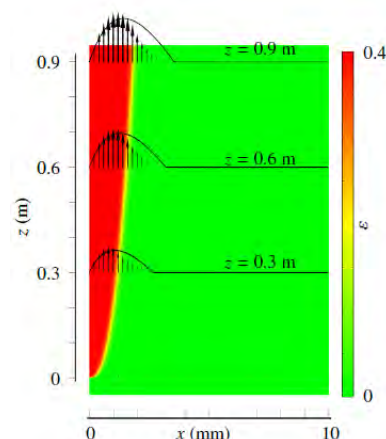


Figure 2: The gas fraction is relatively constant at an imposed maximum of 0.4 and then rapidly drops off. The resulting buoyancy induces a velocity profile that is reasonably accurately captured by the assumed analytical profile.

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Redox flow battery multiscale modelling approach using mass transfer coefficient

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In this work, a multi-scale flow battery simulation approach which highlights the connection of a micro-scale resolved 3D model¹ with a simple homogenized cell scale model is presented. For this purpose, the mass transfer coefficient is extracted from the pore scale simulations and compared to empirical relations from the literature² using the cell scale model. Both models are parameterized with the promising model chemistry of the aqueous, organic 4-OH-TEMPO system³. In addition to that, an experimental validation of the micro-scale model using the *redoxme* cell is presented.

The microscale model resolves the real geometry of the electrode microstructure obtained by experimental image reconstruction from X-ray computed micro-tomography. It 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. The model is suitable to study battery performance e.g. power density as a function of different concentration, electrolyte velocity or discharge rate. With this, the mass transfer coefficient is extracted under operating conditions where transfer limitations are most likely to occur. In order to do this, bulk and surface concentration of active material as well as reaction rate obtained by Faraday's law are used.

The 2D homogenized cell-scale model considers a flow battery half-cell incorporating single species transport and reduced order reaction mechanism. The simple and arbitrary cell design is inspired by experimental cells in the literature. The extracted mass transfer coefficient is a function of state of charge and distinctive for specific flow velocity, initial concentration and discharge rate. It is used to calculate the reaction rate for the evolving species in the porous electrode. Further, it is compared to empirical relations based only on the flow velocity, showing similar order of magnitude and opposing course directly after the inlet manifold of the cell.

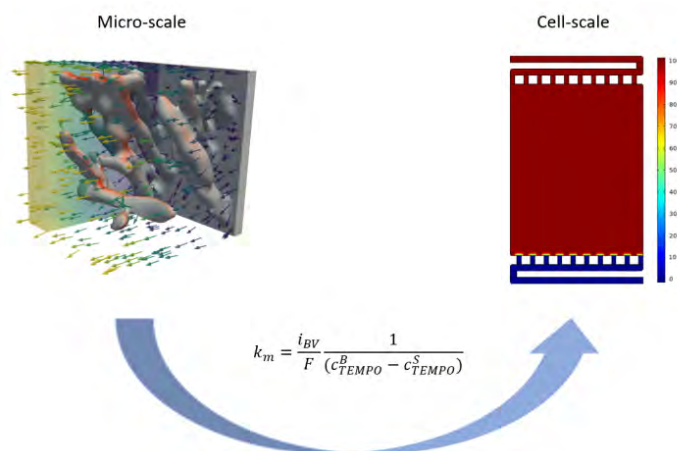


Figure 1: Simulated half-cell compartments of the micro-scale and the cell scale model. Connection via extraction of the mass transfer coefficient from the micro-scale to the cell-scale.

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A Transient Non-isothermal Cell Performance Model for Organic Redox Flow Batteries

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Redox flow batteries are an emerging technology for large-scale grid energy storage of intermittent renewable energy sources, such as photovoltaics and wind farms, thanks to their beneficial properties, such safety and long cycle life. Specifically, organic redox flow battery (ORFB) systems are a promising approach for electrical energy storage. This is due to the vast chemical space available for electro-active redox couples and the prospect for greater sustainability.

To describe and simulate the main processes within a flow battery cell we developed the spatially reduced physics-based 0D-U-I-SoC cell model [1]. To extend the predictive capabilities of the reduced cell model we develop a transient, non-isothermal cell performance model that captures spatial inhomogeneities of the field variables, such as the species concentrations in the porous electrodes.

Error! Reference source not found. illustrates the considered simplified cell geometry in the through-plane direction of the cell assembly. The physics-based macrohomogeneous cell model solves the balance laws for mass, momentum, and energy transport in the current collectors, the porous electrodes, and the ion-exchange membrane.

To account for the effective macroscopic transport properties in the porous electrodes, such as effective diffusion coefficient, we integrate a porous electrode model based on the volume averaging method. Additionally, we develop an effective membrane model that accounts for all important modes of transport including osmosis and the electro-osmotic drag.

The model is parameterized and validated with experimental data of laboratory test cells for promising organic molecules and subsequently used to study and optimize the energy efficiency with respect to the cell geometry and operating condition, such as flow rate and ambient temperature. Furthermore, the model is used to predict time-dependent phenomena, such as EIS measurements and voltammetry experiments.

Cell Performance Model

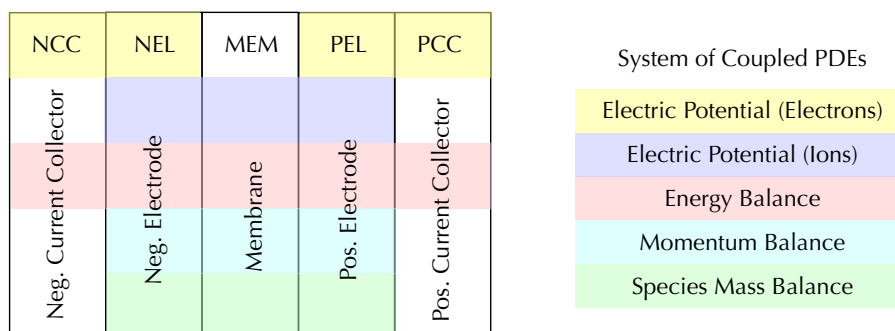


Figure 1: Through-plane cross-section of a simplified flow battery cell geometry.

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Effects of Mixed Gas on Degradation during Start-Up Shut-Down of PEMFCs: A Numerical Study Validated by Segmented Cell Experiment

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Degradation of proton exchange membrane (PEM) fuel cells during the start-up and shut-down is a major issue limiting its application in Automobiles [1]. During the start-up and shut down, the hydrogen and air coexist in the anode electrode, which could cause a sharp increase in the local cathode potential difference and lead to carbon corrosion, namely reverse-current mechanism [2].

Through the literature, much effort has been devoted to model and study the start-up and shut-down of PEM fuel cells, but most works simply divide the anode into "power" and "load" regions through an artificially defined hydrogen/air front interface [2-4]. However, in the real start-up and shut-down operations, such hydrogen/air front interface doesn't exist, and the anode is mostly filled with hydrogen/air mixed gas. In this work, for the first time, the effects of hydrogen/air mixed gas on degradation during start-up and shut-down are investigated and discussed. A transient quasi-2D model is developed with mass transport, electrochemical kinetics, and pseudo-capacitive effects all addressed. Most importantly, the local potential of each segment along the channel is calculated independently based on the local mixture gas concentration with no artificial front interface imposed. The model is developed on in-house code and implemented in Python. With the present model, a more detailed and realistic description of the start-up shut-down can be obtained, such as the distributions variation of concentration, membrane potential, and various electrochemical reaction rate, which helps to reach a deeper insight into the degradation mechanism. Simulation results show the membrane potential is very sensitive to the presence of hydrogen due to its fast chemical kinetic. To validate the present model and simulation results, the start-up shut-down cycles experiments are conducted on segmented PEM fuel cells where the local potential and local electrochemical surface area (ECSA) can be measured. The experimental results show the ECSA loss along the channel direction matches well with the carbon corrosion distribution in the simulation results (Fig. 1), which validates the model.

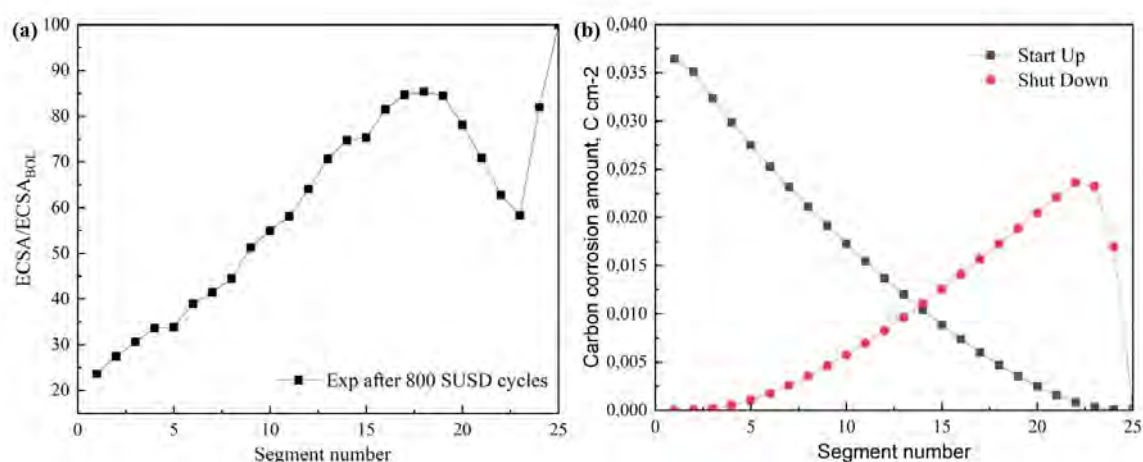


Figure 1. (a) Experimental data: ECSA loss distribution of segmented cell after 800 SUSD cycles; (b) Numerical data: Carbon corrosion distribution in start-up and shut-down process

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Use of a pseudo-3D model for understanding operating heterogeneities in PEMFCs

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Proton Exchange Membrane Fuel Cell (PEMFC) is a promising technology for decarbonized transport. However, the improvement of its performance, cost and durability remains necessary for its industrialization at a larger scale (1). It has been previously reported that operating heterogeneities over a large cell area may induce fuel cell performance and durability decrease (2, 3).

Indeed, in a cell, electrochemical reactions do not take place homogeneously on the active surface area. The magnitude and orientation of the thermal gradient of the cooling fluid, the oxygen concentration gradient between the gas inlet and outlet and other fluid factors, which impact the current distribution, play a significant role on the local degradations of the active surface area (2). The studies conducted so far focus on the relationship between the operating heterogeneities and the local degradation on the active surface area for a few operating conditions (3). The objective of our study is on one hand, to better understand the role of those heterogeneities and on the other hand, to identify strategies to control the current, temperature and water distributions to optimize the performance and durability of the cell. To that end, a numerical study is based on a pseudo-3D multi-physics and single-phase model of a standard size cell, developed on COMSOL Multi-physics (2).

In order to calibrate this model and to simulate the influence of temperature and concentrations gradients, the electrochemical response is measured on a small cell called differential cell. This cell is designed to have in plane operating conditions as homogeneous as possible. In this study, the latter is used to emulate the operating conditions representative of 3 chosen areas (inlet, outlet and middle of the cell). Once calibrated, the pseudo-3D model allows to calculate the distributions from 108 operating conditions. Those 108 conditions are chosen from a full factorial experiment design defined according to the automobile application of PEMFC.

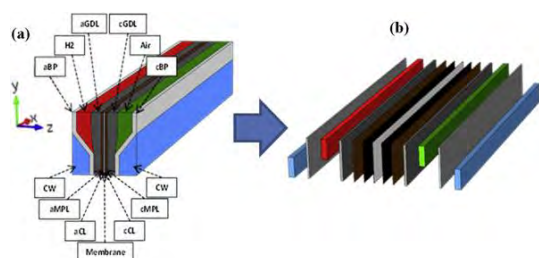


Figure 1: Geometrical approximation from the 3D geometry (a) to the pseudo-3D approximation (b), at the channel/rib scale. (2)

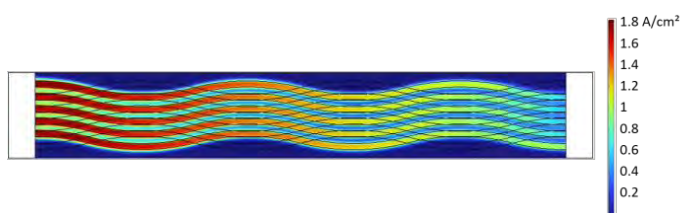


Figure 2: Screenshot of the current density distribution on the active area of the cathode side calculated by the pseudo-3D model. Model of a 5 channels cell with a wavy channel design.

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Modeling of ejectors applied in PEMFC systems

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PEMFCs are usually operated with a stoichiometric factor greater than 1 on the anode side. Therefore, recirculation of the unconsumed hydrogen from the anode outlet to the anode inlet is necessary to achieve fuel utilization efficiencies near 100 %. The recirculation can be done either actively by a blower or passively by an ejector, as shown in Figure 1.

In this work, the efficiency potentials that are possible by using passive instead of active recirculation are investigated. The electrical power saved has a direct influence on the system efficiency, which can be increased by a maximum of around 3 %.

The ejector performance itself is affected by the operating parameters of a fuel cell stack, such as the stoichiometric factor or the anode inlet pressure. This means that the performance of a fixed geometry ejector varies over the entire operating range of the fuel cell stack. Therefore, the objective of this work is to determine an ejector geometry that achieves high ejector performance over a wide operating range of the fuel cell stack.

For this purpose, the thermodynamic processes of an ejector are represented in a 1-D model, whereby the potentials of three basic ejector operating strategies are analyzed. An exclusion criterion for an operating strategy is the formation of liquid water or ice in the ejector. Parameter variations are carried out to investigate the influence of pressure, temperature, relative humidity, stoichiometric factor and mass flows on the ejector operating behavior. The values of these parameters are dictated by the operating conditions of a fuel cell stack and are therefore not constant.

From the knowledge gained, a suitable operating range with high performance of the ejector is determined. Finally, the chosen geometry of the ejector is validated and the potentials for a passive ejector are summarized. With this work, we aim to make further progress in the thermodynamic design of the anode circuit of fuel cell systems.

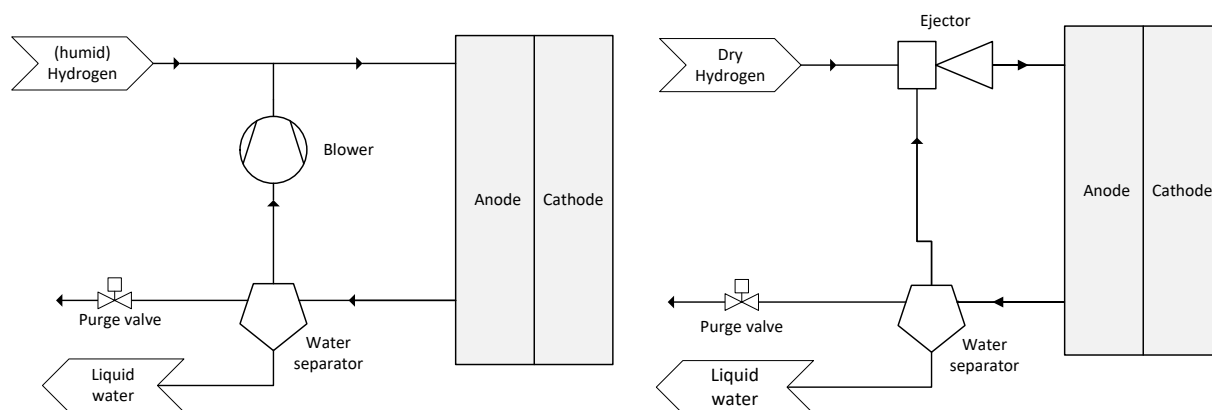


Figure 1: Active recirculation (left) vs. passive recirculation (right)

Spatially resolved, impedance-based PEMFC Stack Model for observation and monitoring

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In applications of polymer electrolyte membrane fuel cells (PEMFC), the correct, simulative prediction of produced electrical and thermal power is highly relevant. Furthermore, harmful operating conditions enhancing fuel cell degradation should be prevented. To achieve this on the FC-system level, the control unit has to consider the interplay between BoP and stack performance and should be able to predict critical states in the stack.

Predicting performance and operational states in a stack reliable is complicated due to spatially deviating operating conditions combined with the nonlinear electrochemical behaviour of the cells. Harmful operating conditions arising locally and temporarily in the stack can hardly be detected during operation.

Therefore, the control of a fuel cell systems would benefit from an observer that predicts the stack performance based on space resolved local operating states and at the same time has a significantly lower computational effort than conventional CFD simulations.

We address this challenge by a multi-physics stack model, which couples (i) the non-linear electrochemistry within the cell, (ii) the fluid pressure drops along the gas channels and (iii) the thermal behaviour within the stack. The spatial resolution focusses on the most relevant directions of each process and thus limits the computational effort.

Simulation runtime is further reduced by modelling the electrochemical behaviour with algebraic equations. These relations and parameter result from a physico-chemically meaningful equivalent circuit model and electrochemical impedance spectroscopy (EIS) measurements. In this approach the interaction of the non-linear loss processes within the cell and the operating conditions can be spatially resolved, quantified and interpreted physically. Therefore, the performance limiting factor can be identified.

Additionally, harmful, local effects as overheating, undersupply of gases or drying out of the membrane are also observed. These information enables the system control to prevent worse damage and extend the achievable operating time. This insight into internal cell state can be transmitted to the control of the fuel cell system and used to optimize performance and efficiency considering durability aspects.

In this contribution a multi-physical stack model considering gradients relevant operating conditions is presented. The local distribution of different loss processes is simulated and physically interpreted. It is also shown how local critical operating conditions within the cell area can be detected during operation. Finally, further challenges in simulation and validation are derived.

1D simulation of fuel cell systems for real-time applications

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Supporting the development of fuel cell systems with suitable simulation models plays an important role in achieving the specified performance and lifetime requirements on the way to zero emission mobility. On the one hand, the precise prediction of operating conditions during the transient fuel cell system operation is required to design and optimize system components. On the other hand, real-time models are crucial for XiL (Software in the Loop, SiL; Model in the Loop, MiL; Hardware in the Loop, HiL) applications. Both predictive and fast 1D simulation models are subject of current development.

In our poster we show an overview over our current work and targets in setting up 1D fuel cell system simulation models for transient simulation. The requirements of a design-oriented system simulation include the accurate prediction of key quantities, like stack power, anode and cathode pressure, water transport and species composition. Specially highlighted are the stack model and its calibration and the modelling and validation of essential components of the balance of plants, like the ejector and the humidifier.

The calibration and validation of the 1D stack model, based on experimental measurement data, is a key requirement for the accurate match of its behavior in the whole operating range. A novel stack calibration strategy, combined with the test of different specialized water transport models (e.g., [1], [2]), is developed focusing on modelling the accurate water transport within the fuel cell stack. Experimental water balance data is used to calibrate the simulated H₂O crossover in the polymer electrolyte membrane (PEM). Figure 1 shows the measured versus the simulated H₂O crossover rate in defined operation points representing the whole operating range of the fuel cell system.

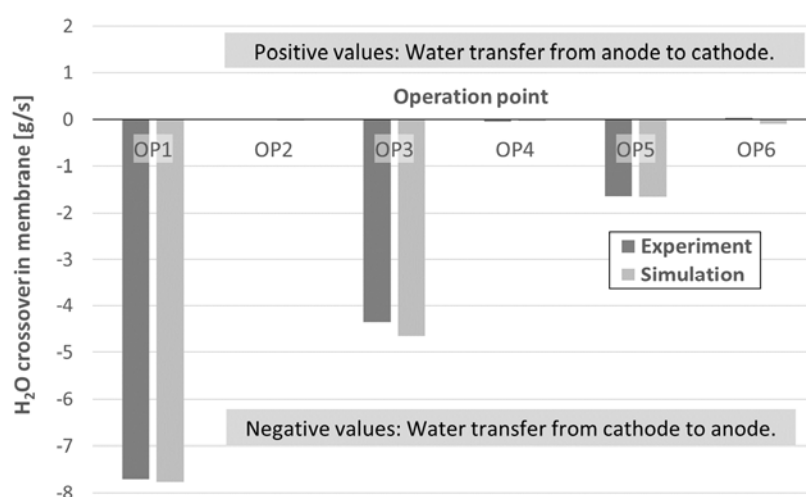


Figure 1: Validation of simulated H₂O crossover in 1D stack model based on experimental water balance data.

A real-time simulation in contrast to the detailed predictive 1D fuel cell system model focuses primarily on simulation speed while minimizing the loss in prediction quality. Regarding simulation speed, currently a dual approach is pursued: a model for near-term real-time requirements and a more detailed 1D model for design simulations. The mid-term goal under current investigation is to derive a real-time model directly from the design simulation, thus avoiding the need for multiple models developed in parallel. This comprises speeding up the detailed model by solver changes, the development of component models designed for real-time and model simplifications. As the simplification process is tedious and time-consuming by hand, a python automation is being developed to do this completely automatic.

Membrane humidifier model for PEM fuel cell systems

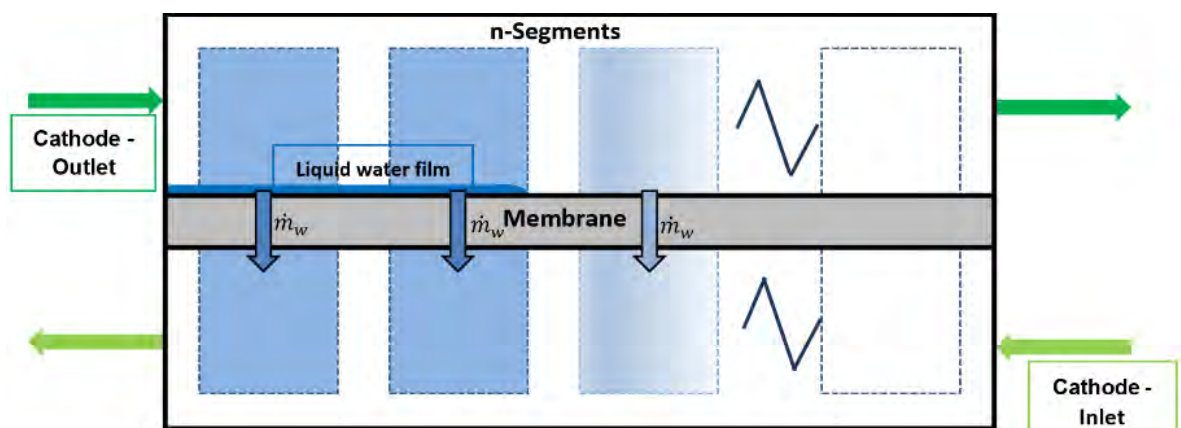
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Humidification within a PEM fuel cell system is mostly realized by a membrane humidifier, which generally transfers the water in the cathode exhaust to the cathode inlet gas. Water transfer and gas separation are usually realized by a PFSA membrane. The polymer chains of these membranes consist of a hydrophobic backbone and hydrophilic side chains. The orientation of these groups and the ability to fill pores varies greatly depending on whether the water present is liquid or vaporized. This results in a strong dependence of the transport properties of PFSA membranes on the physical state of the water. This phenomenon is called the "Schröder paradoxon". Therefore liquid water in the humidifier inlet gas stream affects the water recovery ratio and thus the performance of a membrane humidifier. Liquid water at the humidifier inlet may be present depending on several factors e.g. the fuel cell system operating point, the fuel cell system architecture, the fuel cell, and the environmental conditions. Current membrane humidifier models in the literature neglect liquid water components in the cathode exhaust gas. In this work a new model for this type of humidifier is proposed that accounts for the differences in the water transport depending on the physical state of the water. In the model, the water transport through the membrane is calculated considering mass transport resistances in series. In general, this series connection consists of boundary mass transport resistances and a membrane mass transport resistance. The boundary resistance can be neglected if liquid water is present as shown in experimental data in the literature. The model was implemented in Matlab Simulink and allows a discretization along the main flow direction of the inlet and exhaust air path (along the channel). As a result the humidity evolution along the channel can be calculated and analyzed. Also the change of membrane state and properties along the channel can be plotted, for example the water content or the diffusion coefficient. In addition the presence and the ending of a liquid film at the membrane surface as a consequence of liquid water at the humidifier inlet can be mapped by the model as shown in the figure below. As evidenced by experiments, consideration of liquid water results in higher water transport and thus higher water recovery ratio than commonly used models for membrane humidifiers.



Schematic figure of the segmented humidifier simulation model, the blue color indicates the relative humidity of the gas stream

Transient operation and controller analysis of a fuel cell based powertrain for aviation

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In commercial aviation the necessity to reduce greenhouse emissions is a strong inducement for technical innovations. A promising key technology on the path to emission-free aviation is electric propulsion in combination with polymer-electrolyte membrane fuel cells (PEMFC) [1]. In contrast to most ground-based applications the operation of airborne fuel cell systems is facing some challenges. On the one hand, these are the varying environmental conditions as for example air temperature and pressure. On the other hand, the energy system needs to be able to provide sufficient electric power to the propulsion even in fast transients. As battery storage at present comes with a large weight penalty it is favorable to provide the energy solely by fuel cells [2].

In this study it is investigated how these preconditions affect the transient operation of the fuel cell system in an aircraft and which implications arise on the implementation of the fuel cell system controls. For this purpose, a control-oriented model of a fuel cell system with focus on stack, power conditioning and air supply is used. Subsequently, as depicted in Figure 1 the fuel cell system is coupled with a simple electric motor and propeller model providing the boundary conditions induced by the propulsion unit. The overall system is sized to propel a Cessna 172 airplane which also sets the conditions for a generic flight missions used for a dynamic simulation of the powertrain.

The results show that in the chosen scenario the fuel cell based powertrain is able to satisfactorily provide the required propulsion even in the transients. Furthermore, it can be seen that because of the strong coupling between cathode pressure and air mass flow a centralized control is necessary. In addition the study revealed a tradeoff between power delivery and oxygen excess ratio which in turn is crucial for stack lifetime and needs to be considered when tuning controllers for the powertrain.

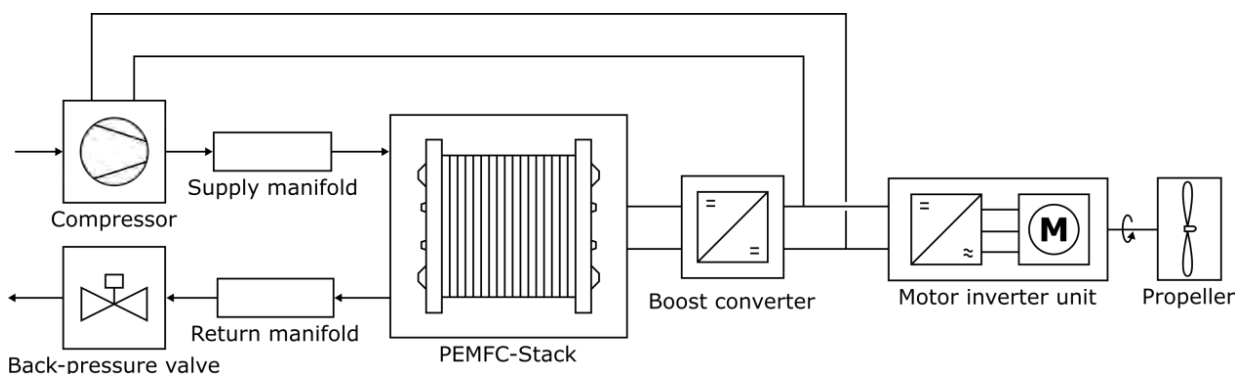


Figure 1: Reduced model of PEM fuel cell based powertrain

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Prediction and modelling of a proton exchange membrane fuel cells performance and degradation using multi-domain and multi-scale models

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The increasing concern for climate neutrality and a pollution-free environment paves the way for ever stricter emission regulations in the automotive and energy sectors. Prevention and reduction of the rate of degradation reactions of proton exchange membrane fuel cells (PEMFCs) while maintaining their high performance and efficiency are a major challenge on the way to their wider market adoption. To achieve these goals, further optimisation at the component and system level is required. In order to meet the demands for shorter product development cycles and lower development costs while approaching the engineering limits in power density and lifetime, it is necessary to rely on modelling and simulation tools in the development process of PEMFC systems.

Innovative and proprietary multi-scale models and scale bridging methodologies devised by the University of Ljubljana enable efficient support of the development process of FC based technologies throughout the entire V-development process. Furthermore, the bidirectional consistency between lower and higher scales in the development phases is of utmost importance as it can accelerate the virtually supported FC research and development from the material to the device level (left arm of the V-development process) and thus make an important contribution to the development of critical components. State-of-the-Art models (1)-(7) are, with the aim of maintaining consistency of models and parameters, which reduces development time and cost while increasing consistency and transferability of models, transferred to the testing and validation phases (right arm of the V-development process), which enable unprecedented interaction of experimental and modelling approaches. This improves the deciphering and understanding of the underlying phenomena and thus the prediction of the performance and degradation of FC under different operating conditions (2), (3), (5), (7). Furthermore, computationally optimized realizations of scalable physics-based models support transferability from early development stages to XiL (Software-in-the-Loop, Model-in-the-Loop, Hardware-in-the-Loop) verification and testing.

Moreover, computationally optimised models also form the basis for customised, spatially resolved SoX observers (State-of-Operational-Conditions, State-of-Health, State-of-Function, etc.), which provide deeper model-based insight into internal states of FC, opening up new perspectives for advanced monitoring and control of FC systems. Component, subsystem and system testing with these models (5) is also very valuable and an important part of advanced cyber-physical platforms to maximise test efficiency in terms of test time and extracted information. In particular, such models are combined with parameterisation tools, parameter identification tools for assessing uniqueness of parameter identification and model-based DoE methodologies (4). This enables the development, verification and testing of a variety of functionalities beyond the State-of-the-Art functionalities, such as virtual sensors in SoX observers on real units under test, in advanced HiL systems where optimal excitations are generated to identify or diagnose relevant phenomena, such as the origin of performance degradation. All of this plays an important role in adapting the system to the respective requirements of the individual cells and stacks and in system optimisation during the phases of the customised development process.

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Investigation of the operating strategy of a hybrid multi fuel cell system powertrain for heavy duty vehicles

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PEM fuel cell drivetrains in heavy duty applications are mostly implemented using multiple fuel cell systems and as battery hybrid systems. The complex architecture of those hybrid system results in various degrees of freedom in the operating strategy. Those have a major influence on aspects such as dynamics, efficiency and durability of the entire system.

In order to be able to analyse and evaluate the capability of an efficiency optimized operating strategy, the ZBT fuel cell model is integrated into a fuel cell system and a full vehicle simulation implemented in AVL Cruise™ M and Model.CONNECT™. The dimensioning parameters are inspired by the Hyundai XCIENT Fuel Cell with 20 t total permitted mass.

Starting from a stable and universal operating strategy, individual aspects are modified and their effects on efficiency and dynamic are investigated. For the investigation urban and non-urban speed profiles are used.

Generally, an optimization focused solely on the fuel cell operation is not sufficient, since this can lead to significantly increased losses in other system components, such as the power electronics or the battery. For this reason, the influence of the load distribution on the individual systems and its effects on the overall system efficiency and consumption is taken into account for the most comprehensive operating strategy possible.

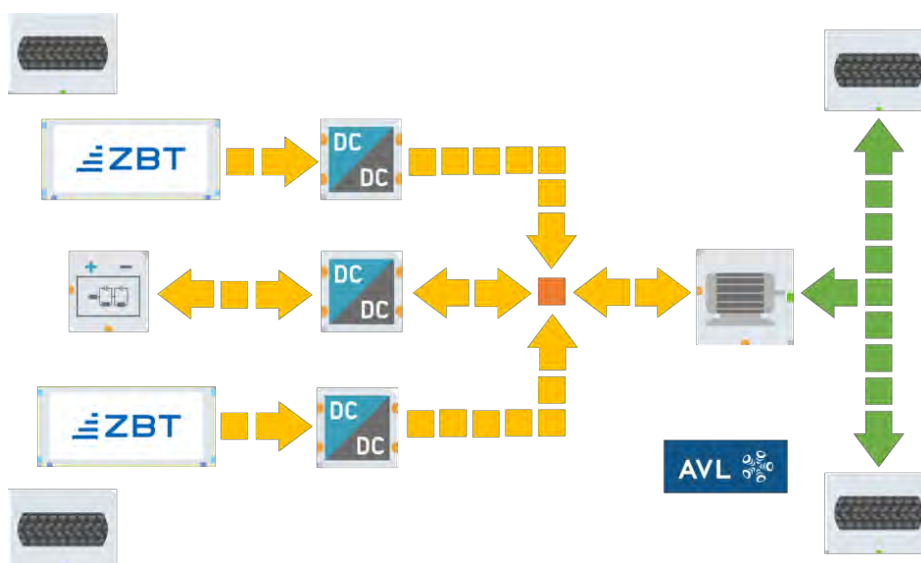


Figure 1: Schematic structure of the hybrid multi fuel cell system powertrain for applications in heavy duty vehicles

Keywords: PEMFC, fuel cell system, heavy duty applications, hybrid control strategy

Optimization of a Fuel Cell System efficiency with respect to the cathode compressor control strategy

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The cathode compressor is the most crucial part for the stoichiometric air supply of a fuel cell stack system and usually represents the biggest power consumer among the other balance-of-plant components. Therefore, the operation of the compressor is one of the most significant influences on the overall system efficiency. Due to its relatively large operating range, the cathode compressor offers a lot of potential to optimize the efficiency of the system. Pressurization can increase the voltage of the fuel cell stack, but in turn results in higher power consumption of the compressor.

For the purpose of this study, a wide variety of steady-state power requirements were conducted in a 10kW system simulation, set up in AVL Cruise™ M and Model.CONNECT™. These power requirements were carried out for several cathode stoichiometries and pressurizations. The ZBT self-developed 1D-2D PEM fuel cell stack model is integrated into the fuel cell system model. The investigated cathode compressor is parameterized with the Celeroton CT-17-700.GB. A cooling circuit and the recirculation of the anode gas are also simulated in the system. Based on the results of the study, a new operating strategy of the cathode compressor is developed. This optimization includes finding the best trade-off between power consumption of the compressor and the fuel cell performance at given power requirements.

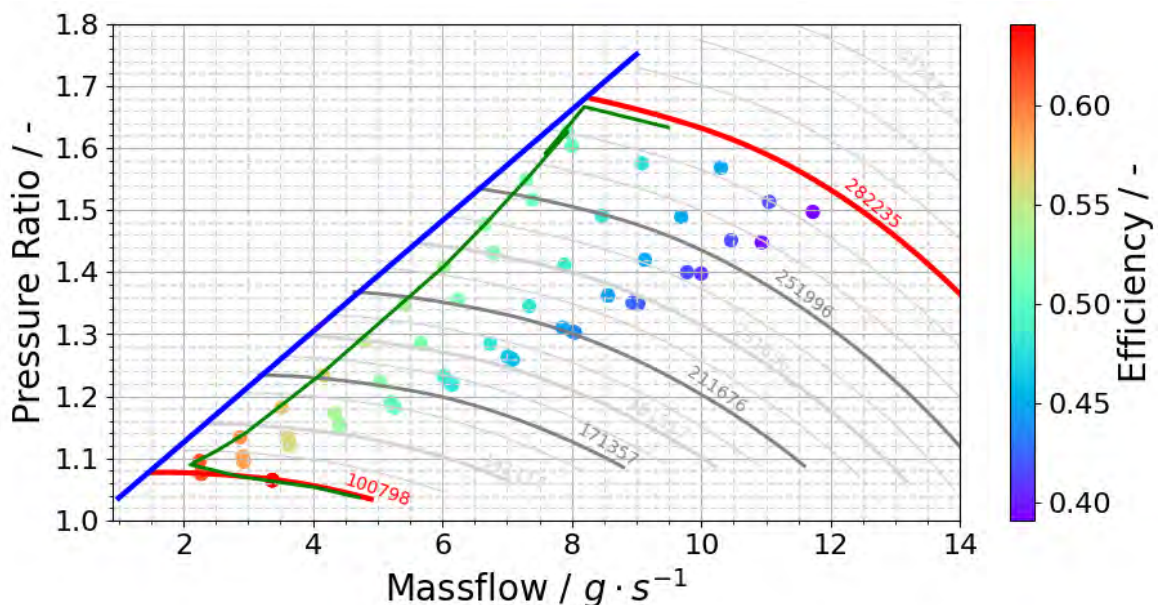


Figure 1: Executed variations of the pressurization and power requirement for a cathode stoichiometry of 2.5 shown in the compressor map (dots). The grey lines represent the compressor speed and the red lines the limiting speeds. The surge line of the investigated compressor is depicted in blue. The green line represents the resulting operation path of the compressor for varying fuel cell power requirements with the highest system efficiency.

Keywords: PEMFC, fuel cell system, cathode compressor, control strategy

Top-down approach of a continuum mechanistic model for high-temperature electrolysis

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Digital twins promise ever-improving prediction of potential defects and component failures. They are used for prototype development to shorten time-consuming measurement series or material development steps by predicting results [1]. Those can be set into relation of the desired project aim. Within the “Power-to-X” technologies, Solid Oxide Cells (SOCs) are investigated with respect to their potential to store renewable energy in the form of hydrogen or couple with the product syngas to the chemical sector [2]. High-temperature electrolysis belongs to the most efficient types of energy conversion systems compared to other technologies [2,3]. Various aspects like degradation behavior, cell performance or alternative electrode materials are experimentally investigated in our group [4-7]. This abstract describes a real-scale high-temperature SOC operated in electrolysis mode. A continuum mechanistic multiphysics model for three types of electrolysis processes (steam, CO₂ and co-electrolysis) is presented. The model is evaluated with respect to the relevant parameters like the exchange current density including parameter variations for e.g. the inlet gas stream, flow rate of the gas or temperature. The electrode kinetic parameters including the operational ones turn out not to be sufficient to properly describe the macrohomogeneous system with respect to measurable quantities like current-voltage (iV-) characteristics. Therefore, microstructure analyses of the fuel (Ni / 8 mol% yttria stabilized zirconia (Ni-8YSZ)) and air electrode ((La,Sr)CoO_{3-δ} (LSC)) from a commercially available button cell from Elcogen were made by Focused Ion Beam Scanning Electron Microscopy (FIB-SEM). The Triple Phase Boundary Length (TPBL), the fraction of electronic and ionic phase in the selected volume as well as porosity and tortuosity are calculated. The TPBL is transformed into a specific surface area to volume ratio for the model computation which decisively influences calculated iV-characteristics. Porosity and tortuosity parametrize a porous structure in order to avoid computationally extensive real geometry calculations. Sensitivity analyses are carried out for parameters that are difficult to vary in experiments. Basis for the comparison are calculated and experimental iV-characteristics. The main contributions of relevant loss mechanisms can be identified and significant parameter intervals affecting the characteristics can be preliminary stated. Both steps together initiate a feedback loop for optimal operating conditions and material optimization. Electrochemical Impedance Spectroscopy (EIS) calculations on the model reveal further details. The spectra together with their Distribution of Relaxation Time (DRT) transformation help to identify single processes and dominant contributions. Parameter variations over few orders of magnitude of the mentioned quantities show the processes' behavior. Similar patterns may be found in experimental results and yield further insights into the often difficult to evaluate experimental EIS data.

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Numerical Investigation of Conductivity Additive Size Distribution in High-Power and High-Energy NMC Based Lithium-Ion Battery Cathodes: Application Based Guidelines

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A lithium-ion battery (LIB) cathode comprises three major components: active material, electrical conductivity additive, and binder. The combination of binder and electrical conductivity additive leads to the formation of agglomerates known as the carbon binder domain (CBD). The preparation of a LIB cathode strongly influences the dispersion of the above-mentioned constituents leading to the formation of distinct pore and electrical conduction networks. The resulting structure thus governs the performance of LIBs. The presence of CBD is essential for the LIB cathode's structural integrity and sufficient electrical conductivity. However, CBD abundance in LIB cathodes leads to unfavorable gravimetric and volumetric consequences owing to its electrochemical inertness. Increasing CBD content adds to the weight of the LIBs, thus negatively impacting the energy density. Furthermore, increased electrical conductivity is won at a cost of ionic conductivity as CBD agglomerates breach the pore networks in the cathode microstructure.

This study provides guidelines for the size distribution of the conductivity additive in NMC-based lithium-ion battery cathodes with respect to its influence on electrochemical performance. The contrasting design strategies as well as operating conditions applicable to high-power and high-energy cathodes lead to significant differences in performance limiting factors for the respective microstructures. Hence, a generalization of the optimum distribution of the passive materials that enhances cell performance in all cases is not possible. In this work, four distinct distributions of conductivity additive agglomerate/aggregate sizes resulting from varying mixing conditions have been investigated with respect to their compatibility with cathode microstructures intended for different lithium-ion battery applications with the help of spatially resolved electrochemical simulations¹. It was found, that in the case of high-power cathodes, wherein ionic transport is the dominant performance limiting factor, a more significant proportion of agglomerates that are bigger in size leads to improved diffusion and intercalation conditions. Conversely, in the case of high-energy electrodes wherein the conductivity additive content is minimized, a larger fraction of smaller aggregates, produced by the fragmentation of the agglomerates during the mixing process are essential to ensure sufficient electrical conductivity.

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Stefan-Maxwell diffusivities for nafion 117 in aqueous sulfuric acid solutions

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Membranes are an essential component in many electrochemical devices, such as redox flow batteries and fuel cells; they not only serve to prevent the catholyte and anolyte from mixing but also provide an ionic pathway between the electrodes to allow redox reactions to proceed. Diffusion across membranes directly affects the efficiency and robustness of such devices and mathematical modelling of the process can aid in understanding the system dynamics, as well as improving the system performance.

One way of mathematically describing diffusion is through the Onsager-Stefan-Maxwell formalism, a framework based on binary interactions among constituent species in the system [1,2]. The key parameter in this framework is the Stefan-Maxwell diffusivity, a coefficient that characterises such binary interactions. Knowing Stefan-Maxwell diffusivities offers great flexibility in diffusion modelling, because often-reported Fickian diffusivities can be constructed from Stefan-Maxwell counterparts. Given Fickian diffusivities change considerably under different operating conditions, having Stefan-Maxwell diffusivities can reduce the need to perform characterisation experiments, in principle. The problem, however, is that accurate Stefan-Maxwell diffusivities are rarely available, especially for membrane systems.

We aim to characterise Stefan-Maxwell diffusivities for nafion 117 submerged in aqueous sulfuric acid solutions of varying concentrations. This is done by revisiting the first set of experimental work by Verbrugge and Hill [3], where a sulfur isotope is used to track the movement of the bisulfate ion across the membrane. Their experimental set-up is illustrated in figure 1 and the resulting concentration dependence of the Stefan-Maxwell diffusivity between the proton and negatively charged nafen sulfonate group is shown in figure 2. The obtained parameters are then validated by comparing Verbrugge and Hill's second experiment from the same paper [3] with simulation results.

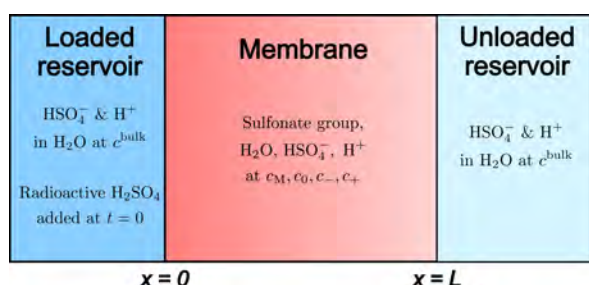


Figure 1: Diagram of Verbrugge and Hill's [3] experimental set-up.

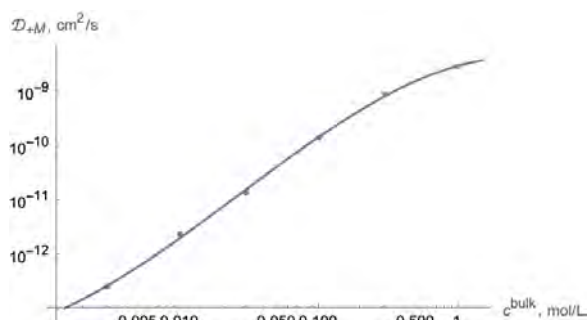


Figure 2: Stefan-Maxwell diffusivity between proton and negatively charged nafen sulfonate group.

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Observation of spatial-temporal evolution of humidity distribution in a segmented PEMFC

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Proton exchange membrane fuel cells (PEMFCs) have become a promising alternative to internal combustion engines, especially in the application of heavy-duty vehicles. Fuel cell operation in a vehicle application however is highly dynamic and therefore requires a good understanding of the transient behaviour of a PEMFC. Thus, we propose an approach for local and transient in operando measurements of humidification along the channel of a segmented PEMFC. Based on the impedances at fixed frequencies and temperature, equivalent relative humidity data is acquired and compared for transient experiments. Based on our results we can show that the classical 1kHz resistance in combination with a proper parametrization is a good choice for monitoring the ionomer humidification. A fast acquisition rate offers high resolution insights into the spatio-temporal dynamics of a PEMFC. It reveals that the current density and humidity distribution response to changes in stoichiometry is highly inhomogeneous along the channel. The data is further used to establish a qualitative model that explains and predicts local dynamic phenomena occurring along the channel during local drainage or humidification.¹ This qualitative model is further used to classify different stages of transient behaviour of a PEMFC, which offers a tool to easily compare different material combinations in their dynamic behaviour.

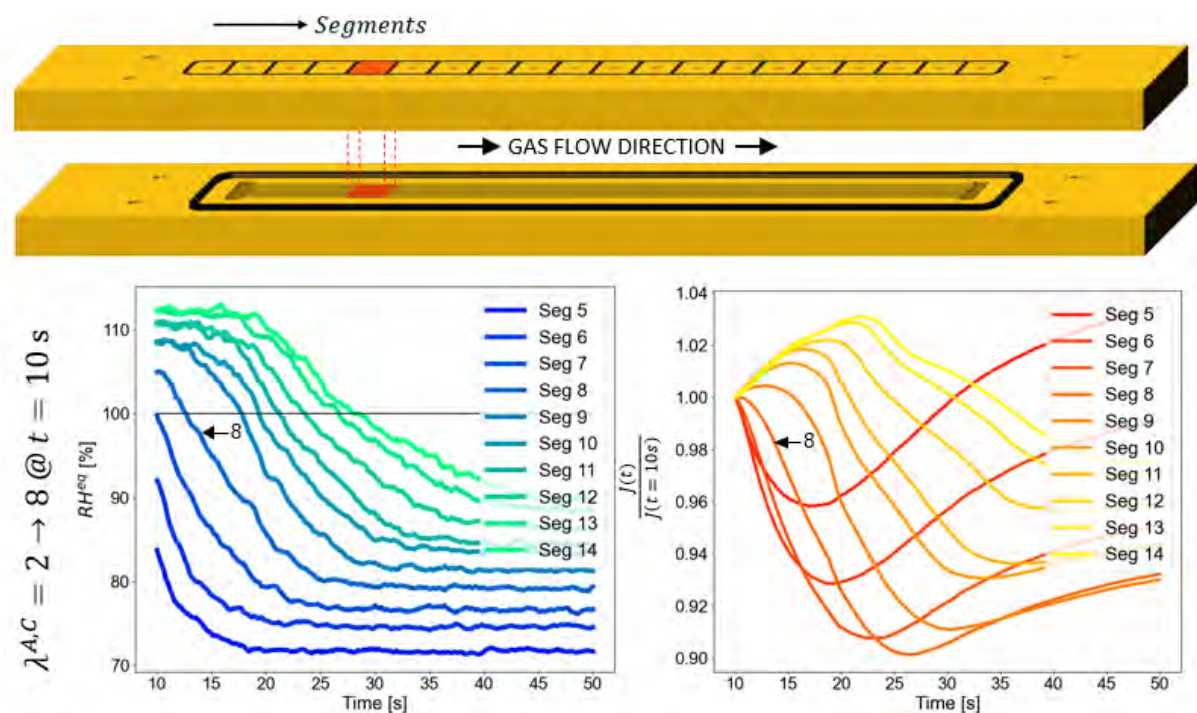


Figure 1: Spatio-temporal resolved evolution of equivalent relative humidity and normed current density. The equivalent relative humidity is based on the 1 kHz resistance and the current density is normed to the local value at $t = 10$ s. Conditions are H_2/O_2 , $T = 70$ °C, and $RH^{in} = 60$ %. After 10 seconds stoichiometry was changed to 8 for both sites

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Monitoring the Operation of PEM Fuel Cells with Machine Learning

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The operation of fuel cell stacks on test benches today is typically monitored by constant alarm threshold values for selected operating conditions. However, due to the wide range of operating conditions of the stacks, this type of monitoring only works for extreme maximum and minimum operating conditions. Wide setting ranges for thresholds prevent the detection of minor faults, whereas too narrow limits will interrupt the tests unnecessarily. A particular challenge is the monitoring of faults that either do not result in a directly measured response from the fuel-cell stack or that only become noticeable with a time delay. The continuous improvement of fuel cell stacks over the last years necessarily requires much-improved monitoring methods, especially for durability tests with an operating time of thousands of hours. For this reason, a novel monitoring concept using AI-based methods for the operation of PEM fuel cells on test benches was developed and is being presented.

Firstly, machine-learning based mechanisms for monitoring the operating conditions as set and controlled by the test bench are shown. Due to the cyclic operation during durability tests, the operating conditions set at a load point can be compared to the past operating conditions at the same load point. This proceeding allows the early and accurate detection of faults caused by the test bench and thereby ensures the usability of the measured data as well as an early alarm in case of problems.

In addition, a digital twin based method for monitoring the condition of the fuel cell stack is presented. The deep-learning based digital twin calculates a probabilistic prediction of the expected voltage of the fuel cell stack based on the current and past operating conditions. The comparison of expected and measured cell voltage taking the model's confidence into account enables the early and precise detection of unforeseen events such as contamination and thus averts consequential damage to the fuel cell stack. In contrast to physical models, the digital twin represents a data driven modelling approach for fuel cells.

The presented methods are applied to real testing data to demonstrate the detection of faults during the operation of fuel cell stacks on test benches that would have remained undiscovered by today's monitoring mechanisms. It shows that the data driven digital twin is able to predict the fuel cell's stack voltage with an accuracy of 2.5 mV over 1000 h of unseen data.

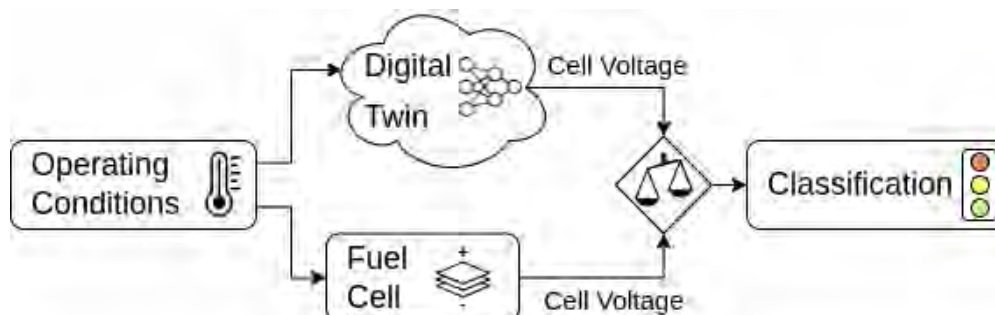


Figure 1: Fuel Cell monitoring with a digital twin

Automated Image Analysis in Nanoscience Using Synthetic Dataset Generator and Deep Learning

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Accelerating the discovery and design of advanced materials is vital for the clean energy transition. Data-driven acceleration methods are rapidly evolving, with the potential to decisively increasing the rate, at which novel energy materials are designed, processed and integrated. Imaging techniques are crucial in the development cycle. Due to the complexity and variety of techniques, a significant number of investigations and the interpretation of imaging data are still performed manually, rendering the overall process time-consuming, labour intensive, and inefficient. This work presents the development and implementation of a deep learning-based methodical pipeline for autonomous image analysis in materials science. As shown in Fig.1, a versatile, system-agnostic, and configurable technology is developed to generate instance-segmented imaging datasets for nanoscience applications. The synthetic generator tool employs a domain randomization technique to expand the training dataset from image/mask pairs for supervised deep learning model training tasks. The approach eliminates the tedious manual annotation step and allows training of the highly performing models based on convolutional neural networks for microscopy image analysis [1,2]. We will demonstrate how the expanded training set helps improving the model performance for a variety of nanoparticle categories, ranging from round-, cubic-, and rod-shaped to amorphous particles. Finally, the trained models are deployed in a cloud-based analytics platform for autonomous particle analysis of microscopy images [3].

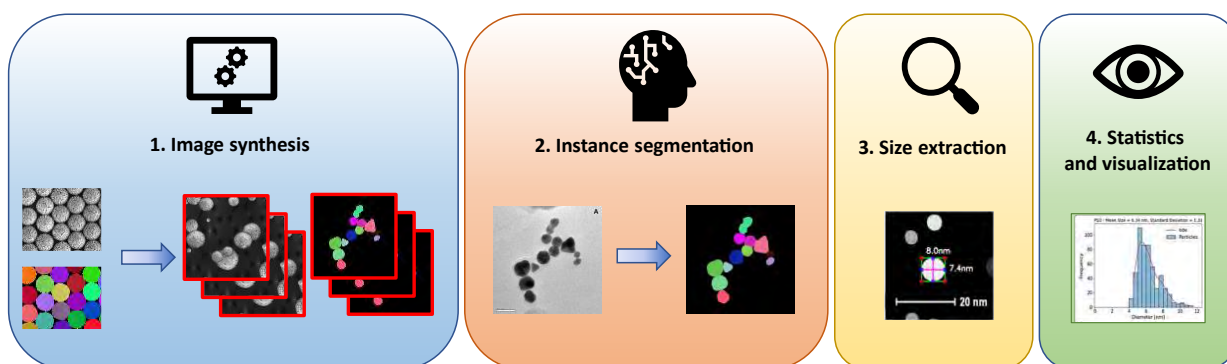


Figure 1. Methodical workflow for deep learning-based image analysis of nanoparticles

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Towards fluorine-free ionomer films for next-generation polymer electrolyte fuel cells

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Research and development of next generation polymer electrolyte fuel cells has intensified as it is viewed as a key technology in the decarbonization of heavy duty transportation (e.g. public transport, land, aviation and maritime freight).¹ However, current polymer electrolyte fuel cell design suffers from drawbacks that hinder wide-spread commercialization in these sectors. Especially, improved catalyst layers with lower amounts of costly platinum group metals, improved mass transport characteristics at high current densities, fluorine-free ionomers and increased durability are required. The key to this is a well-engineered electrode microstructure. It dictates the mass transport of reactant gases and products, while ionomer film chemistry and morphology define proton availability, but also impact oxygen transport and overall catalyst utilization. A careful balance is required between the transport of reactants, products, protons and electrons. The fabrication of conventional catalyst layers rely mostly on wet chemical synthesis which limits the control over the so called triple phase boundary microstructure. In particular, poor ionomer distribution was found to negatively impact fuel cell performance.² While some catalytic sites are inundated with ionomer and experience a high oxygen transport resistance, other uncoated sites might be starved of protons (See Fig. 1). Additionally, studies have reported poisoning of the catalyst active sites by adsorption of sulfonic acid moieties present in most used ionomers. Considering this and the adverse environmental impact of conventional fluorinated ionomers, investigations into alternative ionomer chemistries and coating techniques are warranted.³

To tackle these challenges, our research focusses on developing novel synthetic methods leveraging both electrochemical and chemical principles enabling local control of ionomer coating in the catalyst layer. The interest in these methods originates from their scalability and ability to control the morphology of coatings (e.g. thickness, conformality, porosity and polymer length). At the same time, new fluorine-free ionomer chemistries are being explored and applied using these techniques to impart optimal wettability, ionic conductivity and gas permeability to the materials to enhance electrode performance. The designed materials are thoroughly characterized and will be compared against state-of-the-art commercial materials for their performance and durability in a membrane electrode assembly configuration.

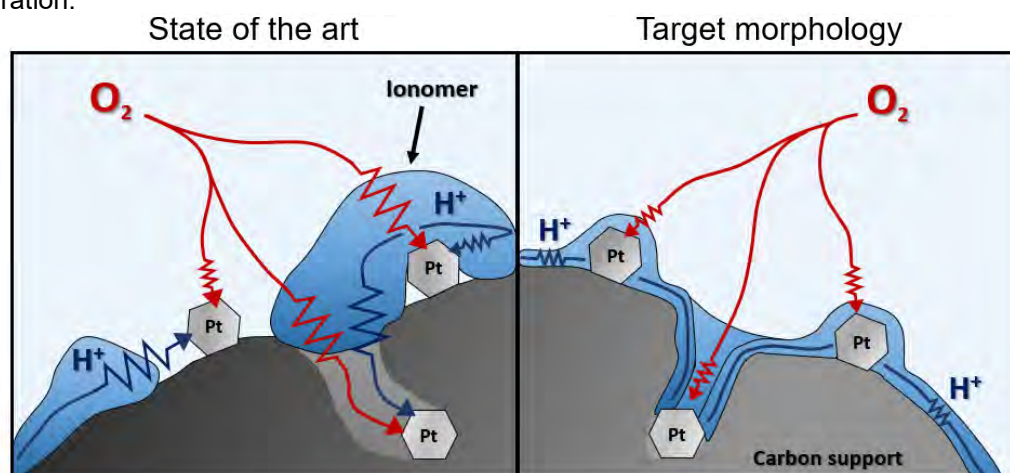


Figure 1: Schematic depicting the expected decrease in mass transport resistances when using conformal ionomer coatings in PEMFCs.

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Towards uniform coatings on carbon fiber substrates for polymer electrolyte fuel cells

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Polymer electrolyte fuel cells are a well-suited technology for the decarbonization of the heavy-duty automotive sector. However, to achieve reliable and cost-effective systems, existing challenges related to performance and durability need to be overcome. Water management is critical to fuel cell operation where, on one hand, water is needed for proton conduction in the membrane and ionomer while, on the other hand, liquid water in the gas diffusion media blocks transport pathways for gas reactants, resulting in mass transport limitations and limited performances. Enhancing water management in the gas diffusion layer (GDL) is, thus, a powerful approach to improve cost competitiveness of the system¹. State-of-the-art diffusion media are made by dip-coating carbon fiber based substrates with a polytetrafluoroethylene (PTFE) dispersion. The treatment provides the required hydrophobicity, but suffers from two major drawbacks. First, the PTFE coverage is heterogenous, which results in uneven distribution of the wetting properties. Second, under operating conditions, the diffusion medium suffers from chemical and electrochemical carbon corrosion, mechanical degradation and, PTFE loss². Fundamentally, the hydrophobicity loss is driven by the weak physical interaction between the substrate and the hydrophobic coating, which does not last long under operating conditions, negatively impacting the overall system performance and durability.

We aim to overcome the existing challenges through an alternative coating approaching leveraging principles of liquid phase electrochemistry. The proposed technique enables the formation of conformal and thin hydrophobic layers covalently bonded to the substrate³, which we hypothesize would result in higher stability and homogeneity of the coatings. In this poster presentation, I will first discuss the alternative synthetic approach to functionalize the fibrous substrates. Then, I will present a set of characterization methods to assess critical properties of the functionalized gas diffusion media. Finally, I will discuss a modelling approach which helps elucidating the relationship between diffusion media properties and resulting performance gains. The ultimate goal is to synthesize advanced GDLs with improved performance and durability.

Acknowledgments

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 101007170. The JU receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research.

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Development of multiphase transport layers with binary pore size distribution

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In electrochemical devices, porous transport layers (PTLs) provide pathways for liquids and gases to be distributed over and removed from the catalyst layer, provide mechanical support as well as thermal and electrical conductivity. As the electrical current drawn from such devices is directly linked to the flow of reactants, the mass transport capabilities of the PTLs become especially critical at high current density operation. However, in two phase counter flow operation, undesirable liquid accumulations and resulting blockage of gas transport pathways can occur which stall out the electrochemical conversion, limiting the achievable power density. To overcome these limitations, improvements to the base material have been investigated to guide liquids and gases into dedicated pathways^{1,2}. While they show success, they require additional processing, adding cost, and are still limited by the morphology of the starting material.

We explore the synthesis of PTLs containing dedicated pathways for each phase, realized by a stark difference in pore sizes through dynamic hydrogen bubble templating³. In this talk, I will discuss the resulting material microstructure and simulated transport characteristics to ascertain the potential of this material as PTL. The simulations showed increased diffusive transport in dry and liquid filled state compared to state-of-the-art materials. This approach could enable a new class of PTLs tailored to the transport requirements the system.

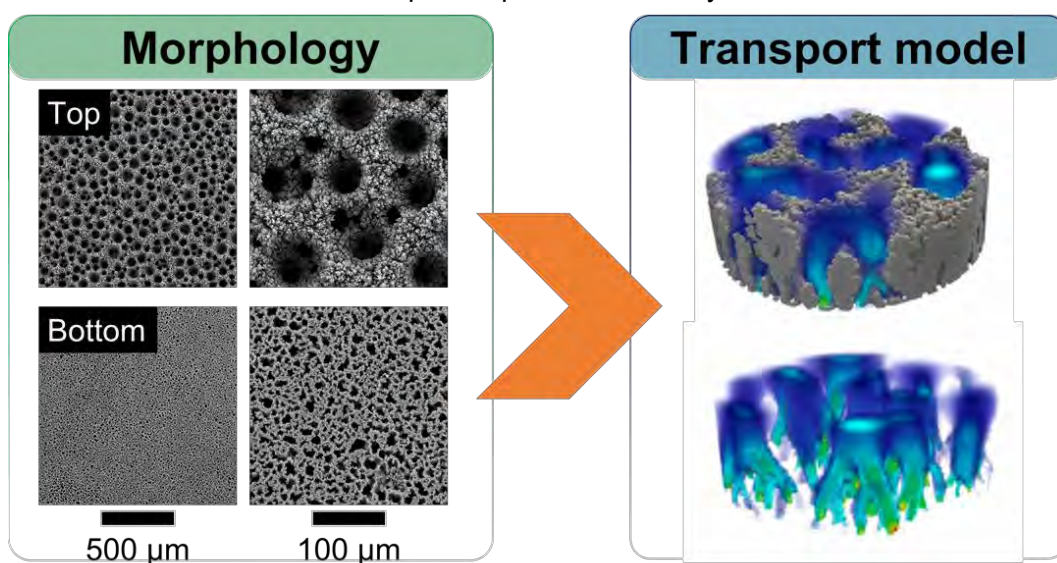


Figure 1: Morphology obtained from SEM. Transport model on segmented tomographic data.

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Optimization of electrochemical model parametrization for incremental PEMFCs

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Physiochemically meaningful PEMFC impedance models are a powerful tool to identify and quantify loss processes in PEMFCs in detail and enable an efficient simulation of PEMFC behavior. In our previous works an impedance data analysis by means of the distribution of relaxation times (DRT) method [1], impedance modeling of porous PEMFC electrodes with a transmission line model (TLM) [2] as well as a stationary 0D performance model [3] was published.

The TLM parameters are determined by means of electrochemical impedance spectroscopy (EIS) in combination with the DRT method and a complex nonlinear least square (CNLS) fit over a broad range of operating conditions like temperature, relative humidity of the supplied gases, oxygen partial pressure and current density.

The parametrization is conducted with incremental gradient-free 1 cm² PEM fuel cells. The high-precision EIS measurements require a steady state of the PEMFC, which is realized by sufficient long holding times at every operating point before the measurements are conducted. The broad range of up to 200 different examined operating points and long holding times of up to 90 minutes, make the model parametrization time-consuming. Unavoidable irreversible degradation effects during the parametrization might negatively influence the results.

Therefore, we want to reduce the duration of the parametrization by optimizing the necessary number of examined operating points and reducing the holding time before each measurement, without negatively influencing the measurement data quality and losing any valuable EIS information. The PEMFC characteristics following a change in operating conditions were recorded, to determine an optimal holding time to reach a steady state at each condition. The influence of different holding times on the EIS data quality was examined by means of the Kramers-Kronig validity test [4]. To optimize the quantity of the analyzed operating conditions, the influence of the number of measurement points on the 0D stationary model parameters was analyzed.

The optimized procedure enables a more efficient parametrization of TLM and 0D models without negatively influencing the high EIS data quality.

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4. Boukamp, B.A. *J. Electrochem. Soc.* **1995**, 142, 1885-1894. DOI: 10.1149/1.2044210

Practical application case of CFD simulation as a tool to develop an automotive PEMFC Design (HyFab-BW – Stack)

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Today, Computational Fluid Dynamics (CFD) is a standard tool within the development process of fuel cell stacks. Design variations can be implemented in short time, which leads to a significant reduction of development costs. A wide range of software is available, including commercial CFD codes like ANSYS FLUENT® and open source codes like OpenFOAM. This contribution provides an example for the designing process of fuel cell flow field bipolar plates using CFD with both of aforementioned tools. The CFD simulations help to ensure e.g. a low pressure drop in the distribution areas while maintaining sufficiently even flow distribution within the active area. Detailed results are presented for the new Generic Stack design (developed within the HyFab-BW project) (Figure 1 to Figure 3). The HyFaB [1] is a research factory (Figure 4) intended to develop automated manufacturing and quality assurance processes for fuel-cell stacks. This project aims to contribute to ramp up this technology to a scale typical for automotive mass manufacturing. The Generic Stack will be used within the HyFaB as an open base development platform. The results presented here will provide detailed insights into the characteristics and capabilities of the open test platform, which will be free accessible for all stakeholders.

The HyFab-BW project has received financial support by the German State of Baden-Württemberg from the Ministry of the Environment, Climate Protection and the Energy Sector (funding code: L7520112).

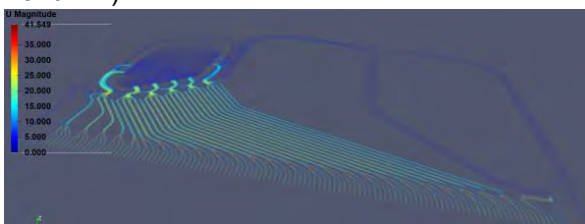


Figure 1: CFD simulation (OpenFOAM) – velocity distribution at anode inlet distributor

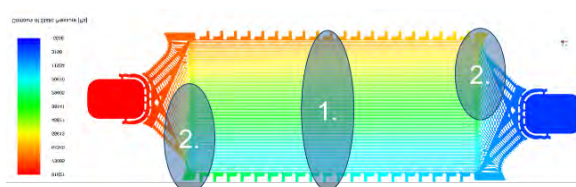


Figure 2: CFD simulation (ANSYS FLUENT®) – pressure distribution over coolant flow field

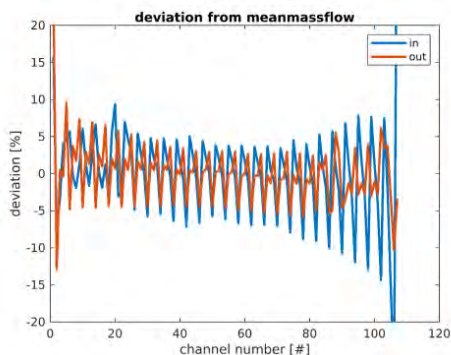


Figure 3: CFD Simulation (OpenFOAM) – relative mass flow distribution at parallel channel in- and outlets



Figure 4: HyFaB ZSW Ulm (17.10.2022)

[1] <https://www.zsw-bw.de/en/newsroom/news/news-detail/news/detail/News/hyfab-a-research-fab-for-hydrogen-and-fuel-cells.html>, 20.12.2022

Investigations on pressure drop in the flow field channels of a PEMFC due to liquid water

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In this contribution, results on product water discharge behavior and the resulting single-channel pressure drop in the flowfield of a proton exchange membrane fuel cell (PEMFC) will be reported. In contrast to various previous investigations (e.g. [1], [2]) focusing on the water discharge ability at minimum flow conditions, here high gas velocities corresponding to the high current densities relevant for automotive or heavy-duty applications will be dealt with, as the resulting pressure drop is of significant relevance for the overall system efficiency. The studies presented here are based on automotive operating conditions and flowfield geometries. The simulations are performed with the open source CFD software OpenFOAM®.

The channel geometry employed represents an advanced automotive metal bipolar plate design. Starting with an empty channel, water is injected at the GDL surface (see figure1 top). The high gas velocity employed implies an inherent conflict between accuracy and computational effort related both to the mesh fineness and time resolution of the transient simulations. This can in part be resolved employing efficient parallelization of the computational tasks. The simulation is running until a quasi-steady state is reached and the amount of water in the channel is not changing anymore (see figure 1 bottom). The resulting pressure curve is analyzed and a method for extrapolating the results of short channel sections to the complete channel length will be introduced.

The analysis shows that in this case the pressure drop due to liquid water transport in the channel could be successfully estimated employing only a short part of the full channel.

This work has received financial support by the German Federal Ministry for Digital and Transport within the framework of the National Innovation Program Hydrogen and Fuel Cell Technology (NIP II, 03B10114D).

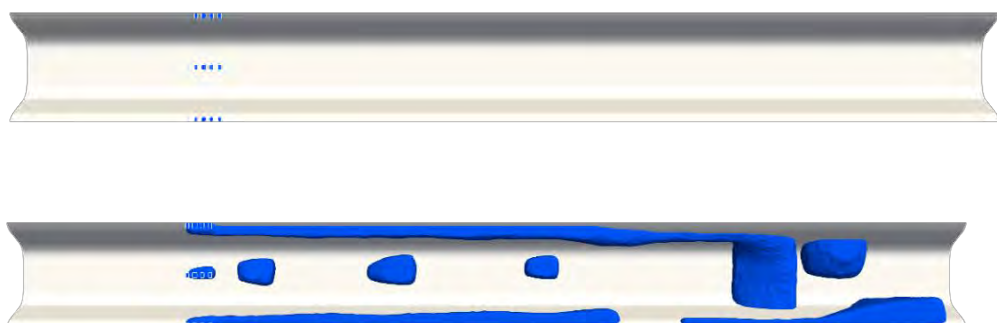


Figure 1: Flowfield channel employed featuring the initial state with water inlets (top picture) and the quasi-steady state situation after 30ms (bottom), flow direction from left to the right (picture not drawn to scale).

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Numerical Study of Two-Phase Flow in a T-shaped Cathode Domain of a Proton Exchange Membrane Fuel Cell

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A proton exchange membrane fuel cell (PEMFC) is considered a promising energy device due to its high electrical efficiency, pollution-free operations, and quick start-up¹. The water drainage process, resulting from the oxygen reduction reaction in the cathode region, is a major challenge for PEMFC applications. Both flooding and dehydration in the gas diffusion layer (GDL) and gas channel (GC) have a negative impact on the PEMFC performance².

Numerical simulation methods present a low-cost and flexible approach to visualize the water drainage process. To investigate the water drainage behavior in the GDL and GC, in the present study, the volume of fluid (VOF) method in OpenFOAM 7.0 is applied to a T-shaped PEMFC cathode domain (shown in Figure 1). A GDL is stochastically reconstructed based on an in-house geometry, with a porosity of 0.82, a domain size of $1000 \mu\text{m} \times 1000 \mu\text{m} \times 300 \mu\text{m}$, and a carbon fiber diameter of $10 \mu\text{m}$. The effect of wettability is considered by varying contact angles for the boundary surfaces. Figure 2 shows the two-phase flow behavior in the GDL and GC at three different time steps, namely, 5 ms, 9 ms, and 15 ms (black color represents liquid water). The left slices show the in-plane water distribution in the middle of the GDL, which indicates that the water distribution in the GDL gradually stabilizes as time proceeds, in terms of appearing position and cluster size. After a certain time, the water breaks through at the GDL/GC interface in the form of water droplets, as shown in the right part of Figure 2. Moreover, the breakthrough water which is close to the side walls attaches and accumulates on the walls (see 5 ms). After merging and accumulation (see 9 ms), it detaches at the GDL/GC interface and then attaches at the top walls (see 15 ms), and finally flows out of the GC.

In future research, the impact of fiber shape, for example, curved fibers will be compared to straight fibers. In addition, the results need to be validated and verified against experimental data.

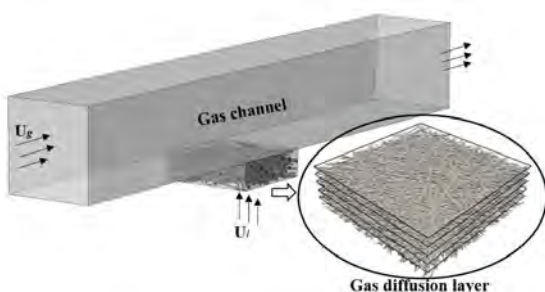


Figure 1: A T-shaped PEMFC cathode simulation domain. U_g and U_l respectively represent the gas and liquid inlets.

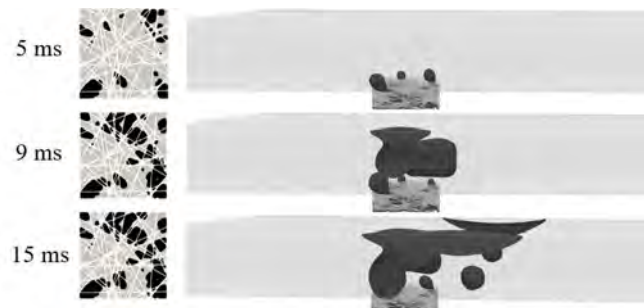


Figure 2: Two phase flow simulation results for three different time steps, i.e., 5 ms, 9 ms, 15 ms (black color represents liquid water).

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Morphology of the iridium oxide catalyst layer for PEMWE under different preparation methods

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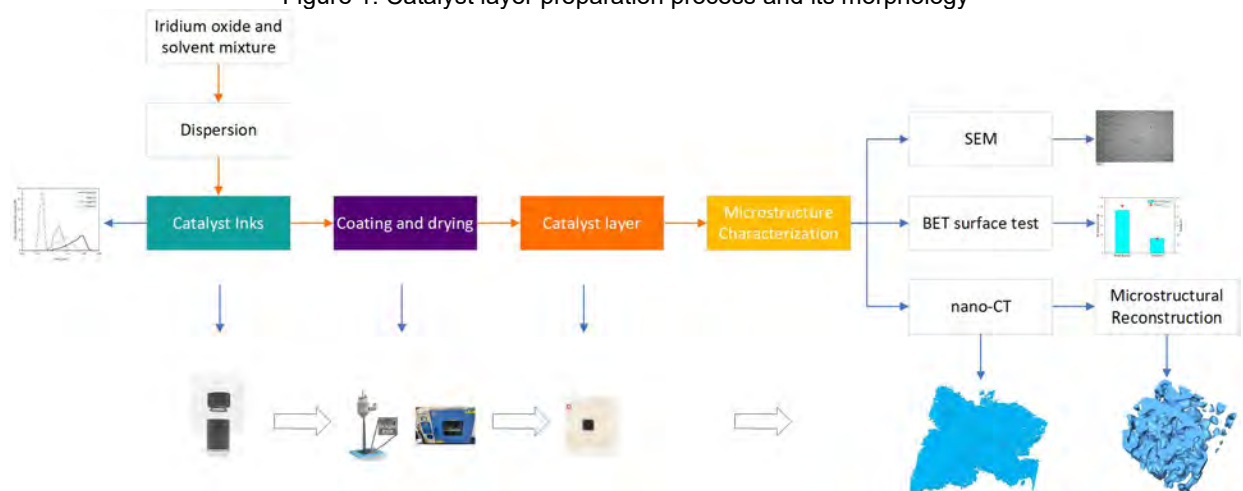
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Proton Exchange Membrane Water Electrolyzer (PEMWE) has emerged as a promising electrolysis technology in the past two decades because of its high efficiency, flexibility, and hydrogen purity. A typical catalyst layer (CL) for PEMWE is composed of catalyst particles and ionomer as the proton-conducting medium. Unlike the well-developed PEM fuel cells, which primarily use carbon-supported platinum (Pt/C) as the catalyst, iridium-based catalysts such as IrO₂ are often used for the anode of PEMWE instead. The microstructure of the catalyst layer greatly influences the mass transfer and, thus, the performance of the Proton Exchange Membrane Water Electrolyzer (PEMWE). The present study focused on the morphology of the microstructure of iridium oxide catalyst layers from catalyst inks obtained by different preparation methods. First, the particle size distribution of the inks obtained by the different dispersion methods was measured; then, we used these inks to prepare different catalyst layers. The morphological characterization of the catalyst layers included SEM tests, BET tests, and nano-CT 3D scans, as shown in Figure 1.

In this case, the two catalyst layers were prepared using sonication dispersion and multiple dispersion techniques for the inks and then prepared by ultrasonic spraying. The results show that the BET surface area of the catalyst layer was 23.3 m²/g, and the porosity was 51.4% when the ink was coated into a catalyst layer prepared using the multiple dispersion technique. In contrast, these two values were 8.2 m²/g for the BET surface area and 16.1% for the porosity when the sonication dispersion technique was used. In addition, the 3D structure of the catalyst layer was obtained by nano-CT scanning, and the reconstruction of the microstructure of the catalyst layer was completed. This will be applied to the pore-scale model.

This study investigates the effects of dispersion methods on the morphology of the catalyst layer for PEMWE. The results showed that the catalyst layer prepared from the ink by the multiple dispersion technique has a larger porosity and a larger BET surface area. The analysis of the structure of the reconstructed catalyst layer is consistent with this conclusion.

Figure 1: Catalyst layer preparation process and its morphology



Dynamic Analysis of an Active Cooling Design for Fuel Cells in Aviation

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In order to advance towards aviation's net zero carbon emission target, proton exchange membrane fuel cells (PEMFCs) are seen as key factor. If PEMFCs supply the main electric power for large passenger aircraft, the produced heat is within the same order of magnitude than today's engines and requires a highly effective thermal management system. In this work, a novel phase-change heat pump (PCHP) cooling strategy is analysed under dynamic operation through a model-based study in Matlab/Simulink®. It could be shown that the operating temperature of the PEMFC system is within the safety margin for all analysed operation modes including extreme hot-and-high take-off conditions (33 °C at 5,100m) and sudden changes in power demand of up to 130%. This is achieved through the implementation of a PID controller which controls the compressor and expansion valve and a variable heat exchanger air inlet. Future work will focus on the optimisation and improvement of the control system.

Experiments on acoustic airflow excitation for effective water removal in PEM fuel cells

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Acoustic excitation of the air supply in Polymer Electrolyte Membrane (PEM) fuel cells is a promising concept to improve the performance of PEM fuel cells at high current densities. In a manageable number of experimental and analytical publications on this topic, the capabilities of acoustic excitation for the enhanced removal of liquid water could be demonstrated. Loudspeakers were successfully used to excite water droplets at their resonance frequencies within artificial fuel cell flow channels, leading to facilitated water expulsion with the (exhaust) air stream. Close review of the open literature reveals significant gaps in the current understanding of why and when acoustic airflow excitation is effective in the first place. Especially the significant frequency dependency of the loudspeaker and its housing to produce the desired sound pressure levels has mostly been neglected. Furthermore, the mechanism of resonance water removal has not yet been demonstrated in a real, operational fuel cell.

In this study, a test-rig is developed that utilizes a woofer to acoustically excite the cathode airflow to a single, water-cooled and operational PEM fuel cell. Here, to the author's best knowledge, for the first time in the open literature a combination of a microphone and a differential pressure sensor is used to quantify the woofer's water expulsion capability from the PEM fuel cell in close correlation to sound amplitude and frequency.

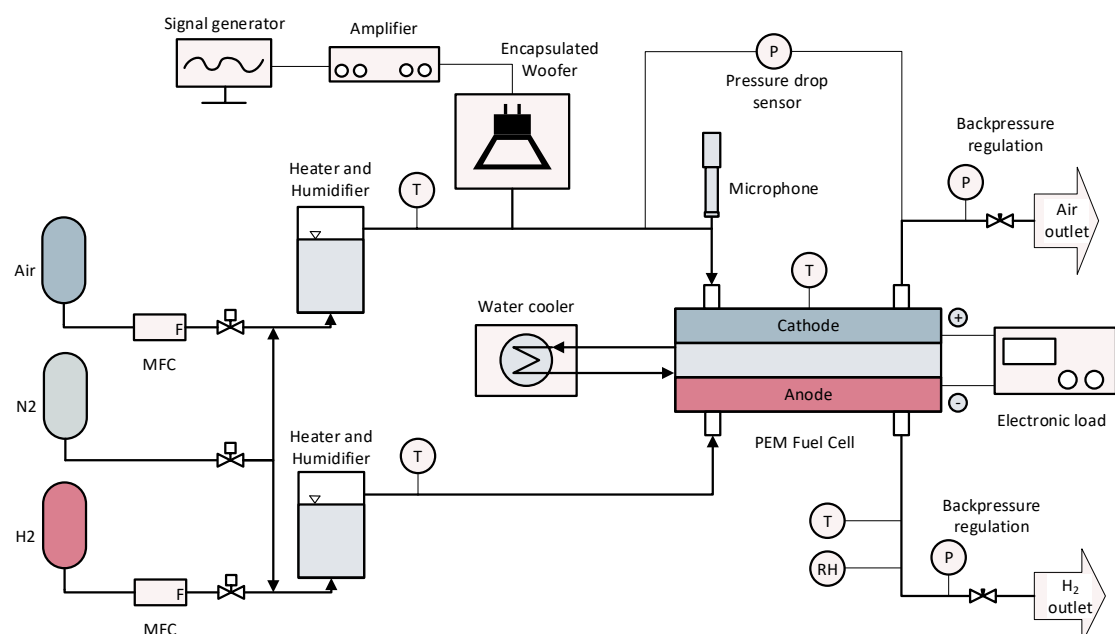


Figure 1: Illustration of the experimental setup.

Fuel cell flow field design assessment using residence time distribution analysis

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Fuel cells allow utilising various gaseous or liquid fuels to produce electricity more efficiently than with conventional combustion methods, reducing harmful gas emissions. Significant attention is paid to direct liquid fuel cells due to the easier fuel transportation and storage, which can accelerate fuel cell technology deployment on a larger scale. Our research focuses on direct formic acid fuel cells (DFAFCs), in which formic acid oxidises effectively at room temperature and is generally considered a safe chemical at fuel cell concentrations.

However, the main drawback of using liquid fuel is more challenging transport conditions due to the 5 order of magnitude lower diffusion coefficients than those of gases, which is particularly significant in the mass transport predominated by diffusion in a laminar flow regime. To mitigate this obstruction in efficient reagent supply to the catalyst layer, mass transport has to be intensified by promoting convective fluxes in the system, which can be realised by baffle implementation into the bipolar plate channels or proposing such a flow field that exhibits better mixing conditions in the system. All these approaches were considered numerically using Computational Fluid Dynamics modelling in ANSYS Fluent Software, and experimentally determining current-voltage characteristics of DFAFC prototypes assembled with the previously designed and virtually tested interconnectors. The proposed flow field designs of the interconnector reagent distribution system were selected for the experimental phase based on the residence time distribution (RTD) analysis comprising mean residence time, hold-back, and segregation determination. The calculated parameters were compared with those obtained for the standard serpentine channel design without any baffles and those characteristic for ideal mixing conditions to assess if the deployed changes in the flow field were beneficial.

The RTD analysis revealed that the hold-back in the serpentine system with right-angled trapezoidal baffles increased by 10.81% for the fuel stream $0.1 \text{ ml} \cdot \text{min}^{-1}$ compared to the system without baffles, which corresponded to the experimentally measured increase in the outlet fuel concentration using high performance liquid chromatography, equal to 7.74% ¹. The second proposed flow field represented mesh of intermixing channels that exhibited the hold-back closest to the value characteristic for ideal mixing conditions and the lowest segregation, which indicates the best mixing conditions.

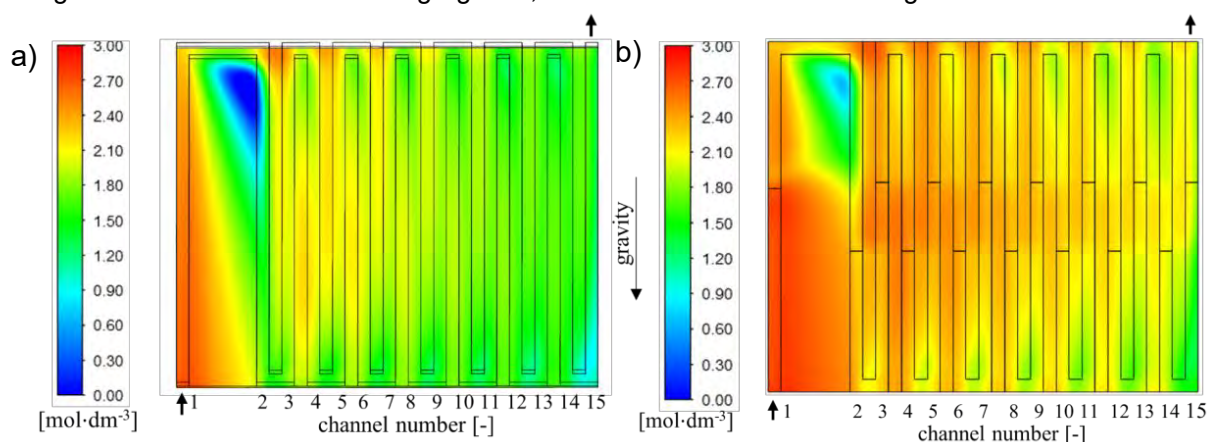


Figure 1: Formic acid concentration distribution $[\text{mol} \cdot \text{dm}^{-3}]$ at the membrane for $Q=0.1 \text{ ml} \cdot \text{min}^{-1}$, $I=0.2 \text{ A}$ for:
a) the standard serpentine design and b) the new channel design with baffles

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Optimised Numerical Simulation of Electrical Properties of Porous Composite Materials

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Lanthanum strontium manganite (LSM) and yttria-stabilized zirconia (YSZ) form a porous composite which is widely used as an oxygen electrode material in the solid oxide cells. The LSM component is an electro-catalyst and a good electronic conductor. The YSZ component is a good ionic conductor with negligible electronic conductivity. With pore, they together form triple phase boundary (TPB) which is the electrochemically active region. The more the LSM:YSZ volumetric ratio closer to 50:50 is in the mixture, the more TPB is present which implies better electro-catalytic performance due to the increase of TPB length, although the lower is a total electrical conductivity of the material. Accurate prediction of electrochemical properties of resulting composite material is a valuable piece of information for cell design development.

A 3D model consisting of equivalent electrical circuits was developed in order to capture electrical properties of a composite material, in form of its electrochemical impedance spectroscopy (EIS) response. In principle, the block of porous electrode is transformed into 3D voxel grid with a specific resolution. The material voxels are connected by a network of equivalent electrical components representing bulk conductivities and double-layers between LSM and YSZ voxels, see Figure 1. Kirchhoff's laws are applied and solving the system of equations leads directly to simulation of EIS response.

This approach has been already presented in the literature for the 2D case [1]. However, the 3D case demands much more computational resources which leads to several optimization adjustments required. The in-house Julia language code with a detailed documentation how to simulate not only LSM-YSZ, but basically any composite, is available at GitHub repository [2].

Validation of the model was performed using multiple samples of various LSM:YSZ:porosity phase composition. Simulated conductivities show excellent agreement with the experimental data.

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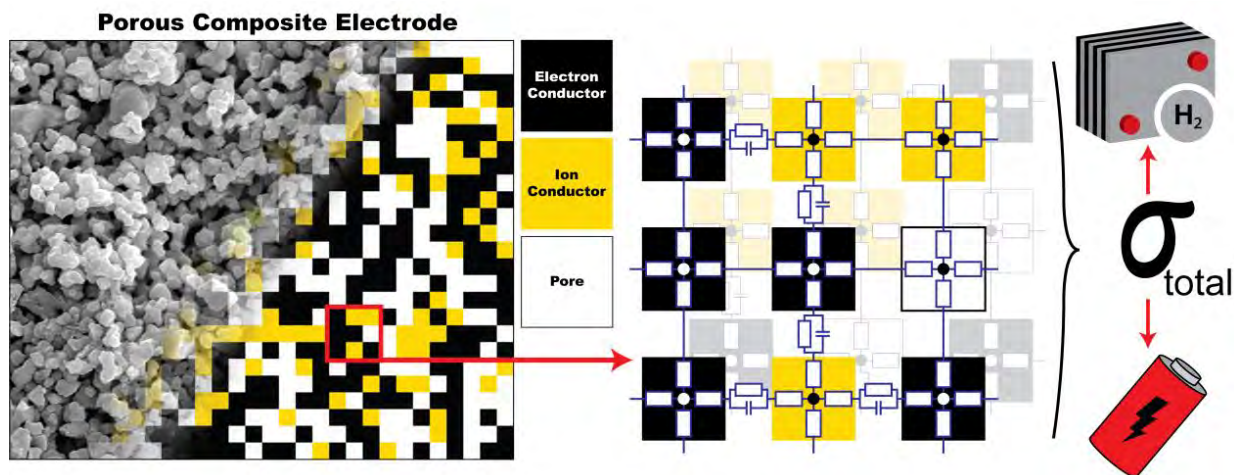


Figure 1: The process of discretizing the electrode material and generating the EEC network.

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Revealing structure and dynamics at catalyst-ionomer interface in PEM fuel cells : a molecular dynamics study

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Understanding and optimization of catalyst/ionomer interfaces in hydrogen fuel cells and water electrolyzers have gained much research interests due to their prominent role in catalytic activity and hence the cell performance¹. Atomistic classical molecular dynamics simulations, being a powerful tool, is employed here to investigate the structural and dynamical properties of a catalyst-ionomer interface that confines a nanopore filled with water and hydronium ions². The effective interactions between platinum based metal catalyst and ionomer skin layer surfaces are monitored and the thickness of interfacial water film is tuned accordingly³. Present study demonstrates the effects of pore width, platinum surface oxide coverage, excess metal surface charge density and ionomer side chain density on the interfacial proton and water density distributions. Moreover, we explore the molecular structure, correlation functions, and dynamics of water molecules and hydroniums ions in the interfacial layer.

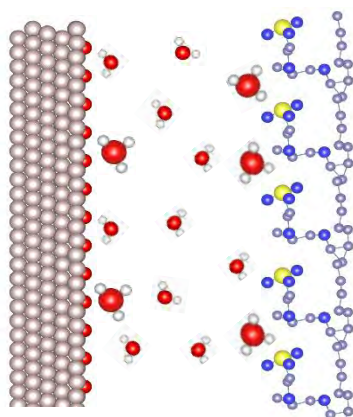


Figure 1: Model schematic diagram of catalyst-ionomer interface with water and hydronium ion

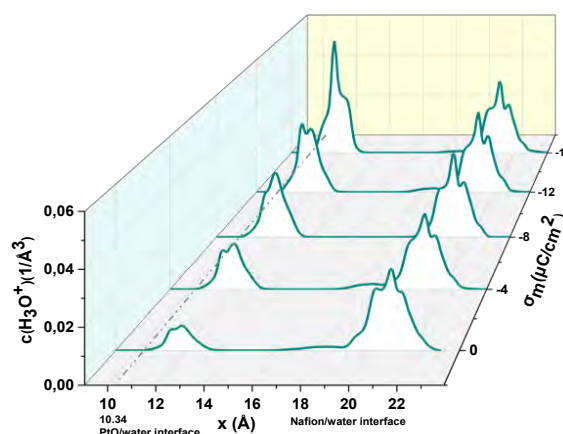


Figure 2: Interfacial hydronium ion density distribution for various excess metal surface charge densities at 25 % oxide coverage over Pt surface. Pore width is 10.2 Å and ionomer side chain density is 1.05 1/nm².

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Iridium Catalyst Dissolution in Single-Cell Polymer Electrolyte Membrane Water Electrolysis

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Electrocatalytic stability at low noble metal catalyst loadings is a main challenge to achieve large-scale implementation of Polymer Electrolyte Membrane Water Electrolysis (PEMWE) for storage of fluctuating renewable energy. Iridium (Ir) dissolution during Oxygen Evolution Reaction (OER) has been commonly investigated in half-cells, however, significant differences by orders of magnitude to the PEMWE environment has been observed. Therefore, catalyst dissolution in application relevant devices is not yet well understood. In this work, for the first time, quasi-online measurements of catalyst dissolution in PEMWE was conducted, by measuring Ir concentration at the cell outlets. Two main influences were studied: The effect of current density and the stabilization over time. Strongly pronounced dissolution peaks were observed during the first anodic stepping up of current density, accompanied by a large decrease in HFR value. Some Ir nano-particle detachment during the first instances of stepping up anodic polarization were indicated, however, only to a small extent. The dissolution rate decreases by around two orders of magnitude during ca. 27 hours of polarization. A large part of this stabilization occurs within the first three hours of operation (ca. factor 35). A quasi-steady-state (QSS) dissolution behaviour is approached with increasing operational time. In this QSS, a clear correlation of an increasing dissolution with current density can be observed, seemingly linear at elevated current densities. The assessed stability-number shows a large dependence on current density. It increases by more than two orders of magnitude with current density and seems to slowly reach a plateau starting from 1.52 V iR-corrected potential. The cathode compartment, which contains water transported from the anode via electroosmotic drag, was also analysed and the amount arriving there was found to be much smaller than the one towards the anode flow channel. Implications of the results on mechanistic understanding of Ir dissolution in PEMWE are discussed. The obtained experimental data can be used as a basis for model-based analysis of catalyst degradation in PEMWE.

Pore-scale numerical analysis of the fluid flow in the Gas Diffusion layer (GDL) using Lattice Boltzmann Method (LBM)

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To accelerate the commercialization of the Proton Exchange Membrane Fuel Cells (PEMFCs), improving the water/thermal management, increasing the durability, and reducing the costs are essential. In the long-term operation of the PEMFCs, the Gas Diffusion Layer (GDL) experiences different types of degradations that results in the formation of ice in the sub-zero temperatures and flooding in the catalyst layer and the membrane. Although different Ex-Situ and In-Situ experiments are available to predict the performance of the PEMFCs in different operational conditions, the existing simplifications in the Ex-Situ experiments, and the time-consuming/costly procedures to perform the In-Situ degradation tests, have directed the researchers toward simulations. Herein, the commercial softwares use the conservative principal equations to simulate the fluid flow in the GDL, which is not correct in the boundaries of the different phases and the capillary transport in the micro-level studies. In this regard, this study characterizes the fluid flow in the GDL using the Lattice Boltzmann Method (LBM) that uses kinetic energy equations instead of the conservative equations. Thus, the existing capillary transport in the GDL can be captured. The utilized geometry of the GDL to be characterized by the LBM has been obtained using the Computational Tomography (CT) scan followed by segmentation and reconstruction for both the pristine and aged samples as it can be seen in Figure 1. Usually macroscopic properties of the GDL are considered for detailed numerical investigation, however, these properties are not compatible with real values in the micro-scale. The pore-scale simulation provides realistic values for the microstructural properties and can make it possible to simulate such problems with more accuracy in large scale. Pore structure of GDL is provided with CT scan imaging with the resolution of one μm voxels to perform numerical simulations.

Keywords: Proton Exchange Membrane Fuel Cell (PEMFC); Gas Diffusion Layer (GDL); Lattice Boltzmann Method (LBM); Computational Tomography (CT) scan.

3D microstructural Modelling of Ni coarsening in Ni-YSZ fuel Electrodes of Solid Oxide Cells

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Microstructure evolution plays an important role in the performance degradation of SOC electrodes. The nickel metallic phase, in the state-of-the-art Ni-YSZ fuel electrodes, is primarily affected by this degradation phenomenon as it has a high mobility and low wettability to YSZ [1]. To enable long term durability prediction and improve the anode performance, it is necessary to understand its microstructural evolution under different operating conditions.

Extensive efforts have been made to understand Ni morphological evolution. In this frame, advanced imaging techniques have been employed to characterize the microstructure of electrodes after aging in a wide range of conditions. In order to support these observations and gain fundamental insights, a number of computer simulations methods such as: multistate kinetic Potts-Monte Carlo models, cellular automata, phase field, and topological boundary dynamics have been successfully employed in modelling grain growth and recrystallization phenomena. Nevertheless, questions still remain on the exact underlying mechanisms of Ni morphological evolution. In the shadow of this lack of clear understanding, a morphological modelling approach aiming at mimicking Ni evolution based on the most fundamental definition of chemical potential and surface curvature minimization would be very helpful to guide researchers into gaining clearer insights of this phenomenon. Moreover, the morphological simulations are very fast compared to the physically based models. Therefore, they can offer the possibility to emulate large database of numerical microstructures in order to study the impact of Ni evolution on the microstructural properties [2].

In this contribution, we present a 3D geometrical model based on operations from mathematical morphology [3]. A wide range of real 3D microstructures of as-reduced and aged electrodes were reconstructed using FIB-SEM imaging and X-ray nano-tomography in order to acquire a large database for model calibration and validation (c.f. Fig. 1). Thanks to the very fast computational time of this morphological model a large database of numerical microstructures can be generated in order to study the impact of Ni evolution on the microstructural properties in an electrode optimization objective.

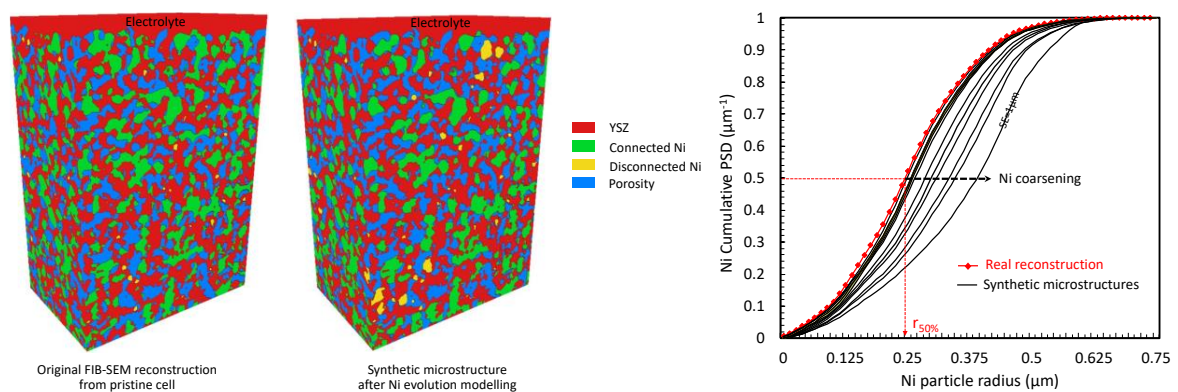


Figure 1: (a) 3D reconstructions of the real microstructure from the pristine cell and the numerically aged microstructure for 1500 h. (b) Evolution of the cumulative nickel Particle Size distribution during the numerical coarsening.

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Numerical Investigation of Two-phase Flow in Structured Porous Transport Layers in Water-Electrolysis Processes

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Water Electrolysis (WE), here specifically the Polymer Electrolyte Water Electrolysis (PEM-WE), is a well-established process for the production of hydrogen. However, to reduce capital costs and increase the electrochemical efficiency, the efficient utilization of the expensive noble metal catalysts must be maximized. Especially at high current densities, the generated gases may occupy active catalyst sites due to incomplete desorption and inhibit the access of water to the active sites required for the electrochemical process. The porous transport layer (PTL) plays an important role in the mass transport efficiency of the process by providing pathways for water to reach the catalyst sites and for the removal of the produced hydrogen and oxygen. Therefore, tools to investigate the two-phase flow in PTLs are crucial to specifically improve the microstructures with regard to their mass transport properties under electrolysis-relevant flow conditions.

In this study, the Lattice Boltzmann Method (LBM) in conjunction with the Multicomponent Shan-Chen (MCSC) pseudopotential model¹ is employed to model the two-phase flow in PTLs and the wetting behaviour of the fluids in contact with the solid matrix. The simulations are performed using the open-source software Palabos². The inherent numerical parameters for the LBM and the MCSC are calibrated by comparing corresponding single bubble simulations with the Volume-of-Fluid (VOF) method. The LBM is finally used for simulation of two-phase flow within PTLs, where the domain is initially filled with water and then infiltrated with oxygen. Two different types of industrial PTLs are analyzed: a woven and a sintered fibre structure (Figure 1). For each sample, the influence of the wetting properties (hydrophilic and hydrophobic) on the gas distribution in the porous domain is investigated. From a purely fluidic perspective, the woven PTL with hydrophilic wetting properties indicates advantages due to lower break-through pressure and lower hold-up for the gas phase.

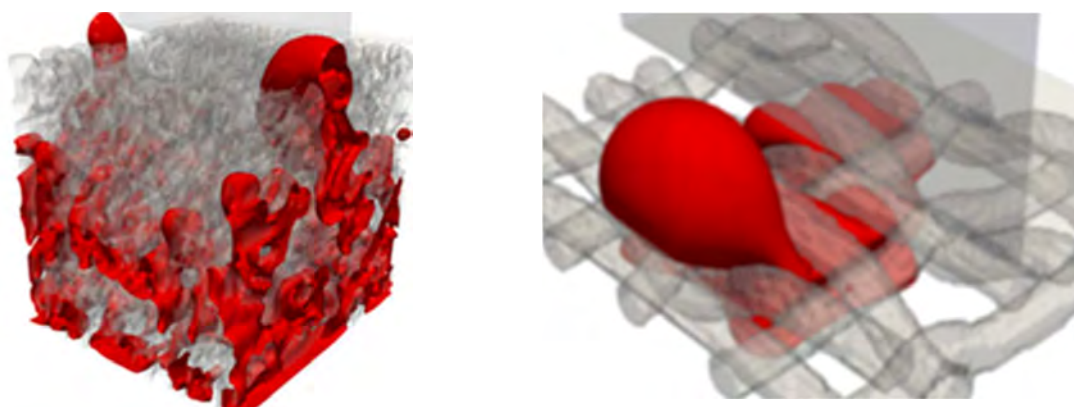


Figure 1: Gas (red) invasion into hydrophobic PTLs: comparison of an unstructured sintered fibre morphology (left) to a structured woven morphology (right).

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2D-FVM Model for locally resolved and dynamic predictions of an ammonia cracker

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The decomposition of ammonia to hydrogen and nitrogen catalyst is an important step in the use of green ammonia as a carbon free hydrogen carrier. This is most commonly achieved with monolithic or fixed-bed catalytic reactors utilizing Ni or Ru as catalyst. These reactions are happening at high temperatures of $\sim 700^\circ\text{C}$ and $\sim 400^\circ\text{C}$ for Ni and Ru catalysts respectively, while also being highly endothermic. As such the supply of heat to the reaction sites is of prime importance in both the design of the reactor and the optimization operation procedures. To aid in this design process, a 2D-FVM model based on the quasi-homogenous $\lambda(r)$ -Model proposed by Vortmeyer and Haidegger [1] for fixed-beds has been implemented and modified for giving locally resolved predictions on the temperature distributions and ammonia-to-hydrogen conversion. The model is able to predict these during stationary operation as well as during dynamic phases such as changes in ammonia load.

To perform a first validation of the model it has been applied to the geometry of a small tube reactor. The model predicts a strong temperature gradient in excess of 150 K over the 23 mm radius from the heated outer wall of the tube reactor to the core of the fixed-bed, that is dependent on both outer wall temperature and the magnitude of the ammonia feed flow. Using a modified tube reactor equipped with several sets of thermocouples in varying radial positions, shown in figure 1, we were able to verify the predicted gradient with an average error of 8 %. Graphs showing the comparison between measured and predicted temperatures for several operation points is shown in figure 2.

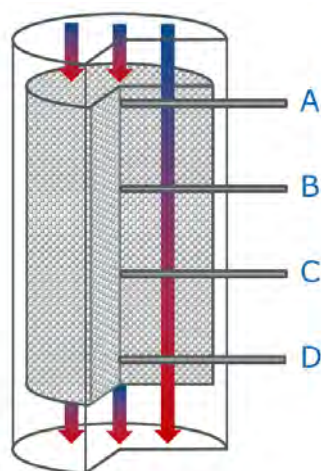


Figure 1: Representation of ammonia cracker with positions of multi-step thermocouples A, B, C and D shown

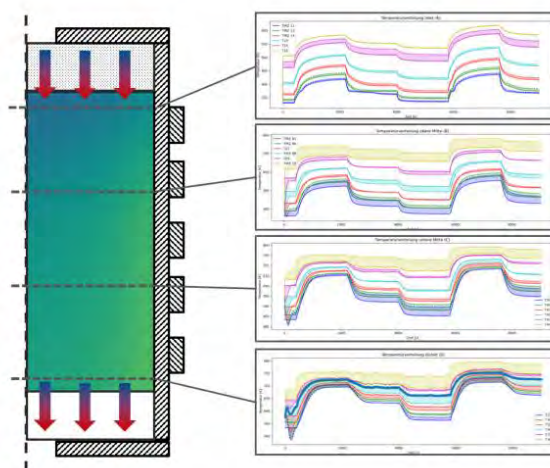


Figure 2: Comparison of measured and simulated temperatures at multi step TCs for dynamic operation of the cracker

1. Vortmeyer, D.; Haidegger, E. *Chemical Engineering Science* **1991**, 46 (10), 2651 - 2660. DOI: 10.1016/0009-2509(91)80058-7

CFD analysis of the efficiency limitations of an electrochemical cell for CO₂ capture

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An anion exchange membrane electrochemical cell has been recently developed and demonstrated to regenerate aqueous K₂CO₃ solutions obtained via CO₂ absorption from air with aqueous KOH. If properly optimized, this novel technique promises to outperform the specific energy expenditure (MJ/kg_{CO2}) of currently employed methods. In order to accomplish this, we propose a CFD analysis of the limitations affecting the cell. Here, we isolate the cathode side, where experiments suggest the highest ohmic drop occurs. For speed of computation, the simulations are carried out in 2D. All the physical and chemical phenomena relevant to the electrochemical process are accounted for, including fluid flow mechanics, heat and mass transfer, electrical potential propagation and chemical and electrochemical reactions. The CAD, meshing and discretization are performed using the commercial software ANSYS, upon customization via User Defined Functions. Among the effects we explore are: i) geometric characteristics, such as metal mesh and gap thicknesses; ii) morphological characteristics, such as metal mesh porosity and anisotropic permeability to flow; iii) operating conditions, such as input current density and flow rate and inlet composition of the catholyte. Our analysis shows that the flow structure is currently not optimized to favor the diffusion/migration of CO₃²⁻ rather than OH⁻ anions towards the membrane, thus requiring a relatively large gap between the electrode and the membrane. Although this helps increasing the faradaic efficiency, it also increases the cell specific resistance. We show that this effect can be modified by adjusting the relative ratio between the permeability in the directions of the fluid flow and the current flow, and we show that there exists an optimal ratio of electrode-membrane gap to cell height. Our simulations suggest that a topological optimization of the electrode fine structure might be beneficial to the enhancement of the cell efficiency.

CuCr Catalysts For Ammonia Electro-Oxidation – A Study On Activity and Selectivity

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In the efficient conversion of ammonia to electricity in fuel cell technologies, a major challenge is the identification of a suitable catalyst that can selectively oxidize NH_3 to N_2 at low over potentials, ambient pressure and temperature at high rates. In this work, low cost bimetallic carbon supported CuCr catalysts were prepared and found to be more active than elemental Cu and Cr. PXRD, AFM and HR-SEM was used for characterization. The CuCr activity was found to increase with Cu content, and was higher than pure Cu, revealing a synergistic effect between Cu and Cr in the oxidation of NH_3 , due to electronic interactions between Cr and Cu [1]. Cyclic voltammetry on stable catalysts with 90% Cu in 0.1 M KOH and 0.1 M NH_3 revealed a peak current density of 22 mA/mg (scan rate= 20 mV/s) compared with 0.04 mA/mg for Cr and 6.9 mA/mg for Cu under the same conditions (Fig 1.). Mass spectrometry measurements have identified N_2 as the major product of oxidation along with trace amounts of N_2H_4 . Pre-oxidation of the catalyst in KOH was found to improve the stability of the catalyst over time. Dissolution of Cu and Cr (CrO_4^{2-}) into the solution has also been identified through ICP and UV-Vis spectroscopy. 90% Cu catalyst of CuCr in similar conditions show higher peak current density compared to commercial Pt catalyst (14.8 mA/mg) thus corroborating the potential of CuCr based catalysts for ammonia oxidation in fuel cells in the future.

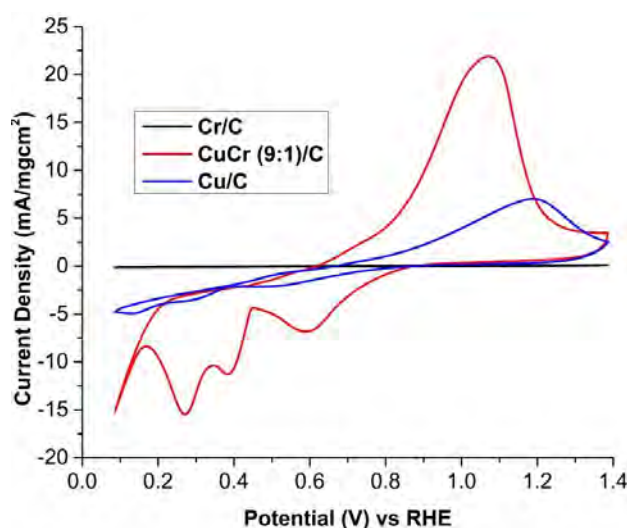


Figure 1: Variation of current density Vs potential of the catalysts in 0.1M KOH and 0.1M NH_3 solution at a scan rate of 20mV/s

1. Xu, Cai, et al. "Synergistic effect between Cu–Cr bimetallic oxides supported on gC 3 N 4 for the selective oxidation of toluene to benzaldehyde." *Catalysis Science & Technology* 9.16 (2019): 4441-445.

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