Proceedings of the 21st Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies

Wolfgang G. Bessler, Marc Kamlah, Philipp Seegert, André Weber, Thomas Wetzel

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Abstract

This Book of Abstracts of the ModVal 2025 symposium offers detailed insights into current research trends in the field of modeling and experimental validation of electrochemical energy technologies. The symposium program featured two plenary lectures, four keynote addresses, 36 contributed oral presentations in two parallel sessions, and more than 100 posters.

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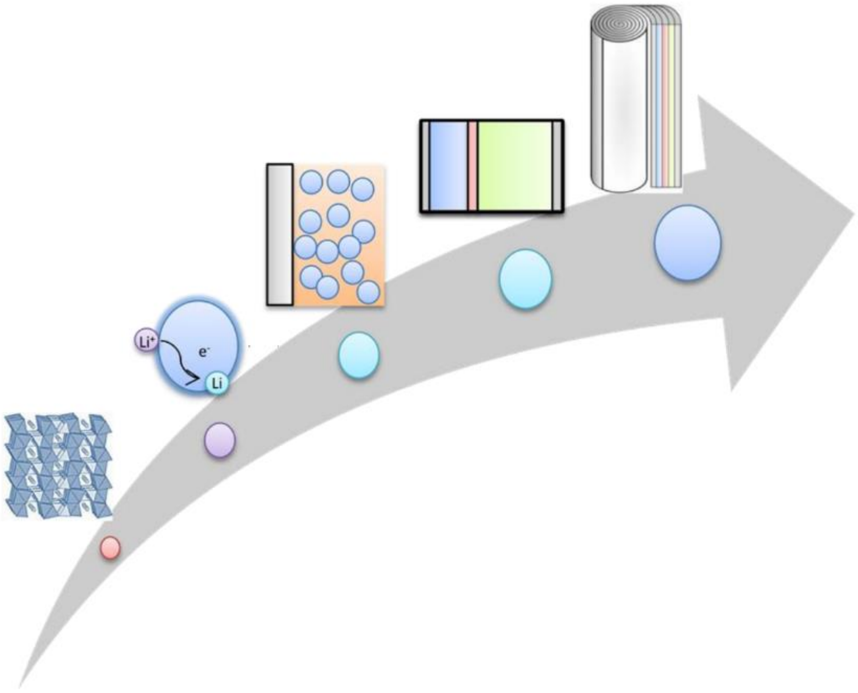

ModVal 2025

11th and 12th of March, 2025
Karlsruhe, Germany

Wolfgang G. Bessler, Marc Kamlah, Philipp Seegert,
André Weber, Thomas Wetzel (Editors)

Proceedings of the 21st Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies

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Editorial: Advancing Modeling and Validation for a Sustainable Energy Future

It is our great pleasure to welcome you to ModVal 2025, the Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies. As we gather in Karlsruhe, Germany, for the 21st edition of this Symposium series, we continue a long-standing tradition of fostering collaboration among researchers from academia and industry, striving to accelerate the transition toward a sustainable energy landscape.

The Modval Symposium was established in 2004 to discuss advances in the modelling, simulation and experimental validation of rechargeable batteries, all types of fuel cells, electrolysers and other electrochemical energy conversion technologies. It takes place every year in spring, alternating between Switzerland and Germany. The symposium is proud of its long tradition of discussing details of model development, numerical implementation and specific validation methods in a specific ModVal spirit. It provides an excellent opportunity to exchange ideas, discuss new approaches and initiate international co-operations. We believe that, over the years, the ModVal series has played a critical role in shaping the evolution of electrochemical energy storage and conversion.

This year’s conference program reflects the breadth and depth of ongoing research, featuring two plenary lectures, four keynote addresses, 36 contributed oral presentations in two parallel sessions, and the record number of more than 100 posters. This Book of Abstracts provides an overview of the contributions, offering valuable insights into current research trends and future directions.

We thank our team members and the administration at Hochschule Offenburg whose support and dedication made this conference possible. We also thank all oral and poster presenters: Your contributions are instrumental in advancing our collective knowledge and driving meaningful innovation in the field of energy storage and conversion.

We look forward to engaging discussions, inspiring presentations, and meaningful exchanges that will shape electrochemical energy technologies. Welcome to ModVal 2025!

The ModVal 2025 chairs

Wolfgang Bessler, Marc Kamlah, Philipp Seegert, André Weber and Thomas Wetzel

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Exhibitors

Batemo GmbH
www.batemo.com

GFS Fuel Cells GmbH
www.gfs-fuelcells.de

Math2Market GmbH
www.math2market.com

Zahner-Elektrik GmbH & Co. KG
www.zahner.de

Program Overview

Monday March 10th

18:00	Registration opens	
From 18:00	Get-together and evening buffet (open until 21:00) at conference venue	

Tuesday March 11th

07:30	Registration opens	
08:45	Welcome	
09:00	**Plenary 1**	
09:50	Short Break	
	Session A: ***Energy Conversion***	**Session B:** ***Energy Storage***
10:00	Session A1: *Fuel Cell Systems*	Session B1: *Hysteresis*
11:00	Coffee Break	
11:30	Session A2: *PEMFC Stacks*	Session B2: *Next-Generation*
12:30	Lunch Break	
13:40	Session A3: *PEMFC Cells 1*	Session B3: *Aspects of Battery Design*
14:50	Coffee Break	
15:10	**Poster Session 1**	
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16:50	Session A4: *PEMFC Cells 2*	Session B4: *Degradation*
19:30	**Conference Dinner**	

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11:00	Coffee Break	
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12:30	Lunch Break	
13:40	Session A6: *Electrolysis*	Session B6: *Parameterization & Characterization*
15:10	Short Break	
15:20	**Poster Award**, ModVal 2026 Announcement, Closing Remarks	

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Monday March 10th, Evening

18:00	Registration opens
18:00	Get-together and evening buffet (open until 21:00) at conference venue

Tuesday March 11th, Morning 1

07:30	Registration opens	
08:45	Welcome	
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10:20	**Mohammad Shojayian** (Simon Fraser University) Investigation and Optimization of a Battery-Hybridized Fuel Cell Electric Vehicle for Durability and Fuel Consumption	**Lukas Köbbing** (German Aerospace Center) Chemo-Mechanical Core-Shell Model Explaining the Silicon Voltage Hysteresis and Long-Term Relaxation
10:40	**Dante Fronterotta** (École Polytechnique Fédérale de Lausanne) Long-term Predictive Analysis of a µ-CHP Solid Oxide Fuel Cell System	**Emmanuelle Hagopian** (University of Oxford) Voltage Hysteresis Experiments to Inform Physics-Based Models
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Tuesday March 11th, Morning 2

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14:10	**Martin Andersson** (Lund University) Water Management in PEMFCs: Volume of Fluid Modeling of Two-phase Flow in Gas Diffusion Layers and the Gas Channels	**Niklas Weber** (Karlsruhe Institute of Technology) Thermal Runaway Prevention and Mitigation: From Cell Level Insights to System Level Strategies
14:30	**Sercan Erdogan** (Zentrum für BrennstoffzellenTechnik GmbH) Optical investigation and quantification of liquid water in the cathode side gas channels of PEM fuel cells	**Sunil Kumar Rawat** (Imperial College London) How to Design a Zero-Degradation Battery: Compensating for Loss of Lithium Inventory in LFP Cells with LFO Additives
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19:30	Conference Dinner

Wednesday March 12th, Morning 1

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Wednesday March 12th, Afternoon 1

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Poster Program

A. Energy Conversion

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A 02	**Venu Agarwal** (EPFL) Modelling Water Transport in Bipolar Membranes for CO2 Electrolysis Application
A 03	**Erwan Tardy** (University Grenoble Alpes) Modeling of Anion Exchange Membrane Electrolysis: Impact of KOH Concentration on Electrochemical Performance
A 04	**Roman Kodým** (University of Chemistry and Technology Prague) Multidimensional Mathematical Modelling Study of Mass and Charge Transfer Limitations in Alkaline Water Electrolysis: Effect of Separator
A 05	**Katerina Hradecna** (UCT Prague) Effect of Catalyst to Binder Ratio on the Performance of Alkaline Membrane Water Electrolysis: A Mathematical Modeling Study
A 06	**Vladimir Sovljanski** (EPFL) Accurate Li-ion Cell Parameters Estimation from Impedance Measurements: Methods and Applications
A 07	**Jannik Heitz** (Forschungszentrum Jülich GmbH) Investigating the Role of Ionomer Distribution on Catalyst Stability in PEM Fuel Cells with a Hierarchical Modeling Approach
A 08	**Abhinav Bhanawat** (École Polytechnique Fédérale de Lausanne (EPFL)) Efficiency limits for photoelectrochemical glycerol oxidation combined with hydrogen evolution
A 09	**Lourenço Vieira** (Zurich University of Applied Sciences) Mechanistic study and parameter estimation of a multi-electron transfer organic synthesis
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B 45	**Alexandra Pamperin** (Karlsruher Institut für Technologie (KIT)) Influence of intragranular cracks on effective transport properties of granular cathode material using homogenization
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B 48	**Paul Maidl** (German Aerospace Center (DLR)) Extending multi-scale simulations of sodium-ion batteries

B 49	**Alexander Ruth** (AVL List GmbH) DoE Supported Parameterization of a Five Equation Pseudo Chemical Battery Thermal Runaway Model
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Abstracts for Oral Contributions

Energy Conversion

Advanced Model-Based Framework for State-of-X Diagnostics in Low- and High-Temperature Proton Exchange Membrane Fuel Cells

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Simultaneously achieving high efficiency and a long service life in proton exchange membrane fuel cells (PEMFCs) requires advanced and cost-effective diagnostic methods. Conventional monitoring strategies, which rely on multiple physical sensors to detect local phenomena, are often incompatible with strict economic constraints and do not provide a comprehensive insight into the complicated interplay between electrochemical reactions, transport processes and degradation phenomena. To overcome these challenges, this work presents a novel State-of-X (SoX) diagnostic methodology that combines multi-scale simulation, parameter identification and real-time observation methodology to elucidate both the State-of-Operation-Conditions (SoOC) and the State-of-Health (SoH) of PEMFCs. At the centre of this methodology is a computationally efficient multi-scale simulation framework [1,2] that is applicable to both low-temperature (LT) and high-temperature (HT) PEMFCs. This framework integrates advanced sub-models that resolve key physical processes such as liquid water dynamics, membrane water uptake and gas crossover effects leading to mixed potentials. Owing to an optimised numerical approach, the overall simulation can run faster than real-time, thus enabling sophisticated observer functionalities while keeping the computational effort manageable.

The SoX diagnostics concept consists of two main components, the online SoOC and the cloud-based SoH observer. The online SoOC observer uses an Unscented Kalman Filter (UKF) algorithm coupled with the multi-scale model to enable virtual real-time sensing of intra-FC states using only boundary conditions, lumped voltage and current measurements. By capturing spatio-temporal variations of critical variables such as reactant and product concentrations, membrane humidity, liquid water void fractions and current density, this observer facilitates advanced control and diagnostic protocols and ultimately enables optimisation of performance under dynamically changing operating conditions. On the other hand, the cloud-based SoH observer employs parameter identification techniques to define track parameter values change that is inherently linked to the specific component degradation. By focusing on parameter uniqueness and fidelity, the observer successfully pinpoints root causes of performance decay. This functionality may be invoked periodically during routine maintenance checks or on demand when SoH metrics fall below predefined thresholds.

Experimental validation and numerical analyses confirm the high accuracy of the proposed SoX diagnostics in deciphering the internal states of PEMFCs and tracking degradation phenomena. Crucially, the seamless integration of the SoOC and SoH observers enables continuous updating of model parameters, ensuring robust control strategies even when conditions in the FC change. This synergy provides unprecedented clarity on both short-term operational factors through observation of SoOC and long-term through observation of SoH, promoting greater reliability, service life, and cost savings. By consolidating these advances, the proposed SoX diagnostics methodology significantly advances PEMFC monitoring and management, paving the way for widespread adoption of cleaner, sustainable energy solutions.

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Investigation and Optimization of a Battery-Hybridized Fuel Cell Electric Vehicle for Durability and Fuel Consumption

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Proton exchange membrane fuel cells (PEMFCs) have emerged as a promising candidate to replace the combustion engines due to their zero harmful emissions and high power densities. Despite significant research into the commercialization of fuel cell electric vehicles (FCEVs), cost and durability still pose major challenges that prevent their widespread adoption [1]. In this study, durability and fuel consumption of PEMFCs within battery-hybridized FCEVs are analyzed together as they affect each other. The cathode catalyst layer and membrane were identified as the most vulnerable components to degradation within the membrane electrode assembly (MEA) of fuel cells [2-4]. Therefore, separate durability models for the membrane and catalyst layer are employed and integrated to estimate the MEA lifetime, which is the least of the catalyst and membrane lifetimes. For catalyst durability, a platinum dissolution and redeposition model based on Ostwald ripening phenomenon was developed and extensively validated with experimental results [5]. To study membrane durability, a statistical approach including mechanical and chemical degradation based on ionomer fibrillar morphology was developed and validated with in-house experimental results [6]. A real-world transit bus drive cycle in the city of Victoria, B.C., Canada is considered as a case study for fuel cell durability and fuel consumption. A comprehensive optimization procedure including both durability and consumption as objective functions is required to determine the optimum scenarios. The durability and consumption were found to be strong functions of stack size and cell temperature [5-6]. Therefore, the design variables are stack size, temperature and the energy management system parameters. The energy management system ensures an effective power sharing strategy between the fuel cell and battery at any time considering the power demand and state of charge (SoC) of the battery. The multi-objective genetic algorithm is applied to carry out the optimization. The results show that there is a trade-off between the durability and fuel consumption. Smaller stacks tend to be more durable due to their lower voltages, but consume more fuel as they are less efficient compared to the larger ones. An optimum scenario is then selected by minimizing fuel consumption while ensuring the fuel cell transit bus meets the lifetime target set by the US Department of Energy (DOE). The degradation rate increases at higher temperatures, so smaller stacks should be selected to operate at higher temperatures to meet the DOE lifetime target, although this will reduce fuel economy. However, at lower temperatures, the larger stacks can achieve the lifetime target and maintain a low consumption. The methodology and procedure presented in this research can be leveraged by the FCEV designers to establish optimum scenarios of fuel cell systems, paving the way for greater FCEV commercialization.

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Long-term Predictive Analysis of a µ-CHP Solid Oxide Fuel Cell System

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The demand for renewable energy drives the need for clean and durable technologies, with solid oxide fuel cells (SOFCs) offering a promising solution due to their high efficiency and flexibility. Long-term control of a SOFC system, including degradation impact on performances, remains a critical challenge. This paper proposes three adaptive control strategies:(1) fixed power, (2) fixed voltage, and (3) fixed stack temperature applied to a commercial µ-CHP SOFC system. The research employs a zero-dimensional system model and a degradation model, both constructed using real operational data, with the degradation model further informed by an example from the literature [1], to evaluate these strategies under different end-of-life criteria: power (both at stack and system level), voltage, and cumulative energy. Dynamic single-objective optimization, based on model predictive control theory [2], revealed key findings. (1) Fixed voltage control extends system lifespan by reducing degradation, though at the expense of energy output. (2) Fixed power control maximizes energy conversion and profitability, achieving a 34% LCOE reduction under the operating income optimization scenario, but accelerates system degradation. (3) Fixed temperature control delivers higher efficiencies but lacks long-term stability. The dynamic performance was analysed using real-world building energy data, confirming the model's robustness. Techno-economic optimization demonstrated profitability, efficiency maximization reached the highest value of electrical efficiency, while a degradation-minimization approach tripled the system's lifespan compared to other scenarios. A multi-objective optimization approach assessed trade-offs between minimizing degradation and maximizing electrical efficiency with fixed system inputs over time. The best trade-off was found by balancing each system variable and setting the system's performance limits. Integrating modeling, optimization, and control provides a robust foundation for future research, enhancing performances, efficiency, and durability of SOFC systems in sustainable energy applications.

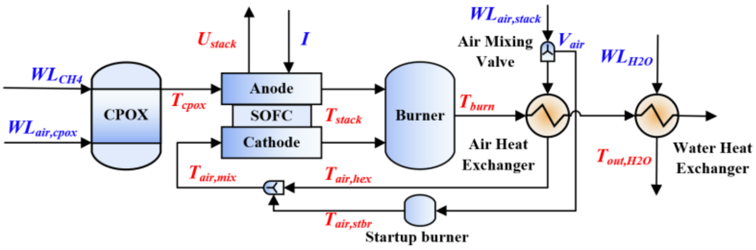

Figure 1: Process flow diagram of the H750 µ-CHP SOFC system developed by New Enerday GmbH, where manipulated system variables (inputs) are shown in blue and measured system variables (outputs) are shown in red.

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Stress heterogeneities inside PEMFC stacks: a homogenization method

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Proton exchange membrane fuel cell (PEMFC) stacks are composed of multiple cells that are compressed between two clamping plates. The performance and durability of the PEMFC are contingent upon the nominal pressure set within the stack by the plates [1]. A pressure that is too low may result in poor electrical contact between the cells and potential leakage. Conversely, a too high pressure may lead to over-compression of the membrane electrode assembly, which could impair the transport properties [2]. The nominal pressure can be set through experimental means or with the use of 2D local mechanical models [3]. However, these methods do not account for the pressure heterogeneities that exist within the stack, nor do they consider the impact of pressure variation during exploitation or during the clamping process. In order to gain insight into the stress distribution within a stack, it is necessary to upscale the numerical models. However, conducting a full 3D calculation at the stack scale is a costly endeavour in terms of both time and resources. We present a homogenised mechanical model of the cell stacking, which allows for the calculation of stress at all points in the stack. In the first part, we develop a micromechanical description of a unit element of the cell and of the cell sealing area. In the second part, we demonstrate how the mechanical properties of unit components can be measured. In the third part, we present the model at the stack scale and explain how it can be used to improve stack clamping design.

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PEMFC with dead-ended anode for hydrogen-powered commercial aircraft

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Polymer electrolyte membrane fuel cells (PEMFC) can provide electrical energy from the reaction between hydrogen and oxygen, with no significant product other than water. Their usage in an electric aircraft is a promising technology to reduce the climate impact of aviation [1]. The supply of PEMFC with hydrogen, air and a coolant medium require several balance of plant (BOP) components. State-of-the-art PEMFC systems use the active anode gas recirculation with a hydrogen recirculation booster (HRB), where non-reacted hydrogen is recirculated and mixed with fresh hydrogen from the tank.

With the investigated concept of a dead-ended anode (DEA), the purge valve at the anode outlet remains closed and no hydrogen recirculation is needed. As nitrogen and water can accumulate at the anode outlet, the purge valve is periodically opened briefly, allowing the hydrogen-poor gas mixture at the anode outlet to escape. The reduced number of BOP components is of particular interest for commercial aircraft PEMFC systems, as power density and failure rate may be increased. However, local hydrogen starvation at the anode outlet can lead to carbon corrosion at the opposite cathode catalyst layer, reducing the lifetime of the PEMFC [2].

An in-house developed dynamic PEMFC stack model [3] in the object-oriented modeling language *Modelica* was enhanced to allow simulations with DEA. Therefore, the two-phase behavior of water in the membrane electrode assembly (MEA) and the gas channels were modeled, a mixed potential approach was implemented to allow the description of electrode potentials at hydrogen starvation, and the carbon corrosion reaction was added. The simulation results could be validated with steady-state and DEA measurements of a PEMFC stack for a wide range of operating conditions. The PEMFC stack model provides insight into difficult-to-measure quantities such as local gas composition in the anode gas channels and interfacial potentials at the cathode catalyst layer. It also allows the prediction of cell voltage and voltage decay for different operating conditions, materials and geometries. The validated PEMFC stack model was used to optimize the purging strategy, i.e. the interval and duration of valve opening. Efficiency and lifetime were increased while carbon corrosion on the cathode catalyst layer was significantly reduced.

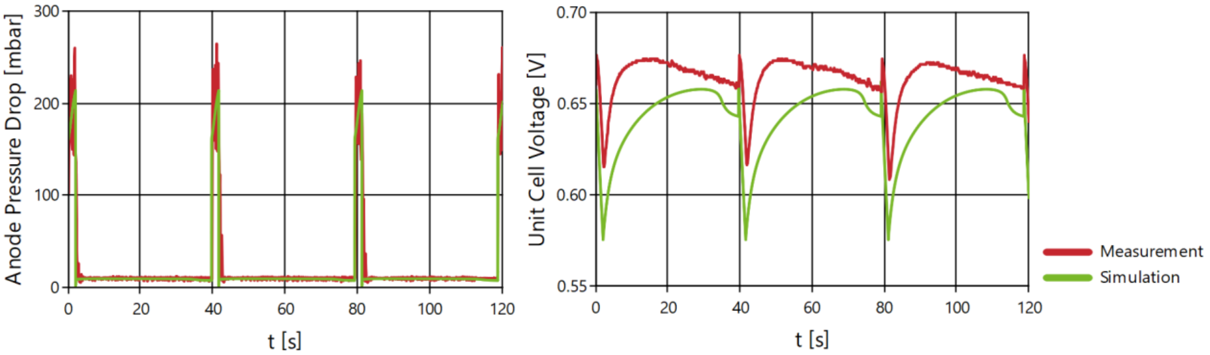

Figure 1: Comparison of anode gas channel pressure drop (left) and average unit cell voltage (right) between simulation and measurement over 3 successive purge cycles

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A network model-based analysis of stray currents in electrochemical stacks and development of design strategies for optimized stack layouts

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Many, if not most, applications of electrochemical systems require the cells to be arranged in stacks to increase productivity and reduce system costs. In all cases where a liquid is pumped to the electrodes from a shared tank, the conductivity of the liquid will cause a stray current that is a fraction of the main current passing from cell to cell. Therefore, in applications like redox-flow batteries, alkaline water electrolysis or even proton exchange membrane electrolysis, stray currents may affect the efficiency, cause side reactions, corrosion or lead to a degradation of the active surface. Thus, there is a strong motivation to quantify the stray current for the design of the stacked systems. This can either be done by focussing on the details of an individual cell or by investigating the entire system in a more abstract form. The latter approach, which has a general view on electrochemical systems and looks for potentials for improvement and optimization, is the purpose of this contribution.

To investigate different stack layouts and different levels of abstraction, we generated a Python-based script that automatically creates resistor networks and implements voltage sources to account for electrochemical potential differences. For the solution of the model, a system of linear equations is generated by creating an incidence matrix from the network and combining it with Kirchhoff's circuit laws (see Fig. 1 (left)).

The model is used for the optimization of electrolyte manifold and channel design, which can lead to already low stray currents under nominal load if length and diameter are properly chosen [1]. However, dynamic operation in the partial load range, start-up and shutdown processes, especially in the case of gas-evolving systems, will affect these optimized design criteria since lower currents and lower gas-void fractions will amplify the adverse side effects of stray currents. Additionally, non-uniform channel and manifold parameters along the stack (e.g. multiple manifold lines, branching lines, varying length and diameter) allow further reduction of stray currents compared to uniform design. This approach is exemplarily shown in Fig. 1 (right) for a stack of 20 cells with individual inlet and outlet channel lengths, significantly reducing the stray current by 25%, although the overall channel length is kept constant compared to the uniform design.

An analysis and explanation of these design optimization strategies to reduce stray currents while considering pressure loss and investment cost effects will be presented in this work.

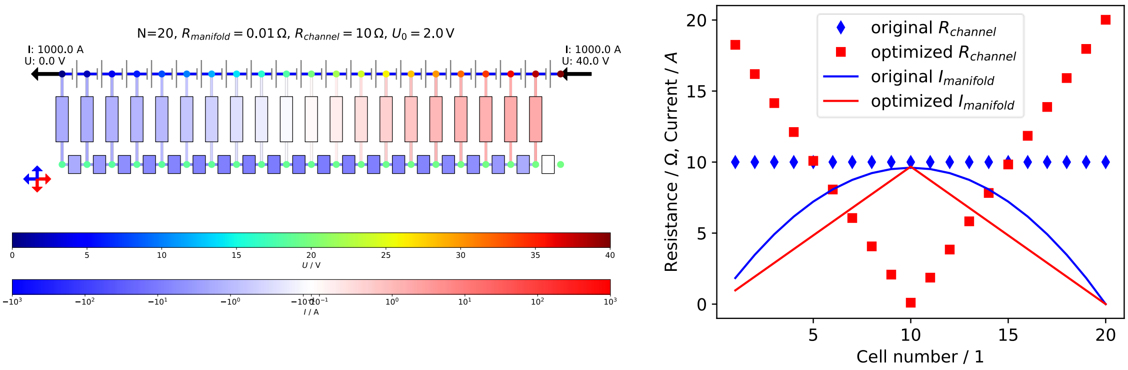

Figure 1: Illustration of a stack of 20 cells with combined channel and manifold resistances, colors indicate current through resistances and potentials at knots (left); distribution of resistances and manifold current before and after optimization (right).

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Towards virtual design of Fuel Cells and Electrolyzers

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Bosch is a technology company with a strong product portfolio in both fuel cells and electrolyzers. Despite having significant testing capabilities and connected products already in the field, experimental data is still a scarce resource. Moreover, not all internal states can be experimentally accessed and experiments at the stack level are very expensive. Therefore, efficient testing on the lowest and cheapest possible scale is crucial. This requires validated simulation models for scale-up and for the derivation of efficient test plans that are consistent across scales.

In an industrial context, the lowest scale of electrochemical testing are typically sub-scale cells operated under differential conditions. Efficient parameterization of scale-up models relies on such in-situ tests [1-5] in combination with ex-situ characterization of individual MEA components [6,7]. Validation of distributed internal states is often only possible indirectly and requires sophisticated experimental tools [8]. First steps towards correlating layer properties to material properties have been made [9,10]. Significant additional efforts will be required until quantitative predictions can be made on the device scale based on inputs on the material scale. We follow-up along these lines with partners in the EU-funded project DECODE [11].

In this contribution, we give an overview to our PEM fuel cell and electrolyzer product portfolio and share some insights into our activities in the field of scale-up modelling of these devices covering aspects of parameterization, validation and application to real world engineering examples. We will also highlight where we see the biggest challenges towards quantitative predictions and towards the integration of lower scales.

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Water Management in PEMFCs: Volume of Fluid Modeling of Two-phase Flow in Gas Diffusion Layers and the Gas Channels

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The coexistence of reaction gases and condensed liquid water in proton exchange membrane fuel cells (PEMFCs) brings complex water management issues. For example, liquid water accumulation blocks gas diffusion and causes uneven reactant distribution, especially at high current density. To provide a more in-depth understanding of the liquid-gas two-phase flow, a series of interface-resolved two-phase simulations in gas diffusion layers (GDLs) and gas channels (GCs) were carried out using the volume of fluid method in OpenFOAM, targeting existing knowledge gaps like inconsistent GC hydrophobicity preferences, random liquid injection methods, and overlooked fibre shape impacts.

Based on observed GC surface hydrophobicity degradation in experiments, two-phase flow in a long GC with varying wettability was studied via three contact angles, see Fig.1(a). The hydrophobic GC had less water accumulation and pressure drop; the hydrophilic one had pressure drop peaks that might accelerate fuel cell degradation. Subsequently, by varying the liquid injection positions, liquid injection near GC side walls was found to increase water accumulation but stabilize pressure drop.

To address simplified GC liquid input, a fibrous GDL was combined with the GC in Fig.1(b). A T-shaped simulation domain was designed considering GDL computation cost, which helps to reveal GDL water dynamics and enables more natural GC liquid injection. The 3D GDL structure was reconstructed with an in-house code, incorporating local and total porosity, fibre diameter and curvature. Results showed a small-fibre-diameter GDL had more internal water but less in the connected GC, indicating a water removal balance between these two domains is required. Water breakthrough at the GC/GDL interface was found to be more irregular than that in GCs without connecting GDLs.

As shown in Fig.1(c), numerical studies on GDLs with different fibre curvatures concluded that large curvature led to slightly more water and higher capillary pressure due to more small pores, while straight-fibre GDLs had more uneven flow transport performance. Furthermore, three types of breakthrough flow detachments were found, i.e., on the GC/GDL interface, attaching the GC side walls, and above the GDL (see Fig.1(c) coloured marking circle 1,2,3). The GCs with a straight-fibre GDL have larger droplets detached close to the GC/GDL interface, while those with curved-fibre GDLs have smaller droplets detached above the interface with a long liquid bridge. Overall, this research provides new insights and data to enhance understanding of complex two-phase flow in key components.

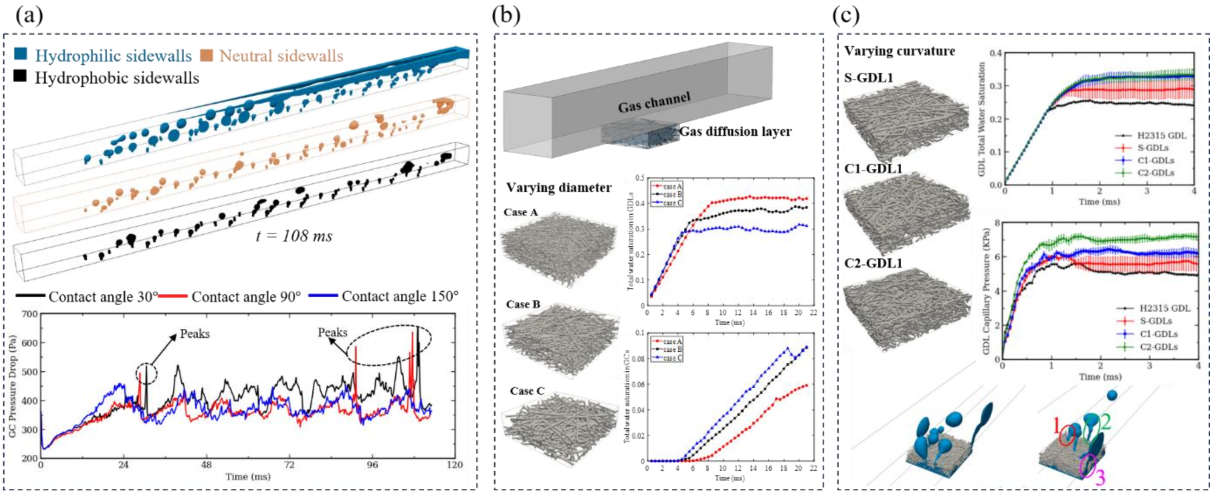

Figure 1: (a) Water flow and pressure drop in straight GCs with different contact angles; (b) Reconstructed GDLs with different fibre diameters and water saturation in these GDLs and their connected GCs; (c) Reconstructed GDLs with different curvature and the resemble results of water saturation and capillary pressure in different types of GDLs, as well as droplet detachment types.

Optical investigation and quantification of liquid water in the cathode side gas channels of PEM fuel cells

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Liquid water management is essential for the performance of Proton Exchange Membrane Fuel Cells (PEMFC). Water is produced electrochemically and removed through reactant channels. However, its accumulation on the gas diffusion layer (GDL) impedes gas transport to the catalyst layer and increases the water content within the GDL [1]. For macro-homogeneous 3D and reduced models [2], interface conditions must be implemented to couple the channel and porous GDL domains. While improvements on the basic assumption of zero liquid water coverage have been proposed, there is currently no generally accepted mathematical description.

We extend the current experimental database with optical measurements of liquid water formation and its effect on the pressure drop in representative channel geometries. The two-phase flow behaviour is analysed in a representative, ex-situ PEMFC mini-channel with optical access from two angles (side and top) and in an optically accessible flow field from the top. Conventional and machine learning methods are applied and compared for the image segmentation to quantify the liquid water in the channels (Fig.1). The area coverage ratio (ACR) of liquid water on the GDL-channel interface is typically determined experimentally using only top-view optical measurements (Fig. 2), which overpredict the water coverage on the GDL. In this study, the ACR is corrected by incorporating side-view imaging to assess the extent and distribution of water droplets on the GDL surface. Information from the single channel experiments are transferred to the complete flow field measurements, where the influence of the full channel length, serpentines and parallel channel interactions can be simulated for typical PEMFC operation modes. The image data and synchronised pressure measurements will be used to calibrate and validate analytical models [3] for the evolution of water topologies in PEMFC channels.

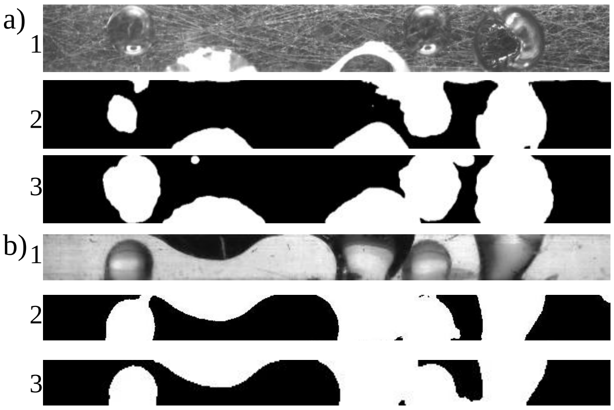

Figure 1: Example images from top (a) and side (b) view for automatic detection of water topologies: (1) reference image, (2) segmentation via machine learning (CNN), (3) segmentation via conventional methods (filtering, thresholding).

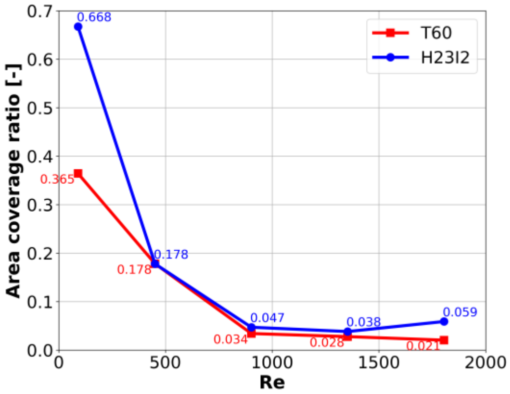

Figure 2: Area coverage ratio as a function of the Reynolds number based on the analysis of the top view images. GDL: Freudenberg H23I2 (blue) and Toray T60-T20 (red).

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Probing 3D-Printed Model-Architectures for Enhanced Water Management in Polymer Electrolyte Fuel Cells

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Water management in polymer electrolyte fuel cells (PEFCs) is significantly influenced by the gas diffusion layer (GDL), which plays a dual role: ensuring uniform reactant distribution to the catalyst layer (CL) and facilitating the efficient removal of product water while maintaining low liquid water saturation in the pores. This work investigates the potential of additive manufacturing (AM) to control liquid water percolation within the GDL.

A digital light processing (DLP) resin 3D-printer is used to fabricate polymer structures with a deterministic cubic lattice design, which are subsequently carbonized in a pyrolysis process. The carbonized samples feature minimum solid dimensions of ~50 µm and pore sizes as small as ~100 µm. The manufacturing pipeline is shown in Figure 1a-d. The structures are assembled as cathode GDLs (see Figure 1e) in a fuel cell specifically designed for X-ray imaging investigations[1]. In the first part the presentation will discuss the results obtained from operando X-ray radiography and X-ray tomography experiments with a focus on the liquid water distribution within the printed GDL. It will be shown that the liquid product water can be guided through deterministic pathways within the tailored pore space. Furthermore, flow simulations reveal an enhanced convective flow within the GDL. The results lead to a GDL design proposal which aims to guide condensed water from under the ribs towards the gas channels while maintaining a thin dry layer next to the MPL. In the second part, an alternative cell architecture (see Figure 1f) in which the conventional channel-rib flow field is entirely replaced by the printed structure is examined. The new architecture shows comparable performance to a conventional channel-rib configuration with commercial GDL materials, even when only an MPL is used as an intermediate layer to the CL.

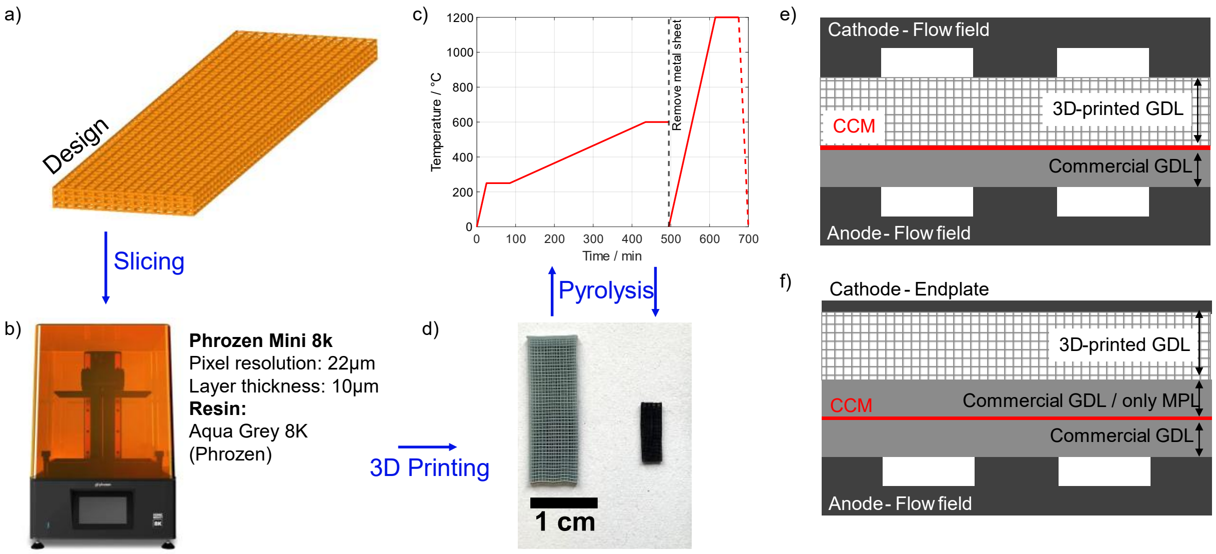

Figure 1: a) 3D rendering of a design example. b) Picture of the Phrozen 3D printer and specifications used for this work. c) Temperature profile used for the carbonization. d) Picture of the printed (left) and carbonized (right) structure. e) Schematic of the tested cells with a conventional channel-rib and GDL architecture. f) Schematic of the tested cells with an alternative cell architecture.

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Simulating Morphology and Degradation of PEMFC Cathode Catalyst Layers with Porous Carbon Supports

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We present coupled physical models for the morphology and degradation of the PEMFC cathode catalyst layer (CCL). The morphology model (MM) considers pore, particle and ionomer distributions and resulting interfaces on the nanoscale, creating a unique mathematical representation of each material at begin of test [1]. In particular, the MM discriminates between Pt catalyst particles on the support surface and inside primary pores of the support and their respective connection to the proton-conducting phase by means of ionomer or water. A central hypothesis to our work is that the amount and size of Pt inside primary pores influences capillary condensation of water vapor. At a given relative humidity (RH), more or larger interior Pt particles are considered to reduce the effective pore size and facilitate capillary condensation as illustrated in Figure 1. Simulations are validated against Pt utilization data in terms of electrochemically active catalyst surface area (ECSA) at varying RH. These measurements are particularly informative as they are sensitive to a variety of CCL properties such as support porosity, catalyst and ionomer loading [2, 3]. In a next step, the MM is coupled to a degradation model (DM) to simulate the evolution of the CCL morphology and associated catalyst utilization in the course of potential-induced ageing. Simulations are validated on data for five different materials which were each aged at three different RH settings, totalling to 15 samples and an overall ageing time of 750 h. The samples were manufactured and characterized in-house and are part of a larger data set which is available for public use [4]. With the coupled MM and DM, the measured ECSA versus RH at begin and end of test can be reproduced. The model allows for in-depth theoretical analysis of the impact of the material composition and the RH applied during ageing on the observed catalyst utilization. Particularly, the model helps identify the position of the characteristic increase in ECSA versus RH as a potential marker for the amount and size of Pt in pores at the given time of characterization. The presented model framework helps establish links both between electrode composition and nanomorphology as well as between nanomorphology and expected degradation.

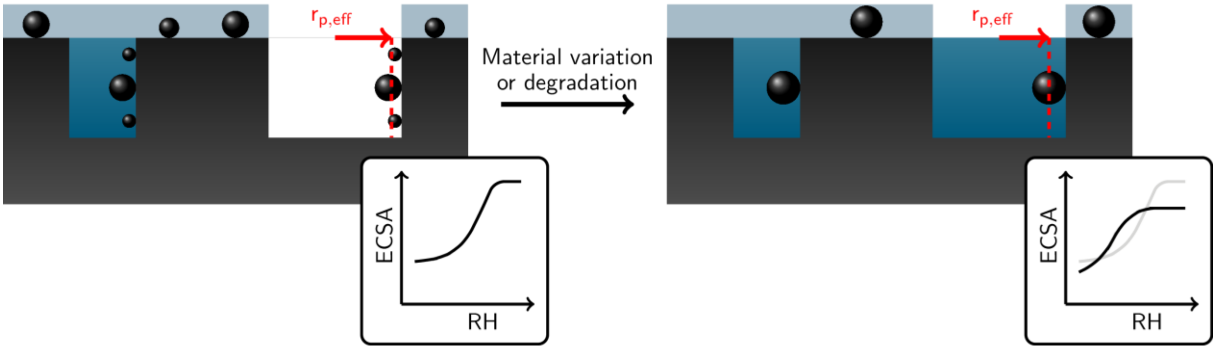

Figure 1: Pt particle distribution on porous carbon support and impact on ECSA versus RH. Larger Pt particles lower the effective pore radius $r_{p,\,eff}$ and result in pore flooding at relatively lower RH. Black spheres: Pt nanoparticles, light blue: ionomer, dark blue: capillary condensed water

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Electrochemical Interface Model Coupling Oxygen Reduction and Degradation Reactions in the Cathode Catalyst Layer of a PEMFC

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Proton exchange membrane fuel cells (PEMFC) are a promising technology to electrify heavy duty vehicles (HDVs) and contribute to the reduction of greenhouse gas emissions. However, current technologies do not meet the requirements of HDVs, especially concerning durability and efficiency.
The oxygen reduction reaction (ORR) in the cathode catalyst layer (CCL) is the single most important contribution to activation losses in PEMFCs, thus representing a significant factor to performance losses. Furthermore, parasitic side reactions in the CCL lead to a long-term performance degradation. Here we consider carbon corrosion reactions in the CCL, which weaken the structural integrity of the microstructure and can ultimately induce a collapse of the carbon support, thereby significantly altering transport resistances. Additionally, the formation of hydrogen peroxide, which is an important reactant in chemical membrane degradation reactions, is explicitly taken into account.
In [2] a unified framework for the ORR was presented, where the surface reactions are coupled to a double layer model [1], which accounts for the formation of oxide and water layers on the Pt surface. By this, the model could account for the local chemical environment at the reaction plane and predict the non-monotonic surface charge behaviour of the Pt surface.
In the current study, we are extending previous models of the electrochemical interface by considering a coupled reaction network, which models the ORR [2], hydrogen peroxide formation [3], and carbon corrosion reactions [4] as illustrated in Figure 1. The model parameterization based on literature data is improved using CV and polarization measurements to reflect material properties. We are investigating the impact of local operating conditions on the performance and degradation reactions and deduce recommendations for material improvements. Furthermore, the developed model is used to improve the parameterization of a macrohomogeneous cell-scale model.

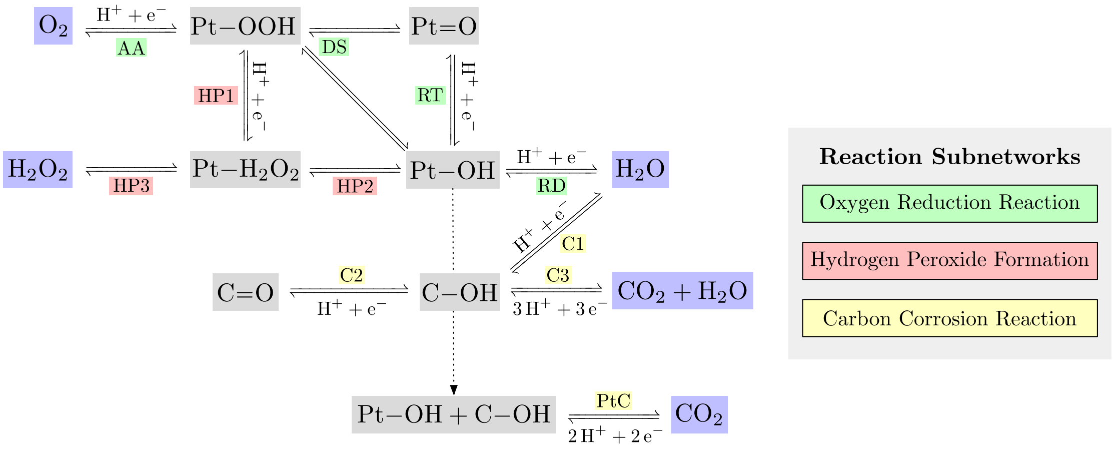

Figure 1: Reaction network of surface reactions on the Pt catalyst and carbon support surfaces.

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Investigating Platinum Gradient Effects on Performance of PEM Fuel Cells Using Agglomerate Models

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Efficient utilization of platinum catalysts is a critical challenge in optimizing the performance and cost-effectiveness of proton exchange membrane (PEM) fuel cells. Graded catalyst distribution along the cathode exhibits a great potential for enhancing cell efficiency and durability [1, 2]. However, full-scale 3D models incorporating in-plane catalyst gradients are not yet fully studied and new insights and opportunities are thus still not explored in this field.

In this study, we present a full 3D mathematical model of a PEM fuel cell based on macrohomogeneous modeling approach [3] with a 25 cm² active area, focusing on the effects of platinum catalyst gradients along the in-plane direction of the cathode. The model incorporates a detailed agglomerate catalyst layer model, volume-averaged flow field channels, two-phase flow, and membrane water saturation to capture the key physical and electrochemical processes. The homogenization of the flow-field lowers the requirements on computation power of the computing hardware while still offering a sufficiently detailed reactant distribution. Various Pt gradient configurations, including a linear gradient and a five-zone distribution from the cathode inlet to the outlet, were investigated while maintaining a fixed average Pt loading of 0.2 mg Pt/cm² on the cathode and 0.1 mg Pt/cm² on the anode.

The results demonstrate that a sharper Pt gradient, with higher Pt loading concentrated at the cathode inlet, yields the best cell performance. These findings suggest that strategic manipulation of the Pt distribution can enhance Pt utilization and reaction kinetics, particularly under the constraints of limited Pt availability. To validate the model, the simulation results were compared with experimental data. The catalyst layers used in the experimental study were prepared using inkjet printing, which enabled precise control over the spatial distribution of platinum.

This study highlights the potential of the spatial optimization of catalyst distribution to improve catalyst utilization and PEM fuel cell performance. Moreover, it provides a tool for integrating advanced modeling techniques with experimental validation to enhance catalyst design and utilization strategies.

Acknowledgement
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Utilization of a validated 0D approach for 1D SOFC performance modeling

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The application of Solid Oxide Fuel Cells (SOFC) in aviation requires lightweight high power density cells and stacks feasible for pressurized operation. Performance increases can be realized on different scales by optimizing materials, electrodes, cells and stack designs [1]. However, another considerable high-impact turning knob to increase the power density are the operating conditions.
In this contribution, an established 0D dc performance model [2, 3] was parameterized for a high-performance anode-supported cell and integrated into a 1D along the channel model that calculates the performance along the gas channel. In comparison to previous isothermal models [4], the temperature increase along the cell was considered by implementing adiabatic conditions and pressurized operation indispensable for airborne applications. The application of this 0D approach in a 1D performance model results in relatively low computation times (< 10 s) compared to complex FEM models [5]. This enables systematic variations of operating conditions in a short time period.
We will show that the parametrized 0D performance model is in good accordance with the experimental current-voltage characteristics of the characterized single cell. With the application of this validated 0D approach to a 1D model, an analysis of beneficial operating points with regards to the power density will be presented and evaluated in terms of feasibility. Performance limiting indicators such as the range of the fuel utilization will be discussed. We will examine the validity of this straightforward 1D model based on a comparison to a former developed and validated 2D FEM model [5]. The results of the pressurized modelling will be set into the context to recent results of pressurized single cell testing [6].

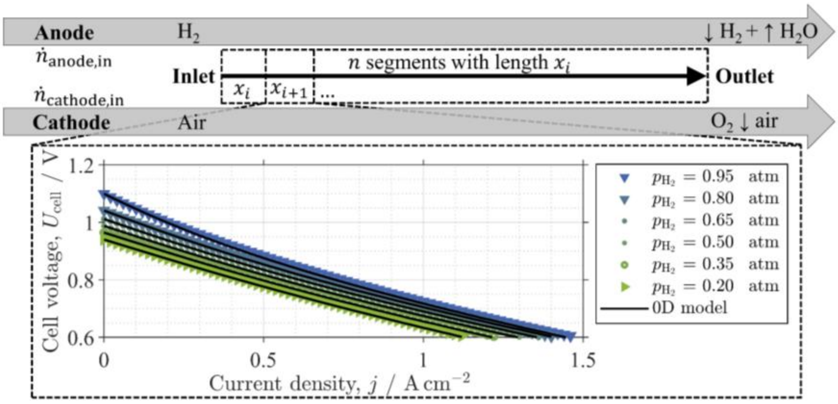

Figure 1: Sketch of 1D performance model with segment-wise solved validated 0D model, exemplary at 650 °C, air at the air electrode and varied partial pressure of hydrogen (balanced steam).

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Numerical simulation of multi-physics and local electrochemical characteristics of hythane-fueled SOFC

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The methane reforming reaction and the electrochemical process inside the solid oxide fuel cell (SOFC) fueled by blending hydrogen with methane occur simultaneously, where heat and mass transport are strongly coupled with electrochemical and chemical reactions, leading to an inhomogeneous distribution of current density and temperature, which severely constrains SOFC performance. A 3D numerical multi-physics coupled model of the hythane-fueled SOFC with multi-partitioned cathode is developed in this study, and the effects of fuel deviation, temperature conditions, and gas compositions on mass transfer and electrical performance are thoroughly discussed. The performance uniformity of the SOFC is subsequently evaluated based on the fuel utilization. The results indicate that concentration polarization near the fuel outlet is a significant cause of the pronounced performance deviation across different segments. The thermal effects of the reforming reaction exacerbate the in-plane performance homogeneity, and, when compared to isothermal conditions, the current distribution uniformity index (UI) is reduced by 3.64%. An optimal fuel utilization operating range of 30%-70% exists, within which the current uniformity index remains above 95%. The research may offer valuable insights into mitigating localized severe operating conditions and improving the performance of hythane-fueled SOFCs.

From Cells to Multi-Stack Modules: Model Validation and Simplification Approaches for Scaled-up Solid Oxide Cell Systems

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Solid Oxide Cells (SOCs) are highly efficient energy converters with significant potential for integrating renewable energy into strongly coupled energy systems. To enable their large-scale application, a thorough understanding of their capabilities and limitations at the system level is essential. One major research focus in the scientific community is to investigate and improve cell performance using single cell experiments in controlled laboratory furnaces, which do not represent the thermal boundary conditions of large-scale commercial systems. Conversely, model-based design of such systems typically employs lumped single cell or stack models. However, this extrapolation overlooks critical factors such as inhomogeneities, stack interactions and heat losses, typically leading to an overestimation of performance.

To address this gap, the German Aerospace Center has developed the simulation framework TEMPEST [1,2,3] in Modelica/Dymola. This object-oriented platform integrates validated models spanning from cell to application scale multi-stack modules, enabling accurate representation of thermo-physical processes with adjustable complexity. For current research questions such as transient capabilities of SOC systems, spatially discretised models are required, as fully lumped models cannot adequately capture temperature and reaction rate inhomogeneities. Central challenges in this effort include developing performant and accurate simplification approaches and validating the resulting models with experimental data.

This presentation will showcase the TEMPEST approach to overcome these challenges for stack and module modelling. Two test environments provide the experimental data for validation: a pressurised short-stack furnace test environment (HORST [4,5], -2 kW…0.5 kW in EC and FC mode), and an ambient pressure multi-stack module test environment (GALACTICA [6,7], -120 kW…40 kW in EC and FC mode). Exemplary fuel cell, steam- and co-electrolysis experimental data from HORST demonstrate the necessity of considering thermal interactions between the stack and its surrounding furnace to successfully validate a stack model. To avoid elaborate modelling of the surrounding, heat transfer parameters of a simplified test environment model are fitted, using a Python-based optimizer that iteratively adjusts the parameters and executes the model in Dymola to minimize errors in temperature profiles and cell voltages. Further, different simplification approaches are presented, including (i) reducing the number of ODEs at the cell level for different flow configurations and (ii) reducing the number of detailed cells within a stack for a multi-stack module model. The simplified module model is validated against experimental data from GALACTICA.

In conclusion, the developed modelling and simplification approaches deliver reliable multi-stack module models that allow to investigate scale-up and the transient behaviour of thermally integrated SOC systems.

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Carbon Monoxide Effect on Hydrogen Production During CO_2 Electrochemical Reduction at Silver Electrodes: A Combined Experimental-Modeling Study

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Electrochemical reduction of CO_2 into valuable chemicals from renewable electricity is envisioned as a means to avoid fossil resources in many applications. As the field is urged to increase its technology readiness, numerical models are necessary tools to accelerate device development.[1,2] Nevertheless, fully reliable and accurate models have yet to be developed. The challenges lie in the complexity of the reaction and the convolution of many effects including mass-transport, microkinetics, and kinetics. In this study, we aim at deconvoluting these aspects by studying the reduction of CO_2 into carbon monoxide at a flat silver electrode, one of the most studied catalyst materials under controlled mass-transport conditions. We hypothesize that one of the major gaps between previous models and experiments is the carbon monoxide affinity for some active sites that prevent other electrochemical reactions from taking place. To model this effect independently, we conducted a series of measurements in the presence of CO and determined equilibrium constants to be fed into a microkinetic model. These experiments confirmed our hypothesis that the produced CO significantly hinders the competitive hydrogen evolution reaction. We then developed a computational model and show that the consideration of the CO effect on hydrogen evolution reaction allows for improved accuracy in predicting experimental observations.[3] The study also provides unexpected insights in the different nature of active sites responsible for CO and H_2 evolution at Ag electrodes.

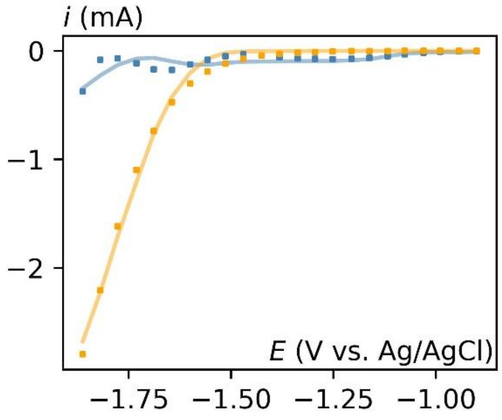

Figure 1 : Experimental (dots) vs. Modeled (plain) trace for H_2 (blue) and CO (orange) production at Ag inverted Rotating Disk electrode. Experimental trace reproduced from [3].

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Data-driven approach for modeling and sensitivity analysis of a Proton-exchange membrane water electrolyzer

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Proton exchange membrane electrolytic cells (PEMEC) have emerged as a promising technology to produce environment friendly green hydrogen. These are complex systems which involve a highly non-linear interplay between mass transfer, fluid flow and electrochemical reactions. To improve the commercial viability of PEMECs, performance optimization of these systems using data-driven models has emerged as a promising approach [1]. In this work, we develop data-driven surrogate models using synthetic data obtained from a physics-based one-dimensional numerical model of PEMEC [2]. The predictive performance of three unique machine learning algorithms [3] (support vector regression (SVR), extreme gradient boosting (XGB) and artificial neural networks (ANN)) were evaluated and their ability to capture the inherent non-linearities of PEMEC were compared. Important transport properties of the system such as operating temperature, anode catalyst and porous transport layer thickness, electronic conductivity and membrane thickness were selected as the input features for developing the data-driven models. Both XGB and ANN models showed better performance in predicting the cell current density when compared to SVR model. The ANN model was deployed to conduct a parametric analysis to investigate the effect of operating conditions and transport properties. Furthermore, an explainable artificial intelligence technique known as SHAP (Shapely Additive Explanations) was employed to list out the important parameters influencing the cell current density. The SHAP analysis highlight that the influence of membrane thickness is higher than the electronic conductivity for supported catalyst layers, and conversely, for unsupported catalyst layers.

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Pore-scale investigation of anodic porous transport layer of PEM water electrolyzer: Experimental and Lattice Boltzmann simulations

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Efficient electrochemical reactions in polymer electrolyte membrane water electrolyzers (PEMWE) rely on the optimal flow of water and oxygen within anode porous electrodes as shown in Fig. 1A. A key challenge is mass transport limitations, caused by the counter-current flow of water (reactant) and oxygen (product) in the anodic porous transport layer (PTL_a). These limitations hinder reaction efficiency and reduce voltage output. To address these challenges, this study combines the Lattice Boltzmann Model (LBM) [1] and optical imaging of a model experimental cell [2] with an electrochemically active catalyst layer (CL) to investigate pore-scale gas-liquid distributions within the anodic PTL of PEMWE as shown in Fig. 1B &1D.

Using multiphase and multicomponent Shan Chen LBM (SC-LBM), the simulations were carried out for different PTL structures which were reconstructed from micro-computed X-ray tomography scans of commercial titanium (Ti) material. The considered PTL structures here are Ti-felt and Ti-sintered which differ in terms of their local pore morphology (presented in Fig. 1C). The results of the LBM show the dependency of the oxygen-water distribution on the local pore structure. To further improve the understanding of gas-liquid distributions within the PTL_a, a transparent PMMA (Poly-Methyl-Methacrylate) based model PEMWE cell was developed. This experimental setup enables direct optical visualization of gas-liquid flow, offering insights into invasion patterns influenced by primary and secondary transport mechanisms, current densities, and flow stoichiometry. The transparent cell facilitates detailed analysis of dynamic transport processes under operating conditions, providing preliminary data for experimental validation and advancing the understanding of gas-liquid distribution mechanisms beyond simulation observations.

The combination of LBM simulations and experimental techniques provides a comprehensive understanding of the dynamic interaction between the pore geometry of various anode PTL materials and flow conditions. Furthermore, straightforward image processing algorithms enable direct comparisons between experimentally observed invasion profiles and SC-LBM simulation results. This study offers valuable insights into PTL transport mechanisms, employing visualization-based strategic approaches to improve the efficiency and performance of next-generation electrolyzers.

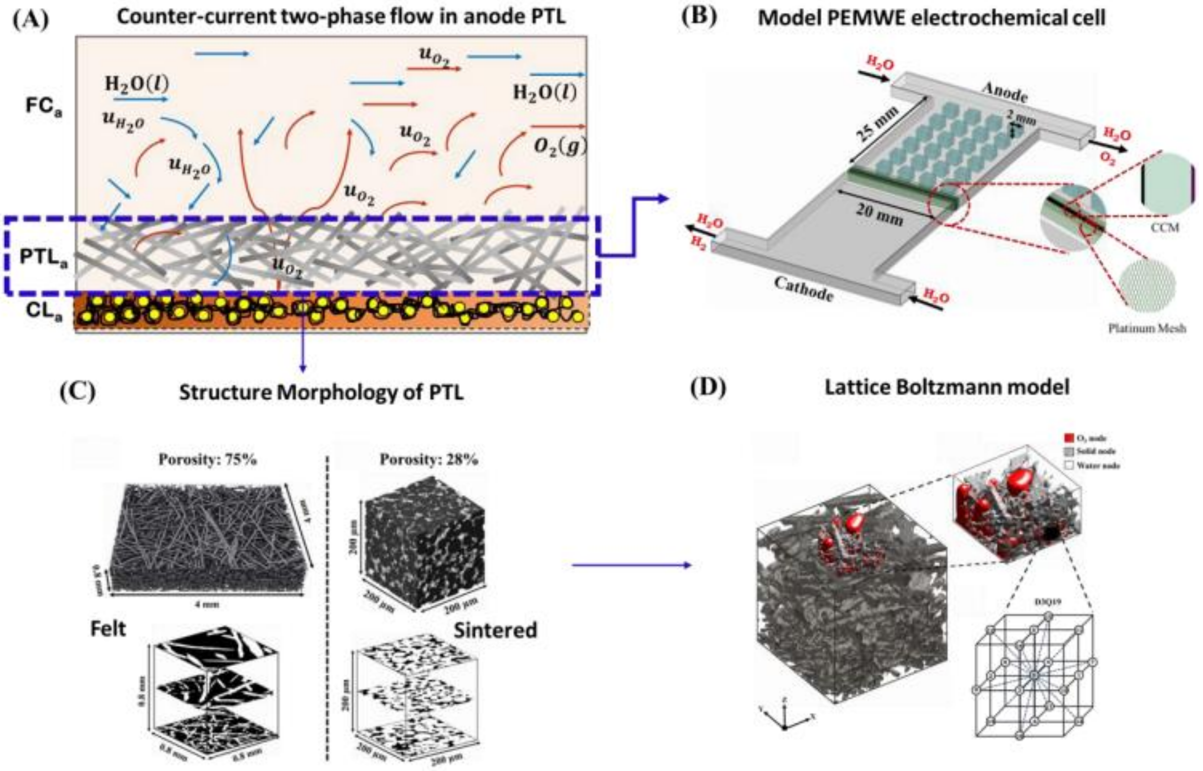

Figure 1: (A) schematic representation of the counter current two-phase occurring in anode side of PEMWE; (B) representation of the model PEMWE cell including dimensions; (C) structure morphology of the Ti- felt and Ti-sintered PTL structure; (D) LBM simulation of oxygen invasion patterns in a 3D domain which was reconstructed from a Ti-felt PTL

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Numerical Investigation of Two-phase Flow Effects on Species Transport in Electro-chemical Systems

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Chemical process industries are energy intensive, with energy often being obtained from fossil fuels. Therefore, an electrolyzer represents a sustainable and cost-effective alternative for synthesis process. In the case of the electro-organic Shono-reaction, hydrocarbons are oxidated at the anode, while hydrogen is produced at the cathode. Evolving hydrogen generates gas bubbles in the vicinity of the electrode surfaces and hence affects the species transport in the liquid electrolyte. Since the diffusion of the reactants to the respective electrodes is the limiting transport mechanism in such electrolysis cells, the hydrogen bubble dynamics influence on the reactants transport requires further research in particular with regard to the cell's productivity. The oxidized hydrocarbons at the anode dissolve in the electrolyte, but detailed information on the influence on the species transport is yet to be determined. Therefore, the presented investigation focuses on the hydrogen bubble dynamics influence on the species transport in a simplified water electrolysis cell.

Due to the complex nature of multiphase flows, a holistic simulation considering numerous influential factors is extremely challenging, particularly when it comes to validation. Thus, the experimental electrolysis cell is used to determine the contact angle between the water and the bubble using the time-resolved transmitted-light shadowgraphy technique [1]. A preliminary proof-of-concept experiment as indicated in Figure 1 was successfully conduced, inducing the bubble growth by a controlled airstream into the cell. Contact angles from the resulting images, as shown in Figure 2, are taken as an input for the numerical simulation. Figure 3 shows the numerical simulation, being able to account for the phase change of hydrogen. The hydrogen bubble is modelled with an interface-capturing Volume-of-Fluid (VoF) Method. The third-party framework *geoChemFoam* based on the open-source library OpenFOAM provides the solver *interTransferFoam*, being able to model bubble formation due to species diffusion [2].

In the conference contribution, firstly the air bubble dynamics between experimental and numerical data from the preliminary investigations are compared. Subsequently, the ge*oChemFoam* framework is extended by multiple functionalities to be applied to the presented problem. In particular, a simplified electro-chemical boundary condition was implemented to account for transport-limited reaction rates. The main objective of this work is the evaluation of bubble detachment and bubble-induced mixing in the bubble wake with regard to the species transport in the vicinity to the electrodes.

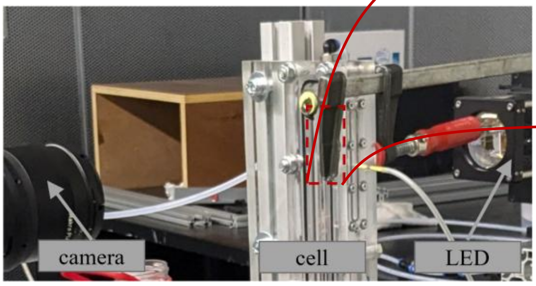

Figure 1: Experimental setup

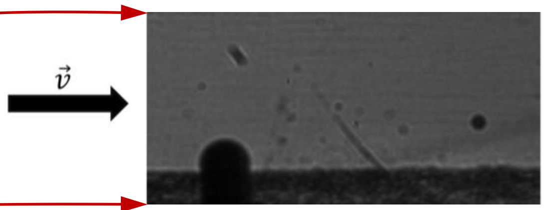

Figure 2: Shadowgram of bubble

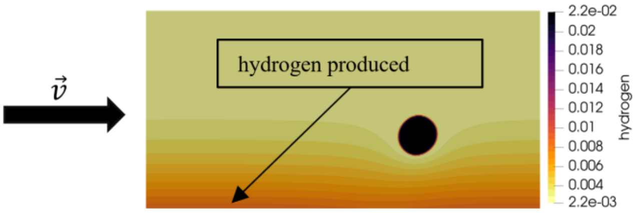

Figure 3: Hydrogen profile in channel with growing bubble

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Abstracts for Oral Contributions

Energy Storage

Impedance as a Battery Modelling and Diagnostics Tool

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Electrochemical impedance spectroscopy (EIS), or what electrical engineers might simply call 'impedance measurement' (!), is a compelling tool for understanding and characterizing electrochemical devices, because switching to the frequency domain enables data-efficient measurements of processes over timescales that can differ by several orders of magnitude.

In this talk I will first give an overview of several aspects of EIS that we have investigated over the past fifteen years, including measuring battery impedance using power converters [1] and using EIS data as a non-invasive battery temperature sensor [2]. Traditionally, EIS assumes that the device under test exhibits a linear stationary response, but it is possible to obtain interesting information and analysis by relaxing these assumptions [3-4], such as *operando* measurements at non-zero operating points.

Finally, I will explore the use of impedance to parameterise and fit electrochemical battery models, with a particular focus on finding parameters from EIS data for simplified models such as the single particle model [5] and single particle model with electrolyte [6]. In this context, I will showcase the use of open-source tools such as PyBaMM (https://pybamm.org/) for battery modelling, and PyBOP (https://github.com/pybop-team/PyBOP) for parameter estimation.

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The Newman model for phase-change electrodes: physics-based hysteresis

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Many modern, commercially relevant Li-ion batteries use insertion materials that exhibit lithiation-induced phase change (e.g. lithium iron phosphate). However, the standard physics-based model – the Newman model – uses a microscopic description of particle lithiation (based on diffusion) that is incapable of describing phase-change behaviour and the physical origins of the voltage hysteresis exhibited by such phase-change electrodes. Building upon the seminal works [1,2,3] we present a simple and rational model of hysteretic lithiation (in an electrode comprised of an ensemble of phase-change nanoparticles) based on a systematic minimisation of the Gibbs energy. Voltage hysteresis arises naturally as a prediction of the model. Initially, equations that model the phase-change dynamics in a single particle of active material are presented. We then generalise to a model, termed the composite phase-change model, of a coupled ensemble of particles in a thin electrode. The composite phase-change model is then incorporated into the framework of a classical Newman model, allowing for the inclusion of transport effects in the electrolyte and electrode conductivity. The resulting modified Newman model is used to predict voltage hysteresis in a graphite/LFP cell. We demonstrate agreement with experimental "major loops", "minor loops" and current pulse/relaxations. Alongside the new model we will demo a simulation tool, Dandeliion (available at www.dandeliion.com), that allows users to replicate, and extend, the results that we will present.

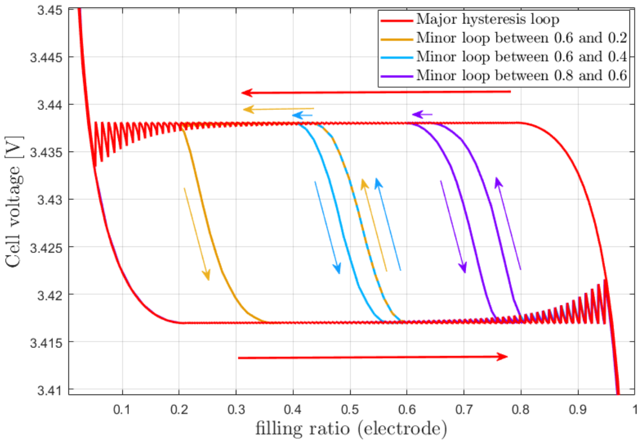

Figure 1: Typical "minor loops" as predicted by the composite phase change model.

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Chemo-Mechanical Core-Shell Model Explaining the Silicon Voltage Hysteresis and Long-Term Relaxation

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Silicon is considered as next-generation anode material for lithium-ion batteries owing to the tenfold increase in theoretical capacity compared to graphite anodes. However, beneath the significant volume expansion of silicon during lithiation, the silicon voltage hysteresis represents a major challenge for the commercial use. The hysteresis causes a reduced efficiency, detrimental heat generation, and complicates the state-of-charge estimation. Our contribution elucidates the reason of the voltage hysteresis phenomenon and identifies approaches to overcome the related limitations.

We developed a chemo-mechanical model accounting for the interaction between active silicon and a surrounding inactive phase in a core-shell geometry. The shell can be considered as solid-electrolyte interphase (SEI), inactive silicon domains, or silicon oxide. The volume changes of the active silicon during cycling cause significant stresses inside the shell, resulting in pronounced degradation [1]. Simultaneously, the visco-elastoplastic shell implies stress to the silicon particle, impacting the chemo-mechanical potential. Therefore, our model reproduces the experimentally observed silicon voltage hysteresis during cycling and after short-term relaxation [2]. Moreover, a recent improvement of our mechanical model allows to describe the long-term, logarithmic voltage relaxation over weeks [3]. Hence, our modeling approach reproduces the observed silicon voltage hysteresis and relaxation consistently. In addition, we derived a reduced hysteresis model, which outperforms the empirical Plett model in terms of physical interpretability and voltage predictions during relaxation.

In conclusion, we explain the silicon voltage hysteresis and long-term relaxation with a visco-elastoplastic core-shell model. Our physical understanding supports the improvement of the performance and state estimation of pure silicon anodes desired for future applications.

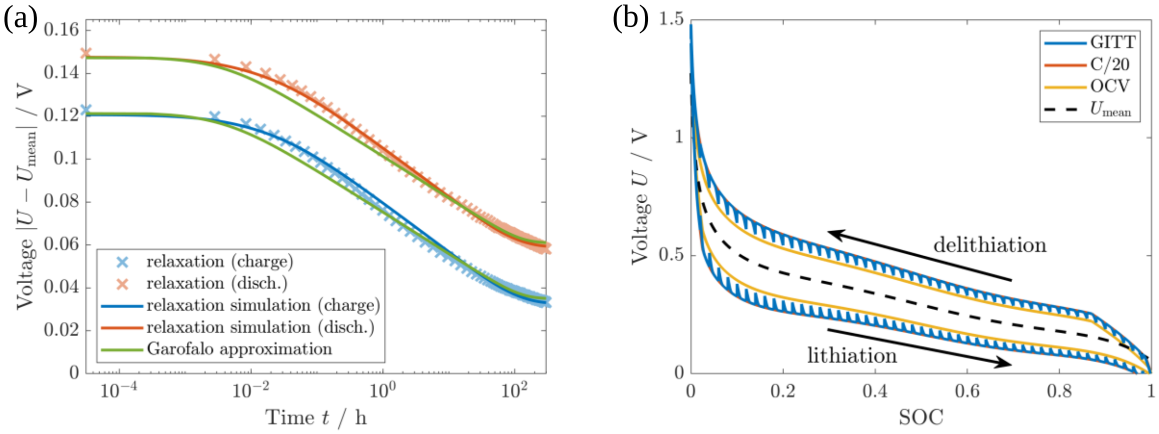

Figure 1: (a) Long-term voltage relaxation in simulation and experiment. (b) Voltage hysteresis during cycling and after relaxation predicted by the reduced hysteresis model. Reprinted from Ref. [3].

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Voltage Hysteresis Experiments to Inform Physics-Based Models

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Battery management systems for LFP/graphite cells—already made more complicated by the large voltage plateau of the cathode—need to incorporate effective hysteresis models. This work focuses on the combined role of graphite and LFP in determining the hysteresis in LFP/graphite Li-ion battery cells. Previous work by our group [1] focused on exploring the empirical single-state hysteresis model proposed by Plett [2], by comparing predictions from Plett's model to pseudo-OCV measurements of LFP/graphite cells. It was found that inaccuracies in the model predictions correlated strongly with graphite stage transitions. This work focuses on the alternative hysteresis model of Dreyer [3], which assumes that LFP voltage hysteresis arises from a single spinodal decomposition among the particles that make up the cathode. Dreyer's mechanistic model is compared to pseudo-OCV hysteresis loops obtained by partially charging LFP-graphite cells across different windows of total cell SOC. These experiments clearly show that the magnitude of hysteresis depends on the SOC range spanned. Comparing model predictions to the experimental data in Figure 1a-c) shows that Dreyer's original model does not account for 'bumps' in the hysteresis loops and cannot match the lower voltage hysteresis when SOC spans narrow ranges around 50% SOC. Both observations may be attributable to graphite hysteresis, with the bumps coinciding with graphite stage transitions [4] and a decreased magnitude of hysteresis occurring when the cell is cycled between graphite stage transitions. The Gibbs free energy surface used by the Dreyer model can be modified to account for additional spinodal decompositions. Here, we probe the impact of graphite hysteresis by modifying the Gibbs free energy surface from the symmetric-well for LFP used by Dreyer to a double-well system centered around 30% SOC (Figure 1d,e) to account for one level of graphite staging. Multiple stage transitions in graphite [4] are modelled through a multiple well Gibbs free energy functional (Figure 1f). The LFP and graphite phases are modelled collectively by creating a Gibbs free energy functional with the stage transitions in LFP and graphite. The findings further emphasise the importance of accounting for graphite hysteresis in physics-based battery models. Further work will focus on incorporating dynamics into the hysteresis model.

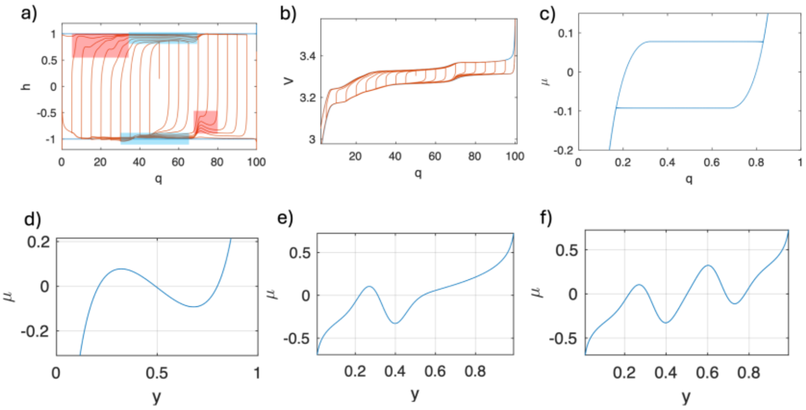

Figure 1: a-b) Data from hysteresis experiments using 1/20 C rate for pseudo-OCV measurements on NX energies LFP/graphite 18650 cells. a) Data plotted as normalized hysteresis versus charge. Red bands highlight bumps in the cycle loops, and blue bands highlight the lack of convergence to full charge and discharge curves. b) Raw data from panel (a) plotted as voltage versus charge. c) Dreyer model prediction for LFP hysteresis. d) Dreyer LFP symmetric two-phase chemical potential [3], e) asymmetric two-phase chemical potential and f) three phase chemical potential.

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Comparative analysis of ethylene carbonate decomposition in Li_2CO_3- and Na_2CO_3-based solid electrolyte interphases

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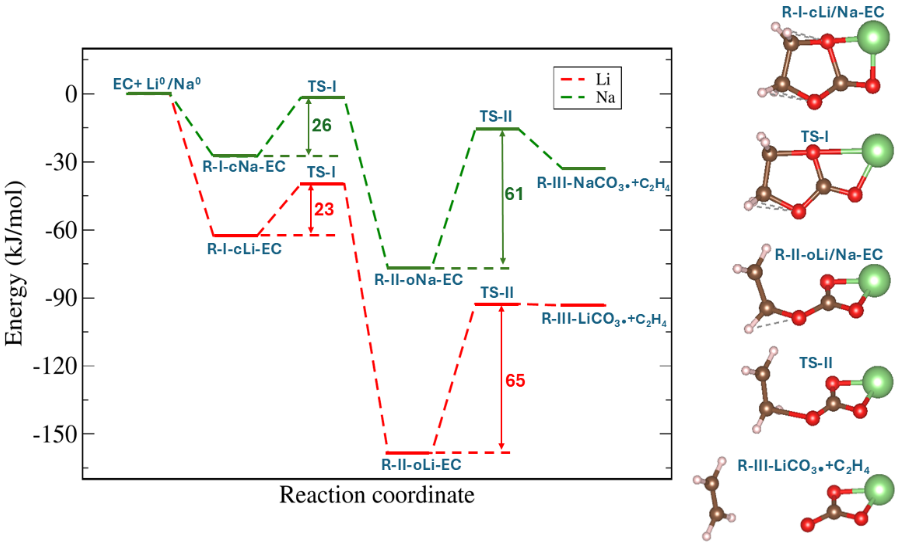
The SEI (solid electrolyte interphase) is a heterogeneous multilayered structure formed at the anode/electrolyte interface due to electrolyte reduction during the first few charge-discharge cycles. This SEI layer protects the electrolyte from further reduction by blocking electron transfer but grows over time, leading to battery degradation.[1] In this study, we investigate ethylene carbonate (EC) decomposition reactions, which primarily drive SEI growth in lithium (sodium)-metal/EC systems [2,3]. To compare the stability and reaction rates of Li- and Na-based SEIs, we simulate EC decomposition pathways and energy barriers in both gas-phase isolation and over inorganic SEI components Li_2CO_3 and Na_2CO_3 using density functional theory (DFT) implemented in the *VASP* software. Within the static approach, the improved dimer method (IDM) [4] is employed to optimize the transition states and calculate energy barriers.

SEI formation begins when EC and Li^0 interact at the anode/electrolyte interface. As shown in Figure 1, EC and Li^0 react to form cLi-EC•, where the electron is located at the carbonyl carbon. This intermediate undergoes a ring-opening reaction (RI) to form oLi-EC• via an energy barrier of 23 kJ/mol. The resulting product can dissociate to ethylene (C_2H_4) and a carbonate radical $LiCO_3$• through RII with a 65 kJ/mol barrier. Further, oLi-EC• can react with Li^0 to form Li_2CO_3. A similar reaction mechanism is also observed with Na^0, but the ring-opening reaction has an energy barrier slightly higher (26 kJ/mol) than Li while the dissociation of ethylene from $LiCO_3$• has a lower energy barrier (61 kJ/mol) as compared to Li. Preliminary results indicate that EC decomposition with Na and Li shows nearly similar stability and reaction rates. However, the static approach introduces significant errors due to reliance on a single calculation representing a complex potential energy surface. Further ongoing investigations of these reactions on Li_2CO_3/Na_2CO_3 surfaces using both static and kinetic Monte Carlo approach will improve the quality of our predictions.

Figure 1: Energy profile for EC decomposition reactions computed in gas phase.



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A Scale-Resolved Numerical Operando Approach for Lithium-Sulfur Batteries

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Lithium-sulfur batteries (LSBs) are believed to have a high potential for aerospace applications due to their high gravimetric energy density. However, despite decades of research and advances, they still suffer from poor rate capability and low power output, eventually preventing their practical implementation [1]. One particular aspect we want to shed light on is the influence of the porous cathode structure on the rate performance during discharge. Therefore, we present a scale-resolved simulation toolbox that aims to provide structural insights into the electrochemical cell behaviour that are experimentally hardly accessible even for modern operando methods. Our *numerical operando approach* employs high-performance computing (HPC) and is based on a coarse-grained continuum model. The latter is spatially discretized with a Discontinuous Galerkin (DG) method and advanced in time by an adaptive controller. The models and methods as well as HPC aspects of our toolbox will be presented, finally showcasing the capabilities of our workflow to improve LSBs.

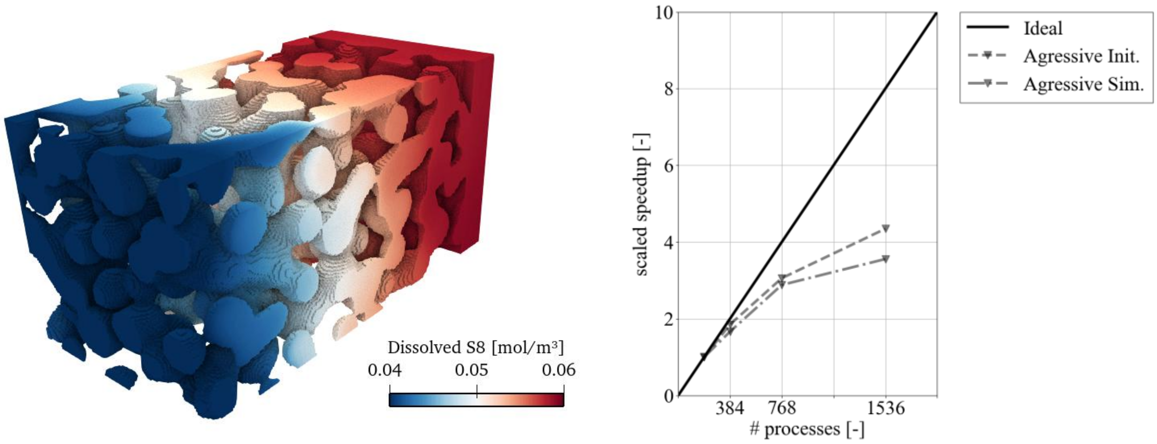

Figure 1: (Left) Snapshot of dissolved S_8 in a sulfur-carbon composite structure shortly after beginning of discharge at 0.5C and (Right) strong scaling plot for 0.2C. The model comprises 35 Mio. Degrees of Freedom (DoF).

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What is Missing from Current Li-S Models to Predict Coin-Cell Behaviour?

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To meet the growing demand for batteries, alternative battery chemistries beyond lithium-ion (Li-ion) are required. A promising alternative is lithium-sulfur (Li-S). As most of the materials and morphology development in Li-S batteries is conducted at coin-cell level, it is essential to understand the mechanisms that limit coin-cell performance and how they translate to larger cell form factors. The ability to test assumptions and predictions through a model saves experimental time and cost, and enables simulation of behaviour under different conditions. Physics-based models are being used successfully for Li-ion cell design, and has created an opportunity to achieve this level of maturity with Li-S models. One key difference is that, for Li-S batteries, the mechanisms governing cell performance depend on factors such as electrolyte-to-sulfur (E/S), and electrolyte-to-cathode ratios, which change significantly when scaling-up from coin-cell to pouch-cell.

Li-S battery models are predominantly designed for pouch-cell batteries. Whilst these models provide the fundamental tool to analyse the behaviour of a pouch-cell, they have not been tested for coin-cells. The physical differences between coin and pouch-cells result in differing mechanisms, leading to the question: can a pouch-cell model be re-parameterised to accurately predict coin-cell behaviour? To answer this question, several published zero-dimensional (0D) pouch-cell models [1], [2], [3] were analysed and upgraded. The experimental data published by Boenke et al. [4] was used for parametrisation and validation.

The new model comprises of the key mechanisms from existing models, including those required to capture charge and discharge behaviour, precipitation dynamics and polysulfide shuttle. With the addition of several features, including the separation of particle growth and nucleation precipitation, and updated derivation of terms including the cathode porosity and surface area, the model can accurately account for behaviour relating to sulfur utilisation and accessibility of active material. The model captures all behaviour relating to the scaling of cell format, including the geometric size and E/S ratio. Unlike existing Li-S models, this model can retrieve C-rate dependence in terms of both capacity and voltage. Whilst maintaining low dimensionality, this is achieved via transport of species between the cathode, separator and a reservoir of excess electrolyte, along with introducing a dependency between the change in area and the precipitation dynamics during cycling.

Despite its simplicity, these changes have significantly improved the causality and accuracy of model predictions when compared to experimental data. From here, further mechanisms or dimensionality can be added if needed to capture additional features, such as cell degradation, with the confidence that the correct causality for coin-cell behaviour is captured. Based on the remaining number of unknown, or not yet agreed upon mechanisms occurring within a Li-S battery, this methodology ensures trust in the model predictions.

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The role of computational fluid dynamics in battery cell development

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The automotive industry is in a transition from fossil fuel powered combustion engines to electric powered drivetrains with battery cells to store energy. The BMW Group has acknowledged this transition already in an early stage with the introduction of the BMW i3 and BMW i8 and today the BMW Group has a battery electric vehicle in every segment of its portfolio. In recent years the BMW Group has built the Battery Cell Competence Center (BCCC) to further increase its competences to develop battery cells for automotive applications, including facilities to produce battery cells on a prototype line. Furthermore, the BMW Group has built the Cell Manufacturing Competence Center (CMCC) to acquire an improved understanding of cell manufacturing on a pilot line level. This presentation will start with an impression of battery cell development and manufacturing at the BMW group, both from the BCCC and the CMCC.

The main objective of this presentation is to highlight the role of computational fluid dynamics in battery cell development. This role will be shown by two interesting examples of fluid flow phenomena in battery cells. The first example shows how fluid flow of a liquid electrolyte can be induced by swelling/shrinking of active material during charging/discharging, which can cause spatial gradients or local inhomogeneities in the salt concentration. This phenomenon is elaborately introduced in [1], where it is called “electrolyte motion induced salt inhomogeneity” (EMSI). Focus of this presentation will be on challenges to simulate this phenomenon, which requires a coupled simulation of electro-chemistry and fluid dynamics. Furthermore, the simulation requires a time-dependent computational domain/mesh with a moving interface to account for the squeezed electrolyte.

The second example is simulation of fluid flow phenomena before and during a thermal event, including venting after opening of a battery cell. There are multiple levels of fluid flow: fluid flow in the porous structure of electrodes, fluid flow in the empty spaces around a jelly roll and fluid flow from a battery cell into its surrounding during venting. Main challenge for this kind of simulations is to capture the appropriate balance for interactions between chemistry, heat release, thermodynamic state (temperature and pressure), conductive/convective heat transport, and fluid flow (mass transport of reactants and products in the chemical reactions). This presentation will show results of simulations that account for this combination of phenomena, which will be compared with experimental results of either an accelerated rate calorimetry measurement or a nail penetration. Study of these phenomena forms an essential part of simulation-based safety assessments of battery cells during a thermal event and provide the required input data (viz. boundary conditions for fluid velocity and particle distribution) for simulations of thermal propagations in a battery pack.

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Thermal Runaway Prevention and Mitigation: From Cell Level Insights to System Level Strategies

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Under thermal, mechanical or electrical abuse, lithium-ion batteries can undergo a thermal runaway causing safety issues for humans and environment, including massive heat generation, release of toxic gases and potentially fire. Battery pack designers strive for maximization of energy density on cell and on system level while still guaranteeing safe operation under any circumstances. Experimental evaluation of a battery system's safety is complex and costly. Therefore, a flexible simulation tool for the prediction of battery cell behavior in these hazardous cases is developed in this work with the goal to optimize the dimensioning and arrangement of the safety system. In this context, flexibility means that the models need to be adjustable to different cell types such as high-energy and high-power cells and to various cell formats. This requires deep understanding of the thermal transport processes and degradation reactions on cell level.

The latter is captured in a comprehensive chemical model which is composed of ten decomposition reactions of the battery components such as anode and cathode active materials, conducting salt and electrolyte solvent. Coupled with a 3D thermal model this allows the prediction of heat release and gas composition during thermal runaway [1]. The model has been validated by heat ramp experiments with various battery cells. The test rig is equipped with temperature and pressure sensors and a gas analysis is performed.

The validated simulation model is applied on thermal propagation processes of pouch cell stacks. Since heat transfer is of major importance in this scenario, it is investigated how the produced gases affects the thermal behavior of the tested pouch cells [2]. It is observed that the gases inside the pouch bag diminish the heat transport with significant impact on the propagation behavior. For this reason, in the numerical setup, the battery cell's thermal resistance is coupled with the amount of produced gas. In this context, it is further investigated how outer pressing forces, as they are usually applied to pouch cells in real battery systems, influence the heat transfer after the beginning of gas generation. This is validated by thermal propagation experiments in a two-cell setup. It shows that the simulation model is able to predict the heating, blow-up and venting of the pouch cells up to rapid thermal runaway as well as the gas composition in these multi-cell trials. Propagation times are estimated within a small margin.

With this entire numerical setup, full pouch cell packs including various cooling systems are simulated under thermal abuse in order to evaluate the effect of safety measures such as heat shields on the thermal runaway behavior of the battery system. Extensive simulation studies with the validated models are performed in order to draw conclusions on the interplay of thermal runaway protection measures and the cooling systems [3]. This allows to derivate recommendations for pack designers regarding the selection and arrangement of safety and cooling components in dependence of battery cell and pack characteristics.

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How to Design a Zero-Degradation Battery: Compensating for Loss of Lithium Inventory in LFP Cells with LFO Additives

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Loss of lithium inventory (LLI) caused by side reactions in lithium-ion cells is one of the primary reasons behind their capacity fade and shorter cycle life. Research in academia and industry has explored additives such as Lithium Iron oxide (Li_5FeO_4) in LFP-based battery chemistries that sacrifice their lithium inventory to compensate for LLI. Over the last ~15 years [1-4], research has proven that LFO can compensate for LLI and help maintain stable cell performance, and more recently, CATL & Rimac [5-6] announced its commercial-level usage, claiming to have achieved zero degradation for extended periods. However, the specifics behind achieving such excellent performance are neither fully disclosed by them nor much explored in the literature.

This work offers deeper insights into how exactly LFO can be employed in commercial LFP cells with LFP/LFO positive electrode (PE) and Graphite negative electrode (NE) using simulations run by building a full-cell physics-based model in PyBaMM. The work digs deeper into the science behind releasing lithium inventory from LFO and its impact on cell degradation (SEI, lithium plating), discharge capacity, and cell life. The work also attempts to find the optimal method to control lithium release from LFO and the optimum weight fraction of LFO to minimize cell degradation and achieve long-lasting, zero-degradation batteries. Work concludes that (a) the release of lithium inventory from additives can be controlled to maximize the benefits of their usage instead of releasing all their lithium inventory at once, (b) controlled slow lithium release maintains the cell balancing and reduces the degradation rates, while rapid lithium release can accelerate cell degradation (c) using optimum weight fraction of LFO is crucial for minimizing cell degradation as excess LFO even though appears beneficial because of its capability to provide more lithium inventory and higher usable cell capacity but is counterproductive as it promotes faster cell degradation resulting in shorter cycle life of the cell. Hence, this study advances and broadens the existing theoretical understanding of employing sacrificing agents, such as LFO, in commercial lithium-ion cells. Additionally, we conclude that merely adding lithium-rich additives does not promise high-performance batteries; instead, it depends on using them in optimal amounts and ensuring the controlled release of lithium inventory through appropriate control methods.

Supporting Figures:

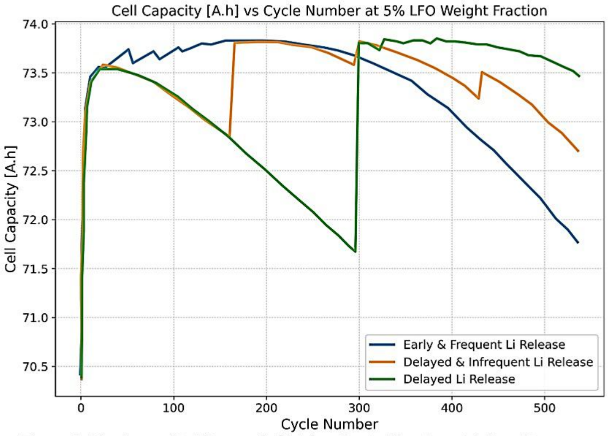

Figure 1: Discharge Cell Capacity [A.h] vs Cycle Number obtained from Aging cycles at different cycle numbers for three cases of lithium release from LFO

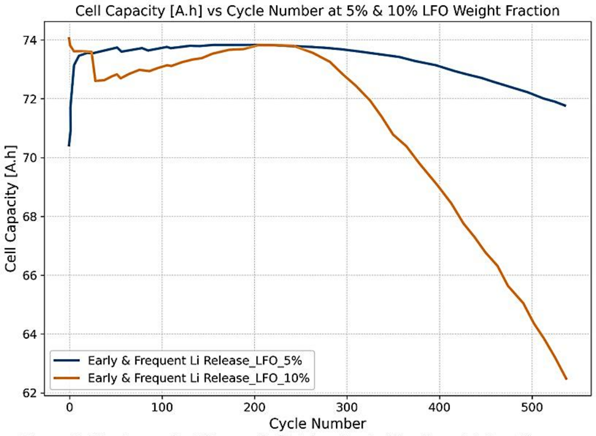

Figure 2: Discharge Cell Capacity [A.h] vs Cycle Number obtained from Aging cycles at different cycle numbers for different weight fractions of LFO in LFP/LFO composite PE

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Beyond Data Correlation: Understanding and Predicting Battery Aging with Fast, Physical and Accurate Models.

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Disentangling the aging behaviour of lithium-ion batteries is difficult, as various degradation processes are taking place simultaneously in the cell that each have individual timescales and physico-chemical triggers. Currently, most aging prediction methods are data-driven, and focus on correlating the battery SOH with measurement results by inter- and extrapolation.

In this contribution, we discuss an approach that is different from a correlation study on aging data: We introduce a methodology that combines aging measurements, intermediate characterizations, and physical aging models. The underlying idea is to use optimized routines to identify aging physically along the different trajectories of aging tests and to integrate the parameters to simulate the full behavior of aged cells under all scenarios. This methodology not only enhances the ability to evaluate and understand the underlying processes, but also serves as foundation for robust aging prediction models.

Through a case study that involves the state-of-the-art technology benchmark of high-power cells – the Molicel INR21700-P50B – we exemplify how a systematic development workflow can be established in practice, how maximum information about a cell's aging behavior can be extracted with a minimum amount of testing, and how different mechanisms can be disentangled. In this way, the audience will learn how to synergistically combine testing and physics-based modelling to enhance battery longevity, performance, design and reliability.

PyBaMM-Aided Analysis of Reservoirs in Lithium-Ion Cells: Strategies for Cell Design and Cycling Protocols

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Enhancing driving range and charging capabilities remains a critical focus in battery research. There is a growing need for guidelines to optimize cell design for specific performance targets, as well as strategies to refine cycling protocols that improve the performance and lifespan of existing cells [1]. These strategies, along with other performance metrics, are largely governed by the cell's design and composition—specifically, the lithium inventory, electrolyte volume, and active material content. These elements can be conceptualized as reservoirs within the cell, with their size and depletion rates dictating overall performance and longevity. Depletion of any reservoir leads to eventual cell failure. While the initial performance of a cell based on these parameters is well understood [2], the evolution of the reservoirs over the cell's lifetime and their role in degradation remain underexplored.

To address this, we use PyBaMM with a DFN model with five coupled degradation mechanisms—SEI growth, lithium plating, electrolyte consumption, mechanical loss of active material, and particle cracking—to compute the lifetime trajectories of the reservoirs under various conditions [3]. For example, we demonstrate that operating an LG M50 battery cell at a slightly elevated temperature under standard charging protocols can extend its lifespan by a factor of 4.4. Similarly, increasing the electrolyte volume by 10% doubles the cell's lifespan. Furthermore, we analyze the interactions between the lithium and active material reservoirs, identifying critical degradation thresholds that guide further optimization.

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An Aging-Sensitive and Physically-Informed Equivalent Circuit Model for Predicting the Lifespan of Lithium-Ion Batteries

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The growing use of lithium-ion battery (LIB) systems in applications like electric vehicles and stationary energy storage highlights the need to predict LIB lifespan under varying usage conditions. Aging is path-dependent [1], such that different aging mechanisms (path or causes) are strongly and nonlinearly coupled leading to nonlinear aging dynamics ("knee" formation) [1], which is challenging to predict. Although physiochemical models can effectively describe aging dynamics, their drawbacks include extended computation times and the complexity of parameter derivation.

An aging-sensitive, physically-informed equivalent circuit model (ECM) was newly developed by integrating aging modes (loss of active material LAM, loss of lithium inventory LLI) and describing their rates using physicochemical aging kinetics. A schematic representation is shown in Figure 2a. The model consists of two voltage sources ($V_{\mathrm{PE}}^{0}(X_{\mathrm{PE}})$ and $V_{\mathrm{NE}}^{0}(X_{\mathrm{NE}})$) with subsequent current leaks from LLI and LAM, two R-RC elements ($R_{\mathrm{PE}}^{\mathrm{dyn.}}$, $R_{\mathrm{PE}}^{\mathrm{stat.}}$ $C_{\mathrm{PE}}^{\mathrm{dyn}}$ and $R_{\mathrm{NE}}^{\mathrm{dyn.}}$, $R_{\mathrm{NE}}^{\mathrm{stat.}}$, $C_{\mathrm{NE}}^{\mathrm{dyn}}$) representing resistance and dynamics of the two electrodes, respectively; and another series resistors (R_{s}) representing resistance offered by the electrolyte and current collection system. The concept of balance equations for charges of the two half-cells ($Q_{\mathrm{NE}}, Q_{\mathrm{PE}}$) allows for the incorporation of aging modes into the model. This model is computationally comparatively simple and allows for the simulation of dynamic, complex, realistic load profiles with long simulation times.

The model was parameterized to a 3350 mAh cylindrical cell with graphite anode and NCA cathode operated with dynamic stress test (DST) driving protocol, which was studied in detail previously [2]. The rate expressions for each aging mode were parametrized manually such that the simulated aging modes match with previously published experimental data [2] as shown in Figure 2b. The ECM successfully predicts the knee in the capacity loss curve (Figure 2c), where the knee formation could be primarily attributed to the onset of lithium plating (Figure 2d). This occurs when increased resistance at the negative electrode causes its potential to drop below the plating potential.

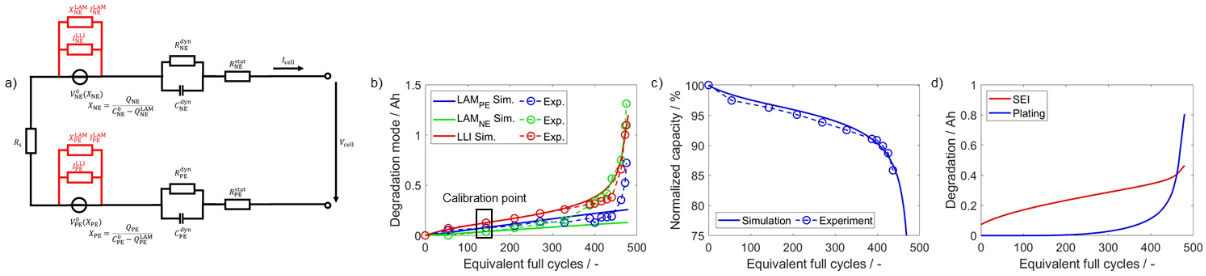

Figure 2: a) Systematic representation of the model and incorporation of aging modes. b) Degradation modes, c) Normalized capacity and d) Cumulated capacity of the formed SEI and plated lithium as a function of the equivalent full cycles.

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A spatially resolved electrode model for the simulation of lithium deposition and stripping in graphitic anodes

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Metallic lithium deposition (LD) is one of the most significant aging mechanisms in lithium-ion batteries (LIBs) especially under fast-charging conditions, which can lead to safety risks in addition to capacity and power fade. Therefore, research and development of operational strategies and charging schemes is essential to prevent LD over the lifetime of a LIB. This work focuses on modelling approaches of LD in lithium-ion batteries. Specifically, an existing transmission line model (TLM) of a graphite anode with spatial resolution at both the electrode and the particle level [1], is extended to include the process of LD. It has been shown that the model is capable of predicting the potential at the particle surface of the active material, which is used for model-predictive control of the charging current [2].The objective of the extended model is, firstly, to predict the amount of lithium metal deposited at varying C-rates and, secondly, to reproduce the experimentally observed phenomena during LD and subsequent stripping. In the extended TLM, LD is modelled as a process occurring in parallel to the intercalation of lithium ions in each discrete electrode segment. This allows the current to be split between the two processes of intercalation and LD. As a result, the amount of lithium deposited in each electrode segment during charging can be calculated. An activation function is implemented to take into account the physical requirements for the onset of LD. Consequently, LD is initiated when the potential at the particle surface in the intercalation process falls below the predefined activation overpotential of LD.

Several simulation studies are carried out using the extended TLM to investigate the influence of the charging C-rate on the electrochemical behaviour. As expected, the amount of LD increases with the C-rate (Fig. 1). Evaluation of the distribution of LD across the thickness of the electrode shows greater penetration depths of LD with increasing current. In addition, the TLM is able to reproduce characteristic features of LD, such as a flattening of the voltage curve and a drop in impedance that can be associated with the onset of LD [3,4], as well as the stripping plateau in the voltage curve that typically occurs during relaxation or discharge after LD [4]. During discharge, it is observed that only a small fraction of the stripping current contributes to the total discharge current, while the larger fraction is used to equalise the inhomogeneous states of charge within the electrode. Consequently, the amount of reversibly deposited lithium cannot be correctly determined by the commonly employed differential voltage analysis using the clamp voltage. The final goal of this work is to use the TLM operando based on experimentally validated parameters in a real-time environment for battery management and model-based fast-charging control.

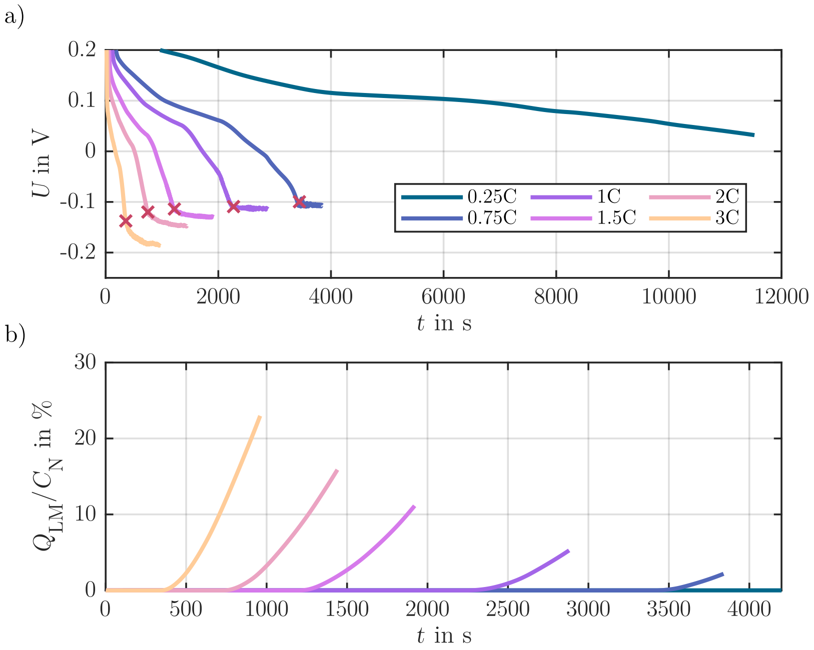

Figure 1: Simulation of a charging process from 0 % to 80 % state of charge at different C-rates. Clamp voltage of the graphite electrode with red marker indicate the onset of LD in a), amount of reversibly deposited lithium Q_{LM}, normalized to the nominal electrode capacity C_{N}, in b).

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Modelling the Impact of Secondary Particle Cracks and Pores on Transport and Kinetics in NCM Cathodes

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Cycle aging of Li-ion batteries can result in a variety of degradation processes. High-nickel cathodes show changes to the surface chemistry, crystalline morphology and particle structure [1]. This results in additional challenges for parametrization using common evaluation methods. Here, multiple degradation effects are lumped into apparent electrochemical and physical properties [2]. As a result, identifying limiting processes and debottlenecking becomes more challenging.

An approach to overcome this limitation is the use of information on particle structure from postmortem imaging methods, such as cross section SEM, Figure 1 (A), in addition to electrochemical characterisation. This contribution provides a method for quantifying the impact of structural changes, extending upon the widely used Newman-P2D-Model [3] by including cracks and pores in the secondary particles. Both the radial charge and mass transport in solid NCM and electrolyte filled cracks are modelled, as well as the interfacial reaction within the particle. This is done by simplifying the complex 3D-structure of cracked secondary particles into an array of representative solid fragments, surrounded by an electrolyte film. The fragments are resolved in radial direction and orthogonal to the radial direction. This provides the capability to simulate evenly cracked or porous particles, as well as the transport limiting impact of large fragments in contrast to small ones. Furthermore, insight into the main reaction side and concentration profiles are gained, Figure 1(B). Furthermore, the beneficial effects of internal porosity on the apparent diffusivity and kinetics are elucidated.

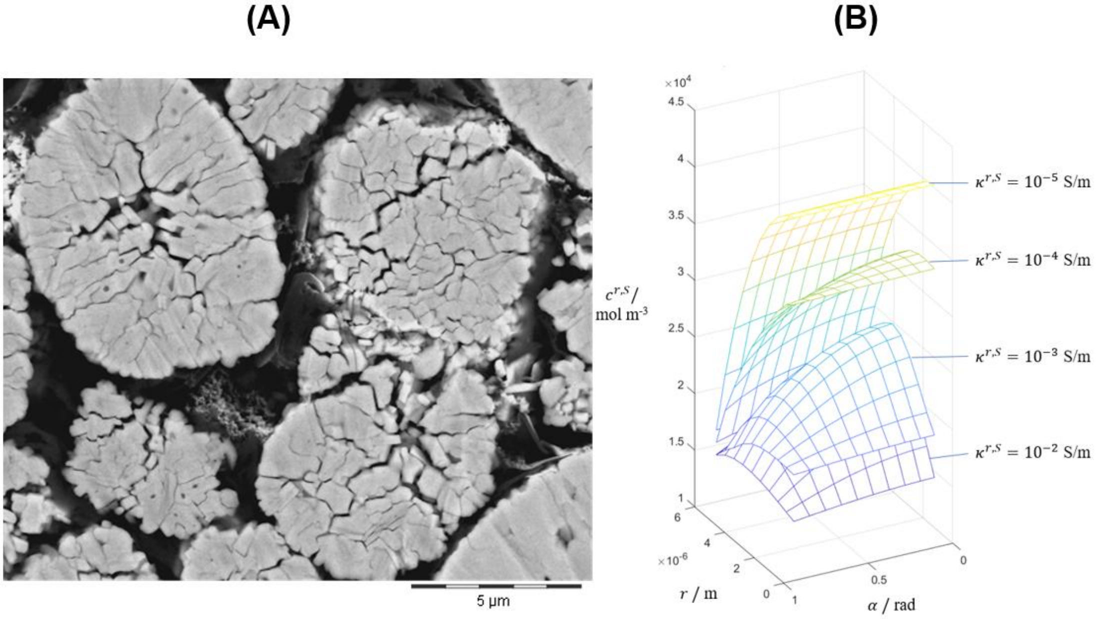

Figure 1: (A) Cross section SEM Image of end-of-life high-nickel NCM. (B) Lithium-ion concentration profiles in the solid fragments after 1C-charge over the particle radius r and the fragment coordinate α for varying electronic conductivities of the solid $\kappa^{r,S}$

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High through-put simulations for battery microstructure characterization and design

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Physical modelling holds promise to guide material and microstructure design but is faced with the challenge that batteries in general and particularly hierarchical electrode structures are a multi-scale problem as sketched in Figure 1. While the rate performance of battery cells is strongly influenced by microstructure, homogenised cell models such as the DFN model are parametrised with effective quantities such as an apparent diffusivity of lithium inside polycrystalline particles and apparent transport of lithium ions in the electrode pore network.

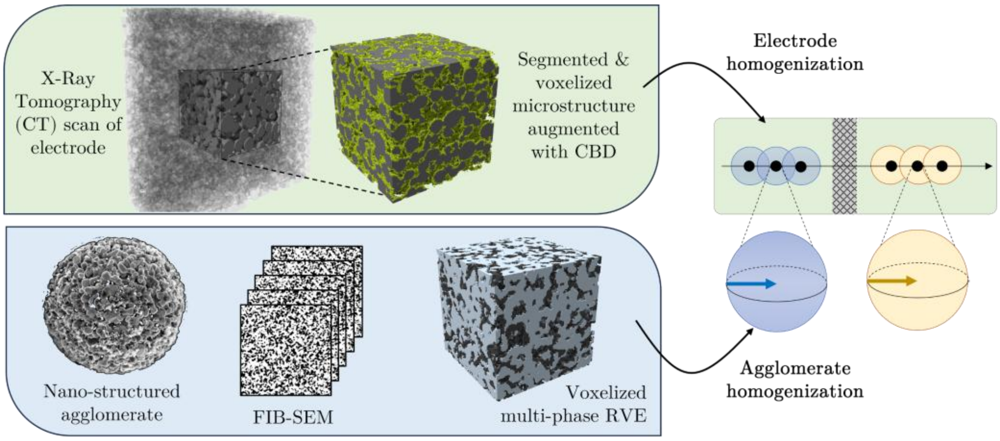

Figure 1: Integration of microstructure information from the electrode scale (∼100 µm) and the active material (∼ 1−10 µm) into homogenized battery cell models

The reliable computation of microstructure metrics is key to bridge the gap between the battery microscale and fast, homogenized cell models. We discuss approaches to compute specific surface areas, connectivity and tortuosity factors of multi-phase electrodes from voxel-based image data [1,2,3]. Utilizing GPU acceleration, we demonstrate that even large microstructure datasets can be analysed in the order of seconds. The code is developed in python and integrated into the openly available repository TauFactor to further accelerate the scientific progress in this field. The speed of the simulations allows them to be integrated into a closed-loop optimisation workflow as described by Kench et al. [4].

Furthermore, we present methodologies to homogenize complex agglomerate microstructures such as polycrystalline NMC particles containing hundreds of grains, strong diffusion anisotropy and potentially nanoporosity [4]. These tools will be vital for designing next generation batteries such as the hybrid electrolyte and solid-state electrodes envisioned by the SEATBELT project (https://seatbelt-project.eu/).

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Data-driven stochastic 3D modeling of the nanoporous binder-conductive additive phase in battery cathodes

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A stochastic 3D modeling approach for the nanoporous binder-conductive additive phase in hierarchically structured cathodes of lithium-ion batteries is presented [1]. The binder-conductive additive phase of these electrodes consists of carbon black, polyvinylidene difluoride binder and graphite particles. For its stochastic 3D modeling, a three-step procedure based on methods from stochastic geometry is used. First, the graphite particles are described by a Boolean model with ellipsoidal grains. Second, the mixture of carbon black and binder is modeled by an excursion set of a Gaussian random field in the complement of the graphite particles. Third, large pore regions within the mixture of carbon black and binder are described by a Boolean model with spherical grains. The model parameters are calibrated to 3D image data of cathodes in lithium-ion batteries acquired by focused ion beam scanning electron microscopy. A visual comparison of 3D image data and a realization of the fitted stochastic 3D model is provided in Figure 1. Subsequently, quantitative model validation is performed by comparing model realizations with measured image data in terms of various morphological descriptors that are not used for model fitting. Finally, we use the stochastic 3D model for predictive simulations, where we generate virtual, yet realistic, image data of nanoporous binder-conductive additives with varying amounts of graphite particles. Based on these virtual nanostructures, we can investigate structure-property relationships. In particular, we quantitatively study the influence of graphite particles on effective transport properties in the nanoporous binder-conductive additive phase, which have a crucial impact on electrochemical processes in the cathode and thus on the performance of battery cells.

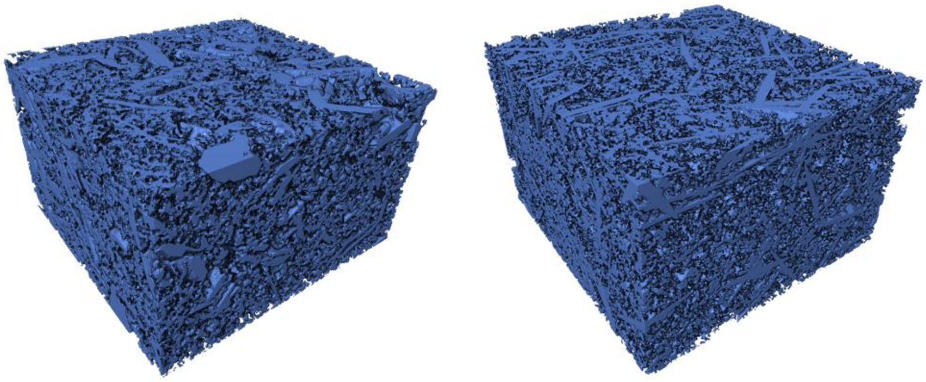

Figure 1: 3D rendering of tomographic image data (left) and
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Pitfalls of Diffusion Coefficient Determination for P2D Battery Model Parameterization

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The pseudo-two-dimensional (P2D) battery model is a cornerstone of battery diagnostics, control, and optimization. However, its utility greatly depends on having a valid parameter set, but parameterizing the model is challenging due to over 30 parameters [1]. Possible parameterization strategies include direct measurement and parameter estimation, while the latter usually requires some form of model reduction due to not uniquely identifiable parameters [2]. In contrast, direct measurement strategies retain the full range of physical parameters, which are crucial for design optimization and aging models, but require extensive experimental effort and are sensitive to parameter interdependence. The diffusion coefficient is particularly critical as it is highly sensitive to battery performance and varies greatly with Li concentration. The galvanostatic intermitted titration technique (GITT) is commonly used to measure it, but assumptions do not hold for phase change materials such as graphite [3], potentially leading to invalid parameter sets.

Here, we present a comprehensive study on the assessment of the diffusion coefficient in heuristic parameterization workflows. We investigate various strategies for determining the diffusion coefficient, focusing on the graphite electrode, which features distinct phase-change regions. Specifically, we investigate (I) the evaluation of all GITT data points regardless of validity, e.g.as shown in Figure 1a, (II) the estimation of constant diffusion coefficients using C-rate tests as shown in Figure 1b, and (III) the evaluation of GITT data points but filtering out invalid points. The latter is enabled by introducing a novel method that estimates the relative error of the GITT measurement. Results are presented for electrodes harvested from large format pouch cells. The results underline the importance of the assessment for consistent and valid parameter-sets. We demonstrate that by filtering invalid GITT measurements, significant improvements can be achieved. This is shown by evaluating the plausibility of dependent parameters, i.e. tortuosity and effective electrical conductivity, being identified in subsequent steps of the presented workflow. Further, we investigate the validity of different strategies for dynamic driving cycles at different temperatures.

To sum up, in the presented work, we elaborate different ways to determine diffusion coefficients and show its importance for the accuracy and validity of the P2D model. Specifically, validity of GITT measurements are crucial but for phase change materials often not given. Future work can build-up on this to further improve automated workflows for reliable P2D model parameterization.

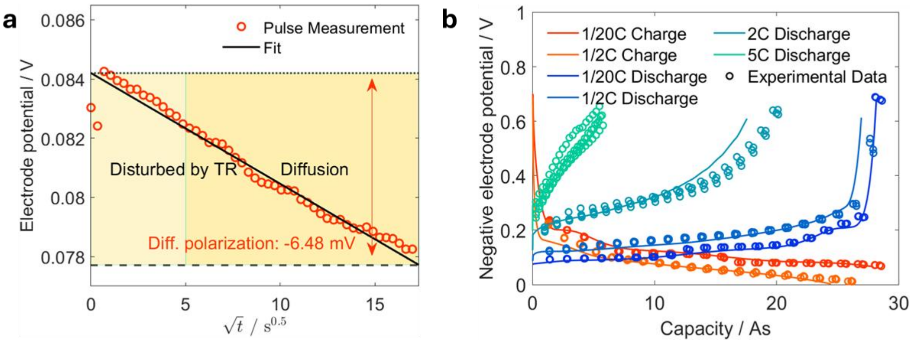

Figure 1: Example for GITT-based diffusion coefficient assessment (a) C-rate fit of P2D model with constant diffusion coefficients (b)

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Parameterizing physics-based degradation models in Li-ion batteries with Bayesian methods

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Modeling physical processes inside a battery is an inevitable step in understanding and improving the lifetime of lithium-ion batteries (LIBs). To assess the validity of a model, it has to be correctly parameterized by comparing it to experimental data. However, modeling the observed degradation is a persistent challenge due to the complex coupling of many different processes [1], leaving the dominant degradation mechanism yet unclear.

To fully understand the measured degradation in LIBs, one has to model several degradation mechanisms and their coupling all-encompassing. As the information about the degradation occurring in the battery is mainly encoded in the measured capacity loss only, disentangling the various mechanisms at once is insurmountable. To still obtain a valid degradation modeling, one must first analyze isolated effects. In a first study, we investigate the responsible growth mechanism of the Solid-Electrolyte Interphase (SEI), as this effect can be isolated for the most part by looking at storage experiments. The ongoing growth of the SEI is considered the primary degradation mechanism during battery storage, but it also makes a significant contribution during battery operation [2]. We inversely model degradation data with an automated parameterization routine based on Bayesian methods [3] to distinguish the proposed theoretical growth mechanisms, i.e., solvent diffusion, electron diffusion, and electron conduction. With a valid SEI growth model, we can analyze the impact and behavior of additional degradation mechanisms in a follow-up study.

We show that sample-efficient Bayesian methods [3,4] are outstanding tools to parametrize physics-based models within reasonable sample numbers, as they successfully tackle obstacles like consistent model selection, reliable uncertainties, and correlations in the parametrization [5]. Suitable feature selection can further improve the algorithmic performance and ensure the correct identification of the physical features. As a result, we identify electron diffusion [6] as the dominant growth mechanism of the SEI during battery storage. Then, we can investigate more complex degradation data and model further degradation mechanisms, such as loss of active material and particle or SEI cracking. In conclusion, our inverse model routine helps to identify and parametrize degradation mechanisms of LIBs and is generalizable to include more mechanisms. This automatable method applies to analyzing battery data, model development, and validation and can, therefore, accelerate battery research.

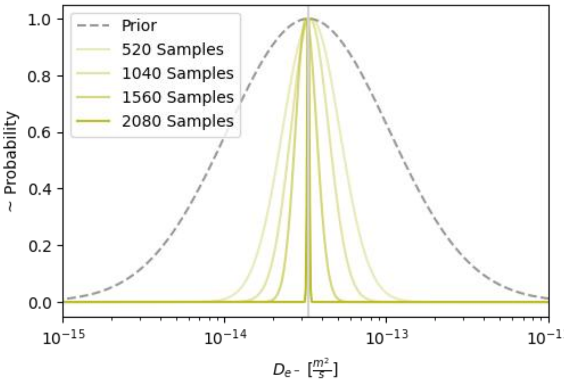

Fig. 1: Convergence of a prior belief about the parameter distribution with increasing knowledge [5]

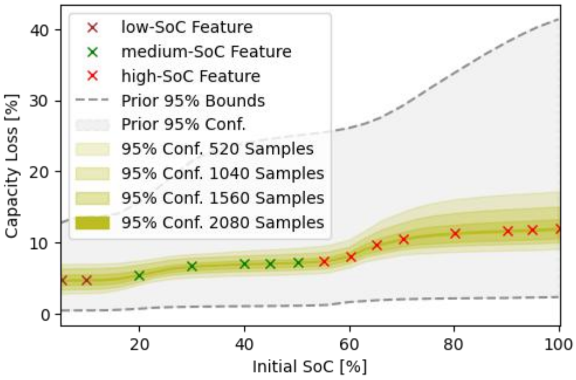

Fig. 2: Consecutive convergence of parameterization and uncertainty for storage data [5]

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Data-Driven Analysis of Relaxation Time Distributions in Electrochemical Systems Using the Loewner Framework

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Electrochemical Impedance Spectroscopy (EIS) has become a fundamental tool for investigating electrochemical systems, however, interpreting EIS spectra is challenging due to overlapping responses from processes with similar time constants. The Distribution of Relaxation Times (DRT) method addresses this by decomposing complex spectra into distinct components, facilitating interpretation. Despite its advantages, DRT computation involves ill-posed inverse problems, even with advanced techniques such as Fourier transforms, Tikhonov regularization, and multi-(RQ) Complex Nonlinear Least Squares (CNLS) fitting, especially when dealing with non-capacitive impedance spectra such as inductive loops and Warburg patterns. This highlights the need for more versatile methods.

In our recent study [1], we introduced a novel data-driven approach for directly computing DRT from EIS data using the Loewner framework (LF). This method is regularization-free, removing the need for parameter tuning, and follows a fixed sequence of steps, ensuring universal applicability to any impedance dataset. The robustness and versatility of this approach have been validated through comprehensive analyses of a range of spectra, including Warburg, Gerischer, and inductive loops, as well as experimental data from ferrocyanide redox kinetics. One of the primary advantages of this method is its ability to uncover the underlying system dynamics, providing deeper insights into physical processes beyond conventional measurement fitting [2]. Our results demonstrate that the LF-based approach significantly enhances EIS data analysis, offering a powerful tool for more accurate characterization and reliable modeling of electrochemical systems.

Keywords: Data-driven analysis, Electrochemical impedance spectroscopy (EIS), Distribution of relaxation times (DRT), Loewner framework (LF).

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Simultaneous Measurement of EIS and MRI of Lithium-Ion Batteries

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Simultaneously measured EIS spectra and MR images of MRI-compatible lithium-ion batteries provide comprehensive information on the electrochemical processes in the battery. MRI offers spatially resolved information on the electrolyte [1] or the lithium [2-4] distribution. EIS spectra can be correlated to physical changes in the batteries.

MRI-compatible lithium-ion batteries were built by WYON using a polymer casing and additional separators. The cells were inserted into the MRI in a battery holder that allows for reproducible orientation and an electrical contact of the battery with a potentiostat or a battery cycler via built-in filters of the MicWB40 probe. Interferences between EIS and MRI have to be considered, due to the large magnetic fields (4.7 T) and radio frequencies (77.75 and 200 MHz) required for MRI. [5] Measurements with an optimized setup show small differences between EIS spectra acquired inside and outside of the MRI probe for $f < 20$ Hz, showing the feasibility of the simultaneous measurement of EIS and MRI.

The electrolyte distribution in a fresh battery (Fig. 1d) is uniform and only shows some gas inclusions indicated by areas of smaller signal I inside the electrolyte volume. The real as well as the negative imaginary part of the impedance Z were at maximum at 4.5 and 1.1 kΩ (Fig. 1b) at that time.

After storage of the battery for 18 months, the battery shows degradation: the signal I in the ^{1}H-MR image (Fig. 1e) shows a significantly lower level (10-15 a.u.) compared to the earlier image (Fig. 1d, 30-40 a.u.), indicating a loss of electrolyte. In accordance, the EIS spectra (Fig. 1c) show significantly larger Z at all frequencies.

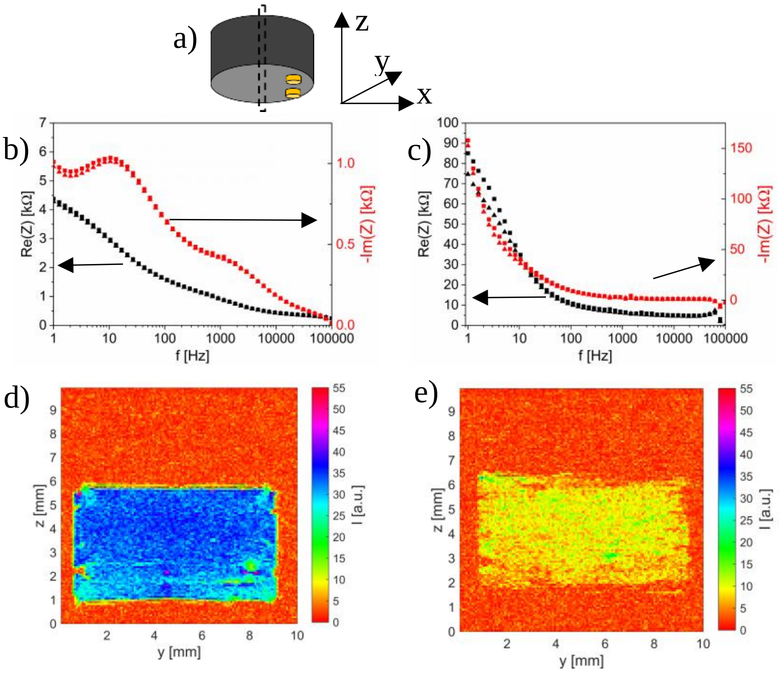

Figure 1: Schematic representation of the cell (a), the dashed line shows the plane of the MR images. EIS spectra before (b) and after (c) storage. The square symbols in b) and c) show the spectra acquired inside of an MRI probe in the magnet, the triangles outside. ^{1}H-MR image of a battery before (d) and after (e) storage. The MR intensity I decreases indicating a loss of electrolyte.

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Abstracts for Poster Contributions

Energy Conversion

Numerical Modeling of Two-Phase Flows in Electrolyzer Channels: Towards Optimized Thermal and Flow Management

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Electrolyzers play a pivotal role in the transition to sustainable energy systems, enabling the conversion of electricity into hydrogen while generating surplus heat. Their operation involves complex interactions of multiphysics phenomena across multiple length and time scales. Challenges in electrolyzer design include optimizing mass and heat transfer, minimizing electrical resistance, and improving system durability. These challenges are compounded by the need to track the interfaces between phases in multiphase flows, which are critical for performance and efficiency.

This research focuses on developing numerical models to investigate multiphase flow dynamics in electrolyzer channels at the cell scale, without incorporating electrochemical reactions. The study will employ OpenFOAM, an open-source computational fluid dynamics tool, to explore and compare various modeling approaches for simulating two-phase flows. Techniques such as the Volume of Fluid method, Level Set method, and Eulerian-Eulerian models will be assessed to determine their suitability for capturing the complex dynamics of bubble formation, coalescence, and detachment. The insights gained will inform the selection of an optimal modeling framework tailored to the unique conditions in electrolyzer channels. The study will draw on insights from prior research on multiphase flows in fuel cells [1] [2], adapting methodologies and geometries to suit electrolyzer-specific conditions. The goal is to provide predictive models that inform the design and optimization of electrolyzer components, with a particular focus on thermal management and flow distribution.

Future work will extend the scope to system-scale modeling, addressing thermal management challenges in alkaline electrolyzers for industrial applications. This research will contribute to advancing the understanding and design of efficient electrolyzer systems, bridging the gap between fundamental studies and industrial needs.

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Modelling Water Transport in Bipolar Membranes for CO_2 Electrolysis Application

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Bipolar membranes (BPMs) offer significant potential for electrochemical technologies, especially in CO2 electrolysis. Their unique ability to create pH gradients provides optimum chemical microenvironments at the cathode and anode for efficient, cheap, and sustainable CO2 electrolysis. However, state-of-the-art BPMs are limited in their performance due to membrane degradation and membrane dehydration leading to low ionic conductivity. Hence, their usefulness for various electrochemical technologies has yet to be proven. Previous studies [1] have identified water transport as one of the main factors limiting the performance of BPM. A multi-physics model of BPM can serve as a useful tool to gain a comprehensive understanding of different performance limiting factors and thereafter propose solutions to overcome these limitations. The goal of the present study is to provide model based design guidelines for a BPM that facilitates efficient water transport, making it a suitable candidate for integration into a zero-gap CO2 reduction electrolyzer operating at industrial-grade performance levels.

We have built a 1-D continuum model of a BPM kept in an aqueous (bi)carbonate electrolyte solution [2,3]. The geometry of the bi-polar membrane also includes catalyst layer sandwiched between cation exchange membrane and anion exchange membrane. We incorporate physical phenomena such as water-dependent transport of ions and neutral species, field-enhanced homogeneous reactions (water-dissociation and acid-base reactions) along with CO2 phase transfer reaction at the BPM-aqueous electrolyte interfaces. We also incorporate water dissociation reaction enabled by the catalyst material and the neutralization reactions of the mobile species with the fixed membrane background charge.

Our model investigates the reverse bias operational modes of the BPM. In alignment with the experimental observation, the model identifies a distinct initial phase where current density is limited, with the majority of the current carried by salt ions at low overpotentials. As the potential increases, there's a rapid increase in current density, indicating a breakdown regime caused by an electric field-enhanced water dissociation reaction at the BPM interface. At even higher current densities (industrially relevant), the polarization curve enters a third phase where the current density plateaus characterized by water transport limitation. This aspect of the BPM polarization curve is uniquely captured by our model. To address the issue of water transport limitation, we conduct various parametric studies focusing on different membrane characteristics, such as individual layer thicknesses and their ion exchange capacities. We also investigate the effect of catalyst layer loading and water dissociation kinetics of catalyst material. The outcomes of these analyses provide crucial guidelines for optimizing these parameters and enhancing water management in BPM-based systems.

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Modeling of Anion Exchange Membrane Electrolysis: Impact of KOH Concentration on Electrochemical Performance

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Anion exchange membrane water electrolyzers (AEMWEs) are gaining attention as a promising technology for green hydrogen production. Operating in an alkaline environment, AEMWEs enable the use of cost-effective, non-noble catalysts and non-fluorinated anion exchange polymer membranes, distinguishing them from proton exchange membrane (PEM) systems. However, their performance and stability are highly influenced by the concentration of the alkaline electrolyte [1].

This study employs a three-dimensional multi-physics model incorporating two-phase flow to analyze the effects of KOH electrolyte concentration and flow rate on AEMWE performance. The model explores current and gas volume fraction distributions considering the ion transport in both the ionomer and KOH electrolyte (Figure 1). Results reveal significant non-uniformities in H_2 and O_2 gas volume fractions at current densities exceeding 1 A/cm² [2]. Local variations in cell performance are observed, particularly at high current densities and low electrolyte flow rates, leading to reduced catalyst utilization. These results will be discussed according a parametric study.

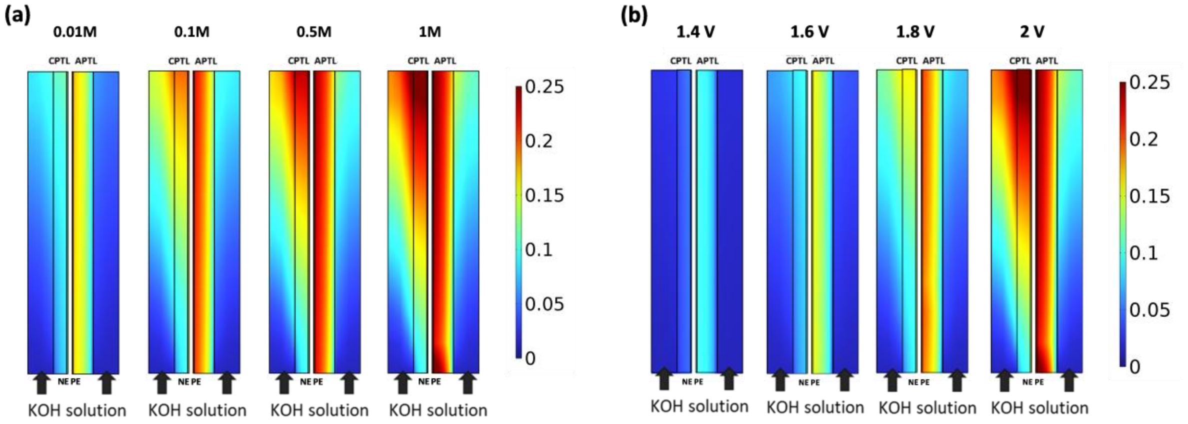

Figure 1: Gaseous volume fraction for: (a) various KOH concentrations (i.e., 0.01, 0.1, 0.5, and 1 M) at 2 V and (b) different cell voltages (i.e., 1.4, 1.6, 1.8, and 2 V) at 1 M along the cell length in the middle of the cell. NE: negative electrode, PE: positive electrode.

Acknowledgements: This work has been performed in collaboration between LEPMI and Michelin in the framework of the CNRS-Michelin joint laboratory, Alcal'HyLab.

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Multidimensional Mathematical Modelling Study of Mass and Charge Transfer Limitations in Alkaline Water Electrolysis: Effect of Separator

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The "hydrogen economy" (HE) represents strategy for transition of our economy based on fossil fuels towards the renewable energy sources. Within the framework of this scheme the water electrolysis plays crucial role as a main method of "clean" hydrogen production. Conventional industrial alkaline water electrolysis (AWE) operates at elevated temperatures (70–100 °C) with highly concentrated caustic solution (KOH, 25–30 wt.%), which significantly limits the operating flexibility and intensity of this process. These drawbacks discriminate conventional AWE employment within the HE. There are several promising innovations of the AWE process developed, e.g. application of an anion-selective membrane (AM) as the separator alternative to the composite diaphragm used in the conventional AWE. The AM allows more compact electrochemical cell design and improves, contrary to diaphragm, the anionic flux at lowered KOH concentration and operating temperature. This results in lower cell ohmic resistance. The application of such AM in the AWE (so called membrane alkaline water electrolysis - MAWE) thus enables reduction of KOH concentration (down to 5–15 wt.%) and operating temperature. The MAWE can thus be operated more flexibly and with improved efficiency as compared to conventional AWE. However, systematic research aimed at evaluation of real application potential and searching for optimal conditions of the AM at diluted KOH concentrations is so far missing.

In the presented work, we have employed mathematical modelling to study behaviour of laboratory scale AWE cell with two types of the separators: AM (MAWE) and diaphragm (DAWE). In parallel an experimental results performed on a short laboratory-scale MAWE and DAWE stack (3-cells) in bipolar zero-gap configuration performed for the model validation purposes [1] will be presented. The separators used are: a) a homogeneous AM (PSEBS-CM-DABCO [1]) and b) a commercial composite diaphragm Zirfon™ Perl. The load curves were recorded to assess optimal performance of the stack with both separators at KOH concentration range of 1–15 wt.%, at operating temperature range of 25-40 °C and at different electrolyte flow rates through the Ni-foam electrodes. 1D, 2D and 3D stationary mathematical models (multidimensional modelling) of single MAWE and DAWE cell corresponding to the laboratory set-up were developed to clarify the differences in the stack load curves recorded for the two studied separators. The models are based on the field-continuum mechanics approach with macrohomogeneous theory used to describe mass and charge transport in the porous electrodes. The Nernst-Planck equation is used to describe migration, diffusion and convection of ions in the cell. The effect of model dimension (1D, 2D, 3D) on the model predictions accuracy is investigated. The effect of mass transport limitation in the porous electrodes and separators, and impact of the gas evolution were analysed. The multiphase (gas-liquid) flow was also described by using simplified macrohomogeneous approach. At all studied conditions, the MAWE outperforms the DAWE; at lower KOH concentrations due to transport limitation in the diaphragm at higher current loads. The presented work clearly identifies interval of operating conditions, in which AM represents an important advantage over porous separator and opposite. Thus, it gives important hint for further development of this technology.

Acknowledgement
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Effect of Catalyst to Binder Ratio on the Performance of Alkaline Membrane Water Electrolysis: A Mathematical Modeling Study

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The water electrolysis process represents technology suitable for hydrogen production from electricity produced by renewable sources. However, the conventional industrial alkaline water electrolysis suffers from the low process intensity and flexibility. These parameters can be improved by using anion-selective membrane as the electrodes compartments separator in alternative technology called alkaline membrane water electrolysis (AMWE). The presence the anion selective membrane and porous electrodes allows more compact zero-gap design reducing cell ohmic resistance. This, together with the fact that anion selective membrane is more effective in transport of OH^- ions between the electrodes, enables utilization of electrolyte with lower KOH concentration and lower operating temperatures. To improve further the kinetics of electrochemical reactions, a catalytic layers (CLs) may be added to the membrane-electrode assembly. As it was found in our previous experimental studies [1], not only the catalyst loading, but also the catalyst/binder mass-weight ratio (CBR) in CLs is a crucial parameter affecting the AMWE performance.

To provide better understanding of the effect of CBR on the AMWE performance and to identify directions for further system optimization, a 1-dimensional mathematical model was developed simulating single AMWE cell with CLs deposited on the membrane surface, i.e. catalyst coated membrane approach. It represents a continuation of the work initiated by Denk et.al [2] focused at AMWE without employment of the CLs. The presented model is based on field-continuum mechanics approach. It employs macrohomogeneous porous electrode theory with Tafel reaction kinetics to describe the charge transport in the porous electrodes and the CLs. The ion transport is described by Nernst-Planck equation in the KOH electrolyte, the polymer binder and the membrane. The proposed model is validated by experimental data from AMWE [1] with CLs of different CBR ranging from 50/50 to 93/7 and concentration of KOH liquid electrolyte from 1 wt.% to 15 wt.%.

The model results indicate significantly nonuniform distribution of both OER and HER in the CLs, especially at high content of polymer binder. Both, HER and OER occur with highest intensity close to the boundary with nickel foam porous electrode. It is caused by notably higher ionic conductivity of the polymer binder than the electron conductivity of catalyst powder. This means that the entire volume of CLs is not effectively utilized and that both the thickness of the CL and the difference between the electron and ionic conductivity of the CL layer (catalyst powder and polymer binder, respectively) dramatically affects the AMWE performance. Further, comparison of model results with and without CLs revealed positive impact of the CLs on the current density. This is attributed to the catalytically enhanced reaction kinetics and enhanced ion transport provided by the polymer binder in the CLs. This study thus underscores the CLs role, together with its structure and properties, in improving overall cell performance at high electrolysis intensity. Furthermore, it demonstrates the high potential of the mathematical modelling in the optimization of CLs with regards to the MAWE performance.

Acknowledgement
This work was supported by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Commenius, call Excellent Research and from the grant of Specific university research – grant No A2_FCHT_2024_073.

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Accurate Li-ion Cell Parameters Estimation from Impedance Measurements: Methods and Applications

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Electrochemical Impedance Spectroscopy (EIS) and Equivalent Circuit Models (ECMs) are widely used to characterize the impedance and estimate parameters of electrochemical systems such as batteries [1]. We use a generic ECM with parameters modelling different frequency regions (high-, mid- and low-frequency) of the Li-ion cell's impedance spectrum (see Fig. 1). We study two formulations of the parameters' identification problem, in polar and Cartesian coordinates, and for each, we derive a noise covariance matrix from the measurement model which is used to properly assign weights for the fitting technique. By leveraging the properties of the ECM EIS spectra, we suggest a method to initialize ECM parameters for the Complex Non-linear Least Squares (CNLS) technique.

The main outcome of this research is a novel algorithm for designing the EIS experiments by applying the theory on Cramér-Rao Lower Bound (CRLB) and Fisher Information Matrix (FIM) to the identification problem [2]. We show that contributions to the FIM elements strongly depend on the frequencies at which EIS is performed. Hence, the algorithm aims to adjust frequencies such that the most information about parameters is collected. It is based on an E-optimal experimental design that aims to maximize the information about the ECM parameters collected by EIS measurements and, at the same time, minimize the overall uncertainty. At each iteration, the algorithm adjusts one frequency point for which the lowest eigenvalue of the FIM has the highest sensitivity. Results of a numerical experiment show that the estimator is efficient, and frequency adjustment leads to more accurate ECM parameters' identification.

Furthermore, we study an application of the proposed algorithm for frequency adjustments to a reduced frequency set where number of points-per-decade is decreased at low frequencies to save the experimental time [3]. In a numerical experiment, we first analyze to which extent reducing the number of measurement points at low frequencies affects the uncertainty of the estimated parameters. Secondly, we show that applying the frequency adjustments, to a reduced set of frequencies, can lead to the same or even improved global uncertainty of ECM parameter estimates as with a higher number of measurements. This is numerically verified through a case study using the ECM parameters of a commercial battery cell.

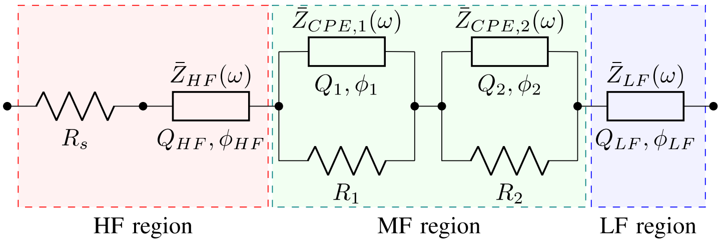

Figure 1: ECM modelling the Li-ion cell impedance (adapted from [3]).

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Investigating the Role of Ionomer Distribution on Catalyst Stability in PEM Fuel Cells with a Hierarchical Modeling Approach

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Proton exchange membrane fuel cells (PEMFCs) will be needed as energy conversion in devices in the transition to a sustainable global energy economy. The development of PEMFCs for mobile applications has seen tremendous progress over recent decades and the technology is nearing commercialization. However, their economic viability remains a challenge due to limited operational life, especially in heavy-duty vehicles (HDV) where a lifetime of 30,000 hours is required. The degradation of catalyst particles remains a major cause of irreversible performance losses of PEMFCs, which is driven primarily by processes that encompass catalyst dissolution (and redeposition), coagulation and detachment. These processes lead to a continuous decay of the electrochemical surface area (ECSA). Based on previous modeling work that helped rationalize the ECSA change [1-3], the present contribution reports on the development of a hierarchical model to link microstructural changes of the cathode catalyst layer (CCL) to the evolution of materials properties and performance over the lifetime of the cell. A specific focus will be laid on the impact of the local reaction environment at the catalyst surface, including ionomer and pH effects, on degradation. The influence of ionomer on the degradation of the CCL is examined by categorizing Pt particles into populations with and without close contact to an ionomer film. This distinction depends on the microstructure and the location of the particles within micropores or on agglomerate surfaces. We analyze the impact of ionomer contact and proton density on Pt particle degradation and demonstrate the capabilities of the hierarchical model to deconvolute and quantify the influence of the ionomer distribution on performance degradation. This analysis provides valuable insights for materials development and cell fabrication strategies, guiding efforts in ionomer synthesis and formulations of ionomer dispersions that aim at extending the lifetime of PEMFCs.

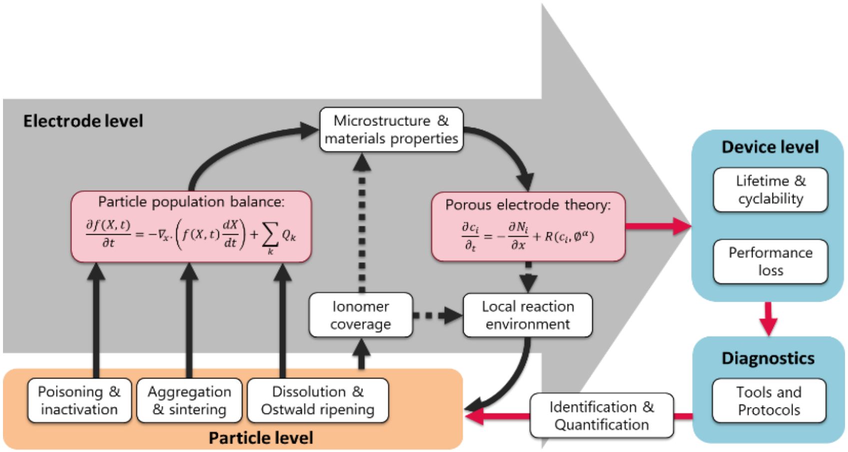

Figure 3: Hierarchical modelling framework. The inner loop (black) shows coupling of degradation on particle level with degradation on electrode level, whereas the outer loop (red) shows the coupling with performance.

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Efficiency limits for photoelectrochemical glycerol oxidation combined with hydrogen evolution

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Photoelectrochemical (PEC) conversion of solar energy to hydrogen is promising but traditionally hampered by the high energy demand of water splitting [1]. Pairing hydrogen evolution with glycerol oxidation, which requires significantly less energy, overcomes this barrier and adds value by converting an otherwise waste byproduct into useful chemicals [1]. In this study, we estimate limiting efficiencies of a PEC reactor featuring transparent, porous, conductive substrates for simultaneous glycerol oxidation (at the oxidising particle) and hydrogen generation (at the hydrogen evolving particle) reactions. A zero-dimensional (0D) model was developed using detailed balance calculations for the photoabsorbers to predict solar-to-hydrogen (STH) efficiency limits and quantify realistic numbers for conceptual designs. We considered both, series and parallel illumination of a tandem photoabsorber. For the realistic cases, the model accounted for scattering-induced optical losses and enhanced reaction kinetics from porous substrates. A wide range of operating conditions – solar concentration, bandgaps of the two photocatalysts, Tafel slope and exchange current densities of catalysts, solution resistance, and fill factor of semiconductor photocatalysts – were studied to assess their absolute and relative impact on reactor performance. The effect of increased temperature on the reactor performance under concentrated irradiation was also estimated by modelling the temperature dependence of bandgaps, solution resistance, Tafel slopes, and exchange current densities. Three different efficiencies were used to evaluate reactor performance: One using the reaction potential of oxygen evolution reaction (%STH), one using the reaction potential of glycerol oxidation reaction (%STD), and one using the reaction potential of glycerol oxidation but also accounting for energy content of glycerol itself as the input energy (%STD_2). The simulations showed that in the limiting case, the STH efficiency reaches 42.3% (resulting in cumulative hydrogen production of 1287.4 kWh/m^2 over 500 hours under solar concentration of 100), while the STD and STD_2 efficiencies reach 13.8% and 2%, respectively. It was found that if both photocatalyst particles had similar bandgaps, parallel illumination was superior since a higher operating current density could be achieved under the constraint of current-matching when both photocatalysts were exposed to the full solar spectrum; otherwise, series illumination yielded better performance. Higher solar concentration increased operating current density but also amplified overpotentials, reducing overall efficiency. Sensitivity analysis identified solution resistance and solar concentration as critical factors affecting the STH efficiency and cumulative H_2 production. Minimizing solution resistance through design and/or operating conditions is thus essential to sustaining high efficiency at concentrated solar intensities.

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Mechanistic study and parameter estimation of a multi-electron transfer organic synthesis

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Unlike traditional synthetic methods, electrochemical synthesis provides a safer, greener and more atom efficient alternative to reaction pathways towards useful compounds [1]. In organic synthesis, chemists are now resorting to electrochemistry to achieve novel reactivities and enhanced selectivity, avoiding toxic chemicals via potential-induced electron transfer instead [2]. However, main reaction pathways are not always fully known, calling for dynamic electroanalytical techniques such as Cyclic Voltammetry (CV) to assess the current-potential curves that evidence the kinetics and mechanism involved [3]. Moreover, dealing with complex processes such as multi-electron transfer with coupled homogeneous chemical reactions may require computational macrokinetic modeling to comprehend competing interactions. This enables the extraction of kinetic and thermodynamic information [4] and the discernment of mechanism candidates [5], when fitted against experimental voltammograms.

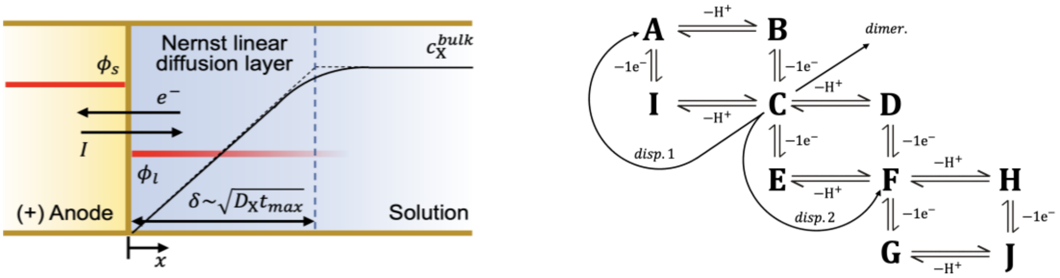

Figure 1: (left) Scheme of the model domain; (right) scheme of possible reaction pathways.

This work presents a model-based parametric and mechanistic investigation of an anodic multi-electron, multi-deprotonation organic synthesis of a hydrazone compound in non-aqueous media. For this end, a 1D continuum-scale diffusion layer model (fig. 1, left) was solved via COMSOL Multiphysics [6]. The model considers an adapted square-scheme, with all its experimentally intuited reaction pathways, accounting for the occurrence of side-reactions, dimerization, and disproportionation (fig. 1, right). In order to estimate the wide scope of kinetic and thermodynamic parameters of a given mechanism, a least-squares fitting procedure was developed in MATLAB. The CV simulations thus grant a prediction of the reaction pathways and kinetics determining the electroorganic behavior, accurately reproducing experimental results across various bulk concentrations. Relevant insight is gained on the effect of mechanistic assumptions, and how applied potential and ratio of diffusion/reaction rates affect product conversion and further oxidation, allowing for the fine tuning of its operating conditions for novel applications, e.g. in flow electrosynthesis. The developed methodology exhibits versatile applicability to other organic processes in electrochemistry.

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Flow Cell Electrolysis of CO_2 in Aprotic Media: Bridging Experiments and Simulations

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To address the increase of greenhouse gases in the atmosphere, CO_2 utilization through electrolysis has attracted considerable scientific interest. This process enables the upcycling of CO_2 into valuable fuels and basic chemicals using renewable energy.[1] Aprotic organic electrolytes offer significant advantages over commonly adopted aqueous electrolytes, including higher CO_2 solubility, suppressed hydrogen evolution reaction (HER), and improved faradaic efficiency for CO production, exceeding 99%.[2] Despite these benefits, current research on CO_2 electrolysis in aprotic electrolytes is primarily limited to small-scale laboratory experiments using H-cells or rotating disk electrode setups.[3] Transferring this process to a flow cell for continuous CO production is essential for practical applications. Flow cells offer several advantages for scaling up CO_2 electrolysis, including improved mass transfer and continuous operation.

This contribution investigates the feasibility and challenges of CO_2 electrolysis in aprotic electrolytes using a flow cell configuration. We developed an experimental CO_2 electrolysis setup using a 10 cm² flow cell with 0.1M $TBABF_4$ in acetonitrile, a polycrystalline Cu foil as the cathode, a mixed metal oxide anode, and an anion exchange membrane as the separator. A physico-chemical 0D model was used to simulate the process assuming well-mixed channels and tanks, and thermodynamic equilibrium between the solution and gas phase.

Our findings demonstrate stable operation for several hours, with CO as the main product. Model-based voltage breakdown analysis reveals significant ohmic losses in the membrane due to limited ionic transport, resulting in high cell voltages that can lead to the degradation of cell components, such as Ni and Zn anodes. This highlights the need for more suitable membranes for use in non-aqueous media to achieve milder operating conditions.

The integration of experimental and modeling approaches in this work provides valuable insights into the feasibility of CO_2 electrolysis using aprotic electrolytes and lays the foundation for the model-based investigation of more complex electro-organic reaction processes.

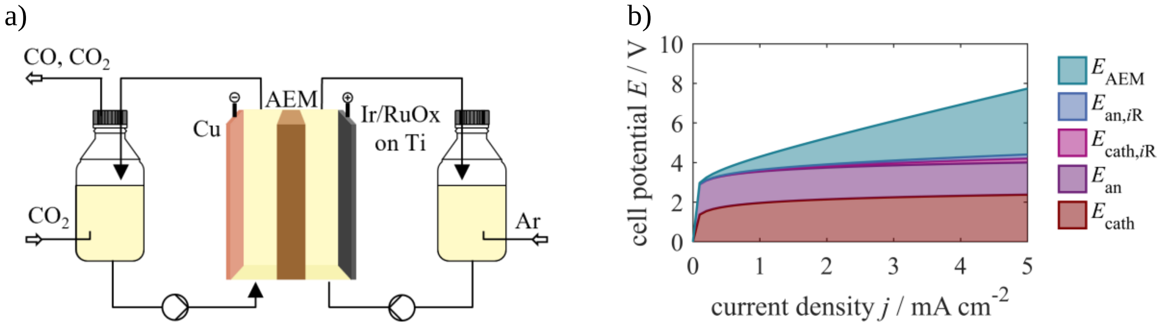

Figure 1. CO_2 electrolysis in a flow cell. a) experimental flow cell configuration and b) model-based voltage breakdown analysis.

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Dynamic Model-based Investigation of the 5-Hydroxymethylfurfural Oxidation and $Ni(OH)_2$ to NiOOH Transitions on Nickel Anodes

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Electrolysis of bio-based molecules promises green hydrogen production and simultaneous conversion to valuable chemicals.[1] The oxidation of 5-hydroxymethylfurfural (HMF) is promising as it produces 2,5-furandicarboxylic acid (FDCA) which is used in the synthesis of biodegradable polymers. Ni-based catalysts have proven active in the electrooxidation of HMF. However, the activity still needs to be improved to achieve higher efficiency and stability under operational conditions. It is essential to analyze and understand the kinetics of HMF oxidation at the Ni-based electrodes to improve conversion rate, product yield, and selectivity.[2] Experimentally validated dynamic kinetic modeling allows to separate complex reaction and transport processes and enables the analysis of individual processes and their interaction with each other.[3,4]

This study combines cyclic voltammetry measurements with dynamic kinetic modeling to investigate the HMF oxidation processes on Ni-based anodes and the competing oxygen evolution reaction. Experiments provide insights into the kinetic barriers and vital mechanistic information for model development. The kinetic model elucidates the interaction between HMF and intermediates with the catalyst. Further, it provides detailed rates for reaction and mass transport. Our findings highlight that the reaction rate is determined by the availability of NiOOH at the catalyst surface. Based on the analysis, we can suggest that more active catalysts and porous or nanoparticle electrodes with a large surface area are needed for high conversion rates of HMF.

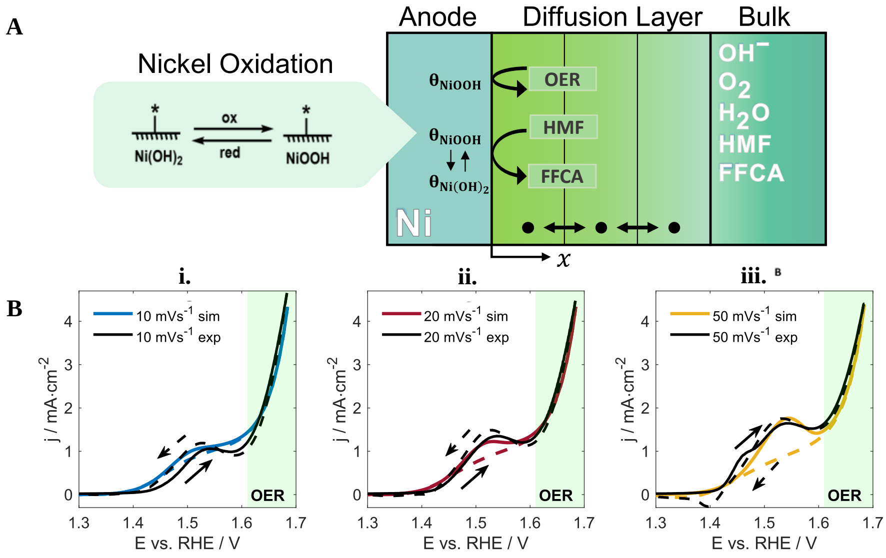

Figure 1: (A) Scheme for the HMF oxidation and the alkaline electrolysis on Ni-based anodes, and (B) simulated and experimental CVs (10 mM HMF) at different scan rates.

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Cations effect on Pt(100) electrodes in aqueous solution studied by Molecular Dynamics at constant potentials

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Electrochemistry focuses on understanding chemical transformations at an electrode-electrolyte interface that involve an electron transfer. Here, the electrolyte is an ionic charge carrier, while the electrode is an active material and an electron conductor. The structure, composition and the dynamical properties of the electrochemical double-layer (EDL) at the electrode might significantly affect the kinetics of electrocatalytic reactions. Interestingly, several studies demonstrated that the electrocatalytic reaction rate and selectivity is impacted by the he nature and concentration of supporting electrolyte's cations, which are typically believed to be chemically inert[1]. As it is difficult to see the EDL experimentally, insights gathered by computational chemistry and more specifically constant potential molecular dynamics are the most promising when aiming to improve our understanding of this complex interface. Recent developments in the charge distribution and fluctuations in electrodes, as within the MetalWalls software, ~~allows~~ nowadays to develop detailed mapping of the EDL. [2] With implications for hydrogen-related technologies, this study intends to employ MetalWalls to investigate how the nature of the cations affect the EDL in alkaline solutions on platinum electrodes and specifically on Pt(100). As illustrated in **Figure 1**, we were able to identify a number of cation-induced patterns in the charge distribution at the interface and inside the electrode, as well as in the water mobility – which might explain the substantial differences in activity observed for the hydrogen evolution reaction as a function of the cation nature that were recently experimentally evidenced [3].

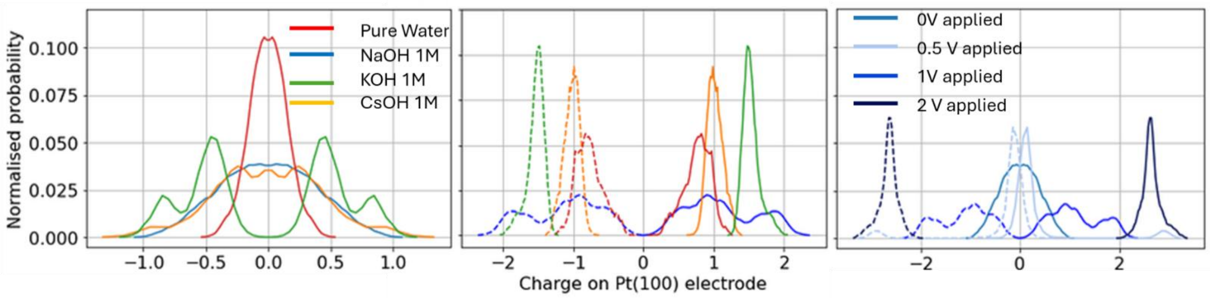

Figure 1. In a simulation box (dimensions = 26.5 x 26.5 x 142.25 Å) of a 1M XOH (X = Na, K, Cs) between 2 x 5 Pt layers in cubic-face-centered configuration with the Pt(100) facet facing the electrolyte, containing 3000 TIP4P water molecules and 54 ions of OH^- and X^+, the charge probability distribution in a given electrode over the entire simulation (*t* = 20-30 ns): a) pure water (red), and different 1M XOH with a potential difference of 0V applied in between the electrode and b) with a potential difference of 1V; c) 1M NaOH with different potential difference between the electrodes. All graphs include both the negative (dotted lines) and positive electrode when a potential difference is applied.

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Predicting electrostatic equilibrium potentials in mixed conductor cells

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The prediction of fuel or electrolysis cell performance requires a reliable estimation of the electrostatic cell potential, which drives electrochemical processes like charge transfer reactions and charge transport. In cells with only a single major ionic charge carrier (SC cells), as is the case in YSZ-based solid oxide cells, the cell voltage can typically be represented through the gas-phase based Nernst equation, directly relating gas phase Gibbs energy differences between the two half cells to an electrostatic cell potential. Cells with multiple mobile charge carriers in the electrolyte (MC cells), give rise to phenomena like defect concentration gradients and leakage currents, thus generally requiring the consideration of ceramic defect chemistry, in order to predict, which fraction of the gas phase energy is available in form of an electrostatic cell potential. An example for MC cells are BCZY-based protonic ceramic cells.

Herein, three different interpretations of equilibrium potentials are distinguished and their relations highlighted. It is shown that contrary to SC cells, these potentials deviate from each other in MC cells, as shown in Figure 1 with 3% H_2 humidity and varying humidity of air.

It is explained why the Nernst equation, if based solely on gas phase concentrations, is ambiguous and not a suitable descriptor in MC cells: While H_2O is mainly produced (fuel cell mode) or consumed (electrolysis mode) on the air-side in BCZY-based protonic ceramic cells at low temperatures, the existence of lattice oxygen vacancies, which become increasingly mobile at higher temperatures, also allows for electrochemical water production/consumption on the fuel-side, leading to an YSZ-like behavior of the cell. Thus, two Nernst potentials could be defined for MCs: $E_{\mathrm{Nernst,BCZY}}$ and $E_{\mathrm{Nernst,YSZ}}$, referencing two different H_2O partial pressures.

A thermodynamic equilibrium potential difference ΔE_{eq} between two half-cells can be derived, based on equilibrated charge-transfer half-cell reactions. Contrary to Nernst potentials based on the gas phase alone, this equilibrium potential ΔE_{eq} also considers the electrostatic energy contribution resulting from defect concentration differences between half-cells in MC cells, which ultimately can be traced back to gas phase partial pressure differences, like varying humidity. This phenomenon is not present in SC cells, where the charge carrier concentration profile throughout the cell is predefined by the local doping. The derivation of ΔE_{eq} is given conceptually for various scenarios, including the presence of multiple charge transfer half-cell reactions and assuming half-cell gas phases which are not thermodynamically equilibrated.

The open circuit voltage E_{OCV} is the only potential that is experimentally accessible. In MC cells it is not the consequence of a system in thermodynamic equilibrium, as otherwise no leakage current would exist. Instead, it is an operating setpoint, which merely fulfills the condition of zero current density. It is further explained why the theoretical prediction of the observable open circuit voltage in MC cells requires knowledge on ceramic thermodynamic and kinetic properties, as well as the numerical solution of a differential equation system.

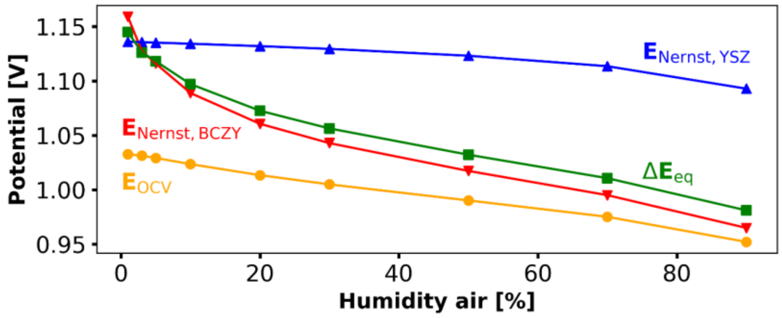

Figure 1: Potentials E_{Nernst}, ΔE_{eq} and E_{OCV} assuming BCZYYb7111 electrodes and electrolyte at 600°C and 3% H_2 humidity. E_{OCV} was calculated by solving a differential equation system, previously parameterized using IV data.

Modified species equation in OpenFOAM to improve the description of species diffusion in porous media

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Computational Fluid Dynamics (CFD) software plays a crucial role in the development of fuel cells, especially in the optimisation of flow fields. Here simulations that provide insights into the distribution of the reaction gases within the cell are of great value. The porous structures of the Gas Diffusion Layer (GDL) substrate, the Micro Porous Layer (MPL) and the Catalyst Layer (CL) are of central importance for gas distribution in the fuel cell. In the current version OpenFOAM-12 [1], however, porous structures are treated like non-porous materials in the species equation, allowing fluids to diffuse freely (equation 1). One option that can be found in literature to correct for the properties of the porous material is to apply a factor to the diffusion term of the species equation that takes into account the ratio of the porosity (ε) to tortuosity (τ) [2]. Such a factor is implemented in some commercial CFD software, such as ANSYS® Fluent. There, the porosity is included as a pre-factor in the diffusion equation, while the tortuosity is taken into account via the anisotropic material parameter K (equation 2) [3]. Though also other formulations are known from literature, this definitely enables a more realistic modelling of species (i, j) diffusion in porous media.

As part of this work, the diffusion term of the species equation in OpenFOAM-12 was adapted accordingly to take a pre-factor formed by porosity and tortuosity into account (equation 3). To validate the modified species equation, simulations were carried out in OpenFOAM and ANSYS® Fluent for the repetition unit of the cathode flowfield in the active area (Figure a). The cathode channel included the porous layers - CL, MPL and GDL - as well as the fluid channel. Figure b shows the oxygen concentration in the catalyst layer at the end of the channel for simulations in OpenFOAM and Fluent. The results demonstrate almost perfect agreement between the two software solutions in both cases. The new implementation in OpenFOAM enables a more realistic representation of species diffusion in porous media. In addition, the clear influence of the pre-factor on the species distribution is recognisable: the oxygen concentration is higher under the channel than under the bar, which further underlines the importance of the correction.

$$J_i = -\sum_{j=1}^{N-1} \rho D_{ij} \nabla Y_i \qquad (1)$$

$$J_i = -\varepsilon \sum_{j=1}^{N-1} \rho D_{ij} \mathrm{K} \nabla Y_i \qquad (2)$$

$$J_i = -\frac{\varepsilon}{\tau} \sum_{j=1}^{N-1} \rho D_{ij} \nabla Y_i \qquad (3)$$

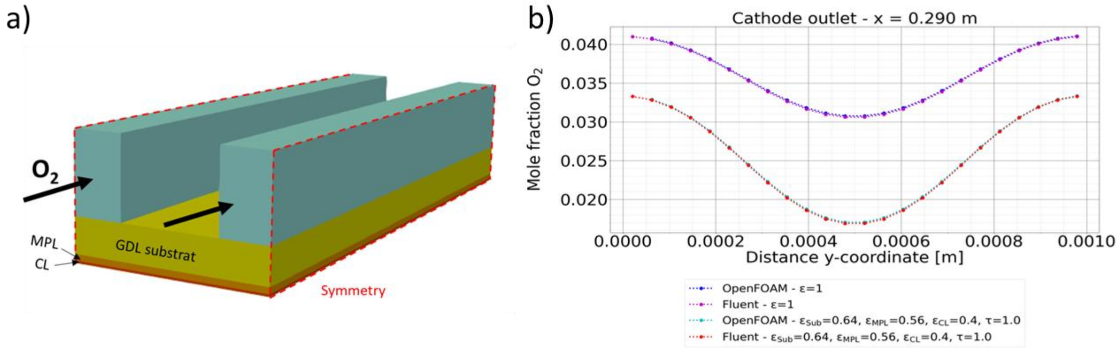

Figure 4: a) Cathode-channel simulation model; b) comparison of simulation results obtained employing OpenFOAM und ANSYS® Fluent in the cathode catalyst layer for different material parameters

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Modeling Charge Carrier Transfer in Photoanodes

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Modeling of photoelectrode performance under varying operation conditions is useful for fundamental understanding and optimization of photoelectrochemical (PEC) devices [1]. While many charge carriers transfer processes have been separately studied, a unified model is harder to find [1]. For example, recent studies use simplified models for the charge transport in the semiconductor [2] or neglect the electrolyte species transport [3]. Also, physics-based current-potential coupling has been seldom investigated [3,4]. Operating parameters beyond the applied potential (such as the electrolyte pH [5], light intensity [2], and electrolyte flow) are usually not studied. Extended output characteristics, including photoelectrode degradation [5] and the simulation of photoelectrochemical impedance spectroscopy (PEIS) have only recently been introduced [4].

We developed a coupled multiphysics model that accounts for phenomena at the electrode-electrolyte interface and extends the input parameters and output characteristics to the frequency domain. Transport of electrons and holes in the semiconductor were modeled with Poisson-drift-diffusion equations including carrier generation and recombination terms. Surface recombination and a degradation mechanism were modelled as competitive pathways at intrinsic surface states, and Marcus-Gerischer theory was used to model the kinetics of charge transfer. Band edge unpinning was modeled through surface state (dis-)charging and allowed to study a surface state-passivating co-catalyst. The model was then used to simulate the impedance spectra, which could be measured by PEIS.

A $BiVO_4$ photoanode with CoPi co-catalyst in phosphate solution for water splitting served as case study. Inaccessible system properties such as recombination lifetimes were extracted from PEIS under standard operating conditions (pH=7, 1 kW m^{-2}, T=25°). The model was then validated against experimental voltammograms, PEIS, and chronoamperometry obtained under different conditions. Simulated voltammograms were able to show *(i)* the effect of illumination direction (front vs. back), *(ii)* pH dependence (between 5 and 12), *(iii)* ohmic losses at high light intensities (< 100 kW m^{-2}), and *(iv)* the effect of CoPi co-catalyst. Simulated PEIS spectra proved useful in differentiating charge transfer processes (e.g. surface vs. bulk recombination). Tendency towards degradation under different conditions was quantified and validated against experimental chronoamperometry. Finally, the inclusion of surface-state mediated charge transfer permits to grasp subtle phenomena not addressed in photoelectrode models yet, such as the light intensity-dependent band edge unpinning.

The presented model is able to simulate transient response (e.g. PEIS) as a function of a wide range of operating parameters in photoanodes for water splitting. The new insights and data gained can help in optimizing PEC devices. The model has capabilities to be expanded to include multiple dimensions and complex photoelectrode structures, which could provide more insights into the heterogeneity and local variation of operation condition in a photoelectrochemical device or component.

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Microkinetic Modeling of Oxygen Evolution Reaction on Ni-Fe Alloy Electrodes

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Anion exchange membrane water electrolysis (AEMWE) is a sustainable hydrogen production technology that integrates the advantages of proton exchange membrane and alkaline water electrolysis.[1] Ni-Fe-based materials have shown great promise as anodes for the oxygen evolution reaction (OER).[2] Developing efficient and stable electrocatalysts necessitates a deeper understanding of reaction mechanisms and pH dependence, for which microkinetic modeling is a powerful tool.[3]

Microkinetic models were employed to simulate experimental OER rotating disk electrode (RDE) data across pH values from 11 to 14. The model accounted for O_2 and OH^- mass transport, Butler-Volmer kinetics, and Langmuir adsorption isotherms. We first conducted microkinetic modeling based on the widely accepted four consecutive proton coupled electron transfer (PCET) steps mechanism. However, the experimental data could not be fitted by the model with this mechanism. To address this, we decoupled the PCET steps into distinct proton and electron transfer steps, revising the model. The updated model, with a single set of reaction parameters, achieved strong agreement with experimental data across all pH conditions.

As a perspective, this microkinetic model will be integrated with a comprehensive electrolyzer model incorporating mass, charge, and heat transport to predict optimal operating conditions for AEMWE systems.

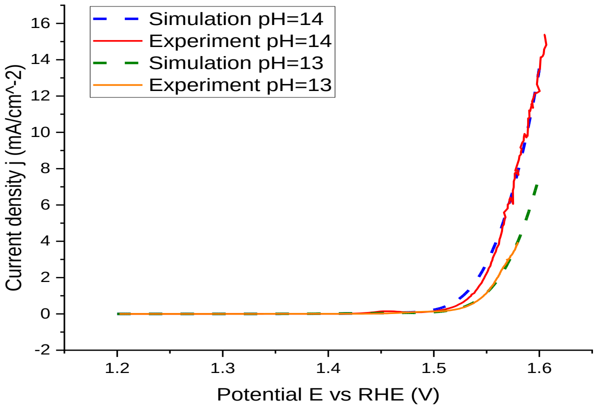

Fig. 1 Comparison of the simulation results using the decoupled mechanism model with experimental data

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Understanding ion-specific interactions in anion-exchange membranes via atomistic modeling

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Anion-exchange membranes (AEMs) are of increasing interest to the CO_2 reduction community as they enable alkaline operating environments that both suppress the hydrogen evolution reaction and facilitate better catalyst stability. When incorporated into a bipolar membrane, AEMs play a crucial role in reducing ionic crossover and maintaining favorable reaction microenvironments at the electrodes. Despite the rise in research interest, understanding of AEM nanostructure remains less well understood than cation-exchange membranes.[1] This gap arises from the diversity of AEM chemistries and challenges in characterizing their nanophase separation, with experimental X-ray scattering data often indicating a loss of or weak nanophase segregation.[2] Recent molecular dynamics studies have investigated the impacts of hydration and cation stoichiometry on hydroxide-conducting poly(aryl piperidinium) and polysulfone polymers. These studies confirm that AEMs do undergo nanophase separation, but the size and morphology of water domains, as well as the ionic coordination environments, is highly dependent upon the chemistry and hydration of the membrane.[2,3] However, as most investigations have focused on OH^-, there is limited understanding of how transport and coordination within the AEM is affected by the presence of common counter-ions (e.g. Cl^-). Furthermore, recent experimental studies of BPMs have found evidence of non-ideal, ion-specific selectivities in mixed-electrolytes that most likely stems ion-specific interactions with the fixed-charges within the AEM.[4,5] As more complicated electrolyte feeds become common for AEM applications, e.g. bicarbonate electrolysis or seawater electrolysis, it will be crucial to have a coherent understanding of how complicated electrolytes interact with ion-conducting polymers. Here, we use classical molecular dynamics to study the nanophase structure of the poly(aryl piperidinium) polymer family which are relevant to CO_2 reduction and for use in bipolar membranes. We analyze the behavior of different counter-ions and their interaction with the fixed charge groups within the AEM, and present insights into the structure-function relationships that dictate macroscopic AEM performance. The results of this study will enable recommendations for chemically selective AEMs and further understanding of ion-specific behavior, in addition to providing parameters directly relevant to continuum simulations of AEMs.

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Machine Learning for the Characterization of Porous Transport Layers

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The geometric micro-structure of porous transport layers (PTLs) affects their permeability, in accordance with Darcy's law. As a material property, it is relevant for transport simulations at higher scales [1], at both the cell and stack levels of fuel cells and electrolyzers.

As a continuation of previous investigations into the application of convolutional neural networks (CNNs) [2], sphere-based micro-structures were investigated, as they can be used for PTLs in electrolyzers. A sedimentation model was developed to create stochastic sphere-based micro-structures (Figure 1). With the permeability calculated by means of a Lattice–Boltzmann simulation, a CNN was developed in order to predict the permeability of a material given by its three-dimensional (3D) micro-structure (Figure 2). The predictions of the CNN were of reasonable accuracy for material that was sintered from spherical particles [3].

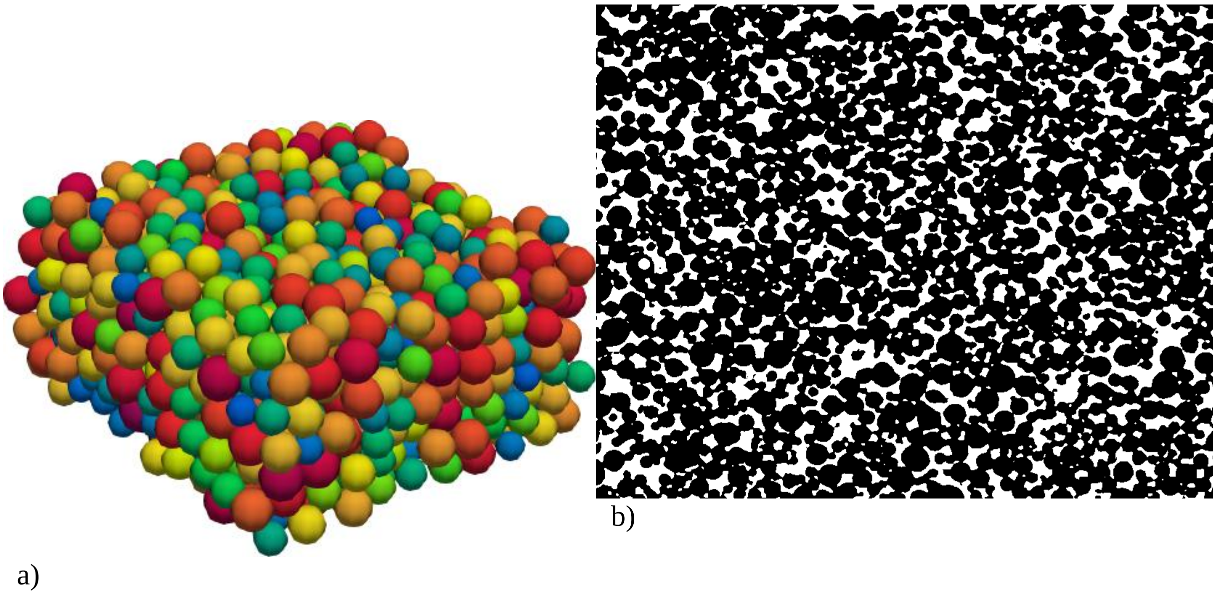

Figure 1. Micro-structures of porous transport layers (PTLs); a) stochastic micro-structure, created by sedimentation of the spheres [3]; b) PTL by sintered titanium spheres [3]. 2D slice from a 3D structure.

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Elucidating Parasitic Currents in Proton-Exchange Membrane Electrolytic Cells Via Physics-based and Data-driven Modeling

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Proton-exchange membrane (PEM) water electrolysis plays a crucial role in green hydrogen production. To accelerate commercial deployment, it is pertinent to use efficient computational models which capture the inherent non-linearities and aid to system optimization. This poster presentation focuses on understanding degradation mechanisms, particularly the impact of parasitic currents on the performance of a PEM electrolytic cell (PEMEC) through macro-scale modeling and uncertainty quantification (UQ) [1]. Parasitic currents due to electron conduction through the membrane are a frequently observed but not fully understood degradation effect, leading to lower Faradaic efficiency. One possible cause of these parasitic currents is mechanical damage in the membrane-electrode assembly (MEA) [2]. To specifically address the effect of such parasitic currents on Faradaic efficiency and cell performance under varying design parameters, we present a one-dimensional steady-state physics-based model for PEMECs. A comprehensive dataset from this model is generated and used to train a machine learning (ML) surrogate model. Its performance is analyzed to assess the potential of ML in accurately and efficiently predicting the effects of parasitic currents in PEMECs. The chosen ML algorithm, eXtreme Gradient Boosting (XGBoost), excels in predicting the polarization behavior while significantly reducing computational demands. Using this ML surrogate model, UQ and sensitivity analysis (SA) [3] are applied to investigate the dependence of PEMEC performance and Faradaic efficiency on the electronic conductivity of the PEM, especially when electronic pathways are existent within the membrane and operating at low current densities.

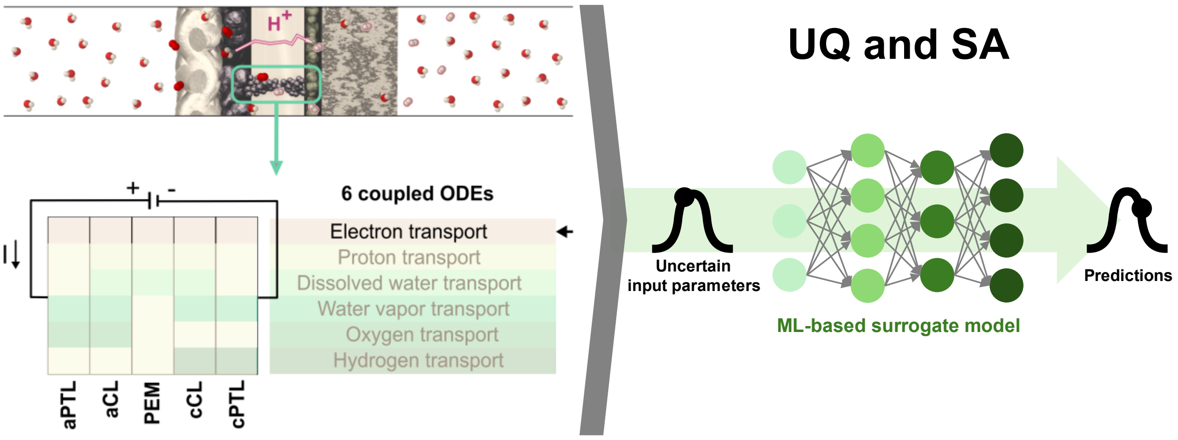

Figure 1: Schematic overview of the proposed framework to elucidate parasitic currents in a PEMEC.

Acknowledgment: Financial support was provided by the German Federal Ministry of Education and Research (BMBF) within the H2Giga project DERIEL (grant number 03HY122C).

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Predictive modeling of proton-exchange membrane electrolytic cells

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Proton exchange membrane (PEM) electrolytic cells (ECs) have gained significant importance in the realm of hydrogen production. With the increasing demand for commercializing PEMECs, there is a pressing need for enhancing their performance and durability. In addition to experiments, macro-scale modeling plays a pivotal role in comprehending the multi-physics processes within PEMECs.

This presentation highlights the development of physics-based [1, 2, 3] and data-based [4] models tailored for PEMECs. They serve as the foundation for elucidating degradation mechanisms of PEMECs, aiming to prolong their lifespan and improve their efficiency for a quick technology ramp up. These models explore the electrochemical processes and transport phenomena occurring within the porous transport layers (PTLs), catalyst layers (CLs), and the PEM, which separates the system into anode and cathode sides. The high-aspect-ratio PEMECs are well-suited for one-dimensional (1D) analysis, where the electrochemistry model comprises a set of 1D steady ordinary differential equations (ODEs). The 1D analysis is implemented in Python, with COMSOL also utilized for 2D and 3D simulations.

Unfortunately, the complex nature of PEMECs as thermal, fluidic, and electrochemical systems poses challenges in accurate prognostics. Modeling these cells involves addressing uncertainties in operational conditions, material properties, and design features. Additionally, uncertainties in experimental data, model selection, parameters, and model inadequacies must be carefully considered during PEMEC modeling. While uncertainty quantification (UQ) and sensitivity analysis (SA) can unveil how uncertainties propagate from input parameters to the output of PEMEC models, UQ has not been extensively integrated into PEMEC modeling. Finally, this presentation underscores the potential benefits of physics-based modeling combined with UQ and SA for PEM electrolysis.

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A numerically highly efficient dynamic quasi-2D PEMFC model including non-isothermal and phase change processes

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Current PEMFC simulation environments are complex and computationally demanding, limiting their applicability for dynamic simulations. To adress these challenges, this work presents a highly efficient non-isothermal PEMFC model with multiphase flow, tailored for dynamic simulations. The model extends the isothermal approach by Murschenhofer et al. [1], bridging the gap between numerically expensive 3D models and fast 0D/1D models that lack spatial resolution by using a quasi-2D approach, see Figure 1(a).

The proposed model captures key phenomena, including two-phase transport by convection, multi-component diffusion and capillary fluxes in the gas channels (GCs) and gas diffusion layers (GDLs), and membrane water transport by electro-osmotic drag and diffusion as well as nitrogen crossover through the membrane. It also accounts for finite-rate mass transfer during sorption and desorption processes between the membrane and the electrodes, as well as heat generation from chemical reactions, finite proton conductivity, and phase changes. A numerical scheme employing linearisation in time (LIT) of the governing equations and a Chebyshev collocation method for spatial discretisation ensures low computational effort. By further utilizing a particle swarm optimization algorithm, it is easily possible to extract otherwise inaccessible model parameters by fitting the model's polarization curve to a desired reference case, e.g. to data from an experimental setup.

Validation of the model is conducted against steady-state computational fluid dynamics (CFD) simulations of a 3D fuel cell geometry performed using AVL Fire™. The results of the LIT model, in terms of polarization curves and the distributions of gaseous species, temperature, liquid water, and PEM water content, show fairly good agreement with the CFD simulations, while reducing the computational effort from hours to minutes. The latter two comparisons are illustrated in Figures 1(b,c). Furthermore, the transient behaviour of temperature and liquid water accumulation in the electrodes qualitatively aligns with data from existing literature [2, 3].

The model's capabilities offer a valuable tool for fuel cell control engineering, facilitating efficient control unit optimization and state-observer predictions. Its computational efficiency makes the presented model particularly suitable for widespread parameter studies and performance analyses.

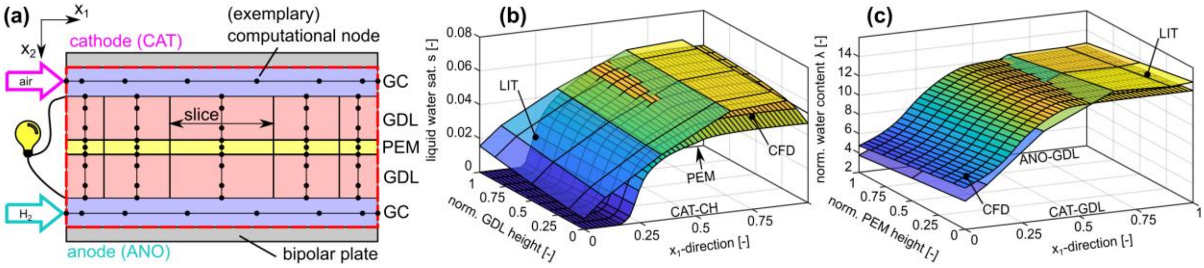

Figure 1: (a) Quasi-2D computational domain. Comparison of steady-state results from the LIT model and CFD simulations: (b) liquid water saturation in the cathode GDL, (c) PEM water content.

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A new generation zero-dimensional physics-based model for proton-exchange membrane fuel cells

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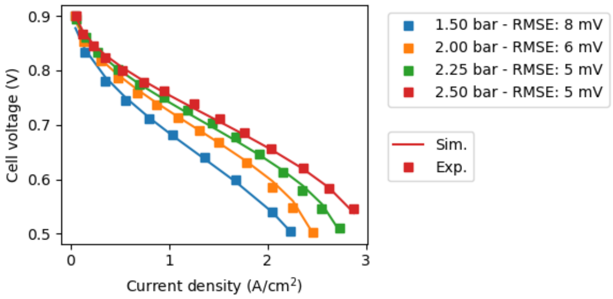
Finding a good trade-off between accuracy and complexity, computational cost of physics-based models of proton-exchange membrane fuel cells is not an easy task. Relatively simple zero-dimensional (0D) models allow for fast simulation and integration in more complex system-level models. On the downside, sensitivity to varying operating conditions is not necessarily well captured, especially for strong current densities where liquid water, gas transport resistance and temperature gradients may be present. Therefore, the current trend in the literature is towards more complex models going from 1D+1D to 3D models, where full transport equations are solved, at the expense of a high computational cost and an impressive list of required input parameters (not always readily available) [1]. Except for a few works, such as the ones from Ritzberger *et al.* [2] or Schröder *et al.* [3], not much effort has been addressed at developing performant 0D models since the foundation works of early 2000s. Here we propose a new generation physics-based PEM fuel cell 0D model which consider recent insights gained from experimental work on oxygen transport resistance [4,5] and catalyst layer proton resistance [6], ionomer thin-film properties [7] and platinum oxidation [8]. An analytical solution for water transport in the PFSA membrane developed by Ferrara et al. [9] is also included. A first validation of the model against experimental data and model results from Gass *et al.* [10] and Goshtasbi *et al.* [11] is presented, which shows that the model captures well the impact of varying operating conditions.



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Revisiting the Gas Diffusion Layer Water Inventory – Benchmarking Leverett

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Significant progress has been made over the last decade in improving Polymer Electrolyte Membrane fuel cells (PEMFC), resulting in usable current densities of up to 3.0 A/cm². Specifically for high current density values, it is important to maintain a well-balanced water inventory inside the fuel cell, particularly within the GDL, to prevent flooding of the porous material by excess product water and maintain high permeability for reactant gases.

While foundational research on modeling GDL permeability and wetting behavior for PEMFCs was conducted two decades ago [1,2,3], these early models have limitations when applied to modern, high-performance GDLs. More recent work [4] has attempted to address these limitations, proposing improved functional forms for describing the behavior of contemporary GDL materials. However, the Leverett J-function [5], originally developed for porous rocks, remains the default description of saturation in many macro-scale fuel cell models. Crucially, modern GDL materials are significantly thinner and more technologically advanced than those used in the original studies.

Thus, this work aims to accurately model the water saturation and permeability of gases in modern GDLs using various simulation methods starting from the micro scale (image analysis and modelling in the software GeoDict, Pore-Network-Modelling (PNM)). The micro-scale simulations are based on high-resolution X-ray scans of the GDL structure. These scans are analyzed and reconstructed with GeoDict to create digital twins that perform statistically identically and allow for virtual material modifications. Parametric studies for various local operating conditions are then performed using these twins, including e.g. different compression rates, temperatures, water production rates, and gas velocities. These simulations provide insight into the behavior of water saturation within the GDL structure and its influence on the diffusion of oxygen and hydrogen towards the catalyst layer. Using the knowledge gained from the microstructure simulations, the default Leverett J-function used to describe water saturation of porous media on an integral level in the CFD software Ansys Fluent® will be benchmarked against a better-suited functional. Depending on the results, ways to improve the J-function parameters or devising a new macro-scale functional description of the GDL water saturation and the resulting gas diffusion properties of the GDL will be explored.

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Influence of the Energy Management System in Fuel Cell-Battery Hybrid Powertrains on the operation of PEM fuel cells

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The energy management system of a hybrid fuel cell-battery powertrain can be designed to obtain a highly efficient and durable drive system for mobile applications. Depending on the available power and energy demand the energy management can control the power distribution from the fuel cell and the battery. The dynamic operation of PEM fuel cells is limited by a maximum power ramp-up rate. If this is not considered in the energy management, it can lead to insufficient gas supply and consequently to performance and lifetime losses. The reason for the insufficient gas supply is the dynamic control of the fuel cell system components, such as the air compressor or the hydrogen recirculation unit.

In this work the influence of different energy management controller on the fuel cell system behaviour is investigated. Therefore, a simulation model of the fuel cell-battery hybrid powertrain was set up considering a 7.5t truck as a use case. For the energy management a state machine controller (SMC) and a fuzzy logic controller (FLC) are compared. The state machine was set with predefined controlling rules and states, corresponding to the fuel cell power levels "low", "medium" and "high". The fuzzy logic controller (FLC) was set with predefined fuzzy sets and fuzzy rules, considering the demanded electric power and the state of charge of the battery. The hybrid fuel cell-battery system reacted according to the requested power demand, set from the energy management controller. The WLTP driving cycle was defined as a test case for the simulation of both energy management controller. To evaluate the two controller the total hydrogen consumption was chosen as a value for analysis of the system efficiency and the total degradation rate as reported by Chen et al. [1] was chosen as value for analysing the lifetime. Regarding the simulation results the SMC leads to fewer load changing cycles as in case of the FLC. This leads to about 7% increased total hydrogen consumption for the SMC. Due to the lower load changing of the SMC the simulation shows that the FLC leads to about 12% more total degradation as the SMC.

As a result, it can be concluded that the SMC is in this configuration more suitable for stationary operation of fuel cell systems, as it is robust in terms of lifetime for systems with very low load changing cycles and the FLC shows a better performance for fuel cell systems with dynamic operation.

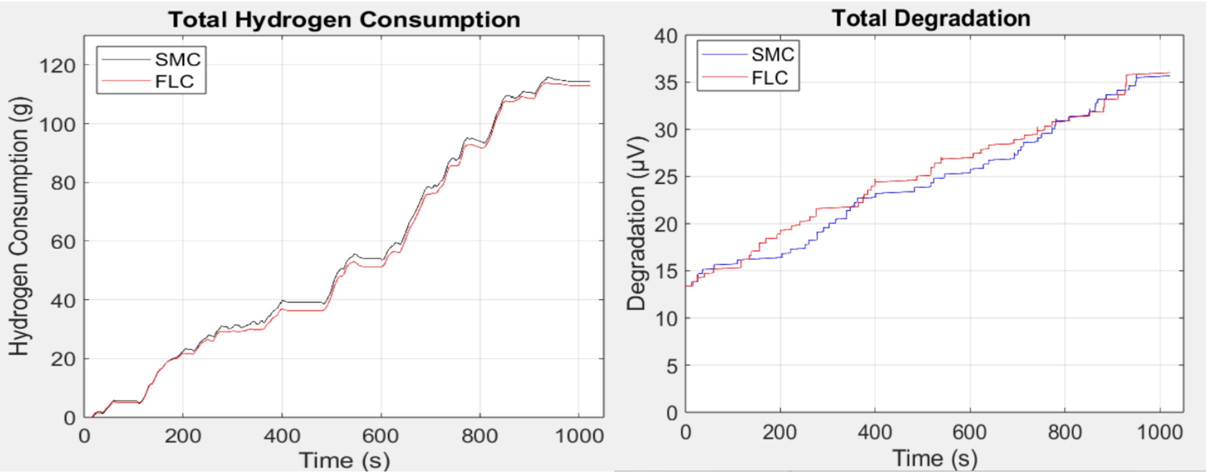

Figure 5: Total Hydrogen Consumption and total degradation for the fuel cell system with state machine and fuzzy logic controller considering the WLTC as a test case

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Bridging the Gap: Investigating the Influence of Clamping Pressure and performance in Full-Size PEM Fuel Cells

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Proton exchange membrane fuel cells (PEMFCs) powered by green hydrogen present a promising alternative for sustainable transportation. While sub-scale cell research provides valuable insights and facilitates rapid material, model, and method development [1], its applicability to real-world scenarios is limited. Real world applications of PEMFC deployments involve significantly larger active areas and stacked cell configurations, introducing complexities not captured in sub-scale studies. Previous research has demonstrated the significant impact of along the channel effects and humidity distribution on cell dynamics and current density distribution (CDD) [2]. Furthermore, clamping pressure plays a crucial role in manufacturing and long-term performance. This study addresses this gap by investigating the effects of clamping pressure and gas diffusion layer (GDL) properties on a full-size single cell PEMFC. Utilizing a segmented intermediate plate (S++ plate) to measure CDD, we conducted experiments under varying clamping forces and with different GDL materials. Our findings reveal that while overall performance may remain stable within the typical range of clamping pressures, high-frequency resistance (HFR) and CDD exhibit significant variations. This underscores the importance of considering clamping pressure and GDL selection in the design and optimization of full-size PEMFCs for real-world applications, bridging the gap between sub-scale research and practical deployment.

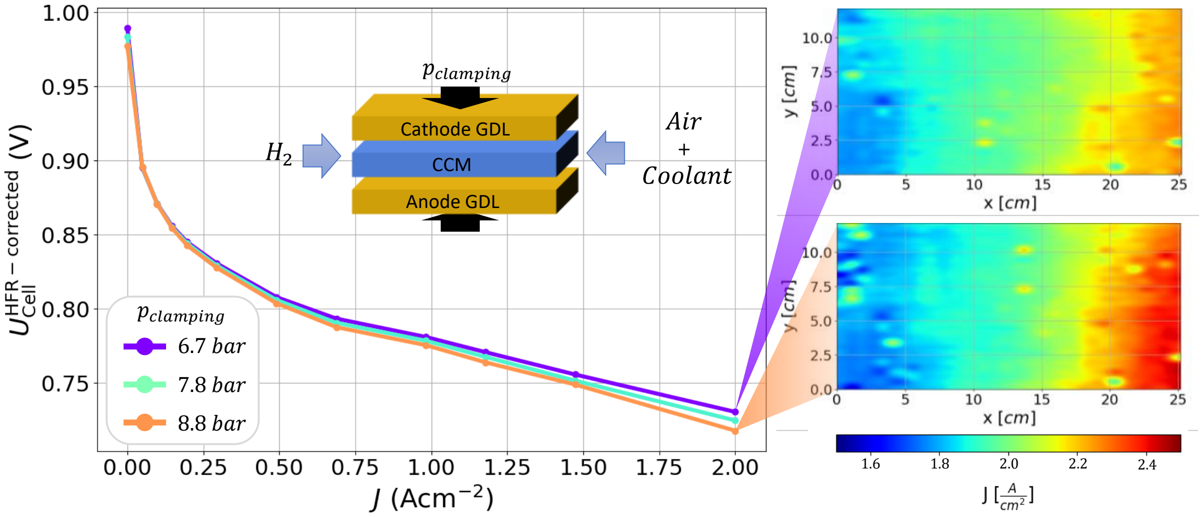

Figure 1: Polarization curve of a full-sized MEA under different clamping pressures and two corresponding current density distributions for 2 Acm^{-2}

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A Modelling Framework for the Simulation of Coupled Performance-Degradation Phenomena in Proton Exchange Membrane Fuel Cells

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Proton exchange membrane fuel cells (PEMFCs) are a promising technology for reducing the carbon footprint in the automotive sector, particularly for heavy-duty vehicle applications. On the other hand, their limited durability remains a significant issue. In the literature, several degradation mechanisms have been identified and individually modelled. At ZHAW, we have been developing a model that simultaneously reproduces chemical membrane degradation and catalyst layer (CL) degradation. The former, caused by hydroxyl (OH) radical attack on the membrane, is a final result of several processes: oxygen crossover, hydrogen peroxide formation, and ultimately multi-step (electro-)chemical reactions involving several species [1] leading to OH formation. Traditionally, implementing these governing PDEs manually for each process requires substantial effort to ensure conservation of fluxes (e.g., molecular diffusion in concentrated mixtures), source terms (e.g., net species consumption and current densities), and the calculation of transport and thermodynamic coefficients. To overcome these challenges, we built a modular model in COMSOL Multiphysics® [2], where distinct interfaces handle specific physical phenomena and degradation subprocess, as shown in Fig.1(a). Additionally, we have coupled a subscale CL degradation model (based on the work of [3]) with a PEMFC performance model. Thereby, we account for the influence of local electrochemical surface area (ECSA) decrease under varying operating conditions, as shown in Fig. 1(b). As result, the coupled performance-degradation model captures the effects of performance decays over time due to FC operating conditions changes, e.g. humidity, potential, and temperature.

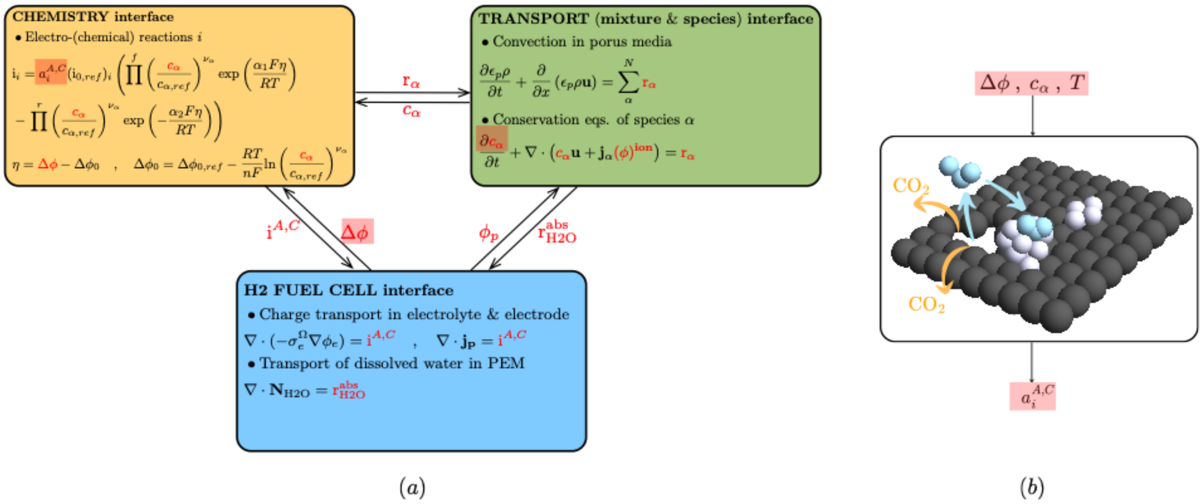

Figure 1: (a) Coupling-diagram of the COMSOL interfaces with linked variables (red)
(b) Inputs-/outputs between 1D MEA model and subscale CL degradation model

Acknowledgements: This work is part of the project PEMTASTIC, supported by the Clean Hydrogen Partnership and its members Hydrogen Europe and Hydrogen Europe Research under the Grant Agreement 101101433.

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Enhancing Gas Diffusion Layer Design: Integrating Simulation and Experimental Methods for Improved Gas Flow in PEM Fuel Cells

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Recent advancements in manufacturing have unlocked new possibilities in the design of gas diffusion layers (GDL) for Polymer Electrolyte Membrane (PEM) fuel cells. However, testing and comparing various designs still demands significant time and resources. This study introduces a simulation method to facilitate the preselection of structures for fabrication and experimental analysis, thereby reducing these costs. The aim of the structure variation in this study is to enhance the gas flow under the bipolar plate (BPP) land areas, which currently contribute negligibly to the overall gas transport in commercial GDLs [1].

Six different flow structures were initially designed and evaluated using both simulation and experimental methods. The GeoDict software [2] was employed for simulations, while laser perforation was used to fabricate the structures from 40 µm graphite sheets for experimental testing. Performance testing was conducted using the qCf 12 High Amp from Baltic Fuel Cell at 50°C and 1 bar. The results are presented in Figure 1 for the simulated resistivity and porosity, alongside the experimentally obtained voltage at a load of 0.5 A/cm^2. These results demonstrate how the simulation complements the experimental testing by allowing separate analysis of different GDL characteristics, which enhances the understanding of how GDL geometry influences PEM fuel cell performance.

Integrating simulation with novel manufacturing techniques promises to yield new scientific insights and improve the efficiency of developing innovative GDL designs.

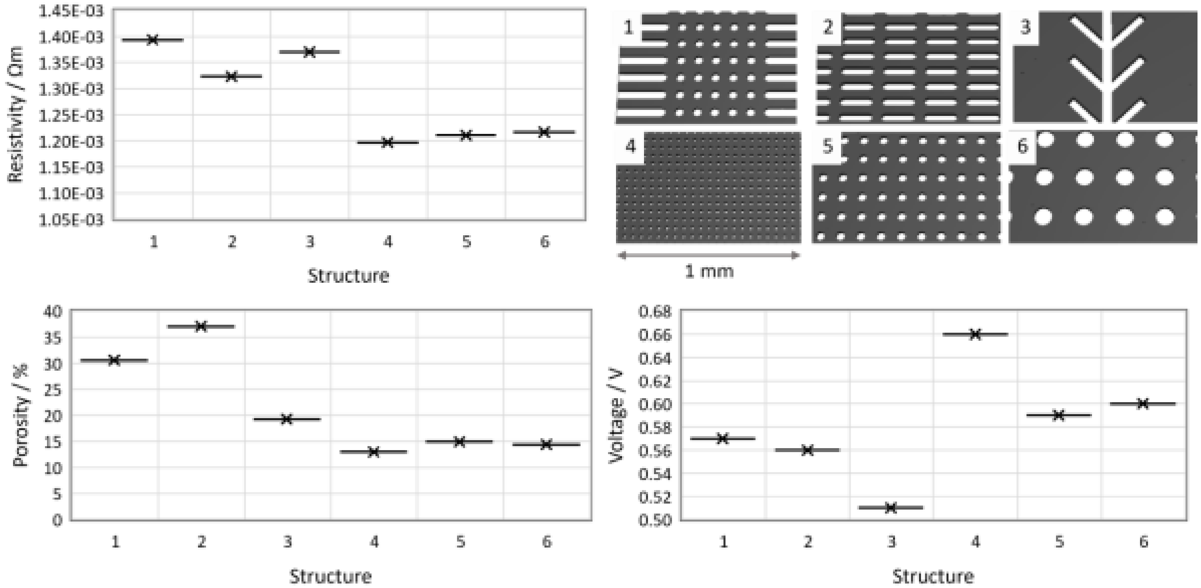

Figure 1: Simulation results for porosity and electric resistivity as well as experimentally obtained fuel cell voltage for the six different investigated GDL structures.

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Simulative fuel cell spatial behavior analysis for enhanced fuel cell control

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Automotive fuel cells are subjected to dynamic load changes which causes fluctuations within the fuel cell in terms of temperature, humidity, pressure etc. These conditions if not maintained properly could result in local critical states such as hotspot formation, flooding or drying. Left unmitigated, such conditions can ultimately result in membrane damage and fuel cell deterioration.

Hence PEMFC operating conditions are critical for its durability and efficiency. System level simulations and analytical calculations can provide a general view on the relationship between operating parameters such as electrical load, stoichiometry, pressure, humidity etc. on the reaction kinetics and its corresponding suitability. But the core component of the fuel cell, the bipolar plates (BPPs), and in particular the sandwiched membrane electrode assembly (MEA) between the BPPs can have different configurations such as co-flow, counter flow or cross flow directions of reactant supply, that directly influences the local gradients of the current density, temperature, humidity and reactant concentration. Hence the spatial gradients corresponding to the respective flow configuration must be analysed and considered while developing the operating strategies.

A sensor integrated fuel cell approach was developed to capture the local conditions across the active area of the bipolar plate. The localised data is then used within the control algorithm to reduce the occurrence of the localised critical states. In addition to the experimental setup, a simulative approach to study the effects of the operating conditions on the local gradients can speed up the development process considerably.

Spatially resolved fuel cell simulation models enable such an approach where the effect of the operating parameters such as stoichiometries, pressures, humidity, etc. on the local conditions along the channel length can be directly analysed. In this work, an open source spatially resolved model was used to study the effects of different operating conditions and different flow configurations on the spatial gradients across the bipolar plate [1]. As depicted in Figure 1, these simulations help in visualising the effects of the operating conditions on critical parameters such as relative humidity, current density, membrane water content etc. A better understanding of these effects enables us in developing operation strategies that incorporate system as well as localised fuel cell state of health, allowing for more durable and efficient fuel cell systems.

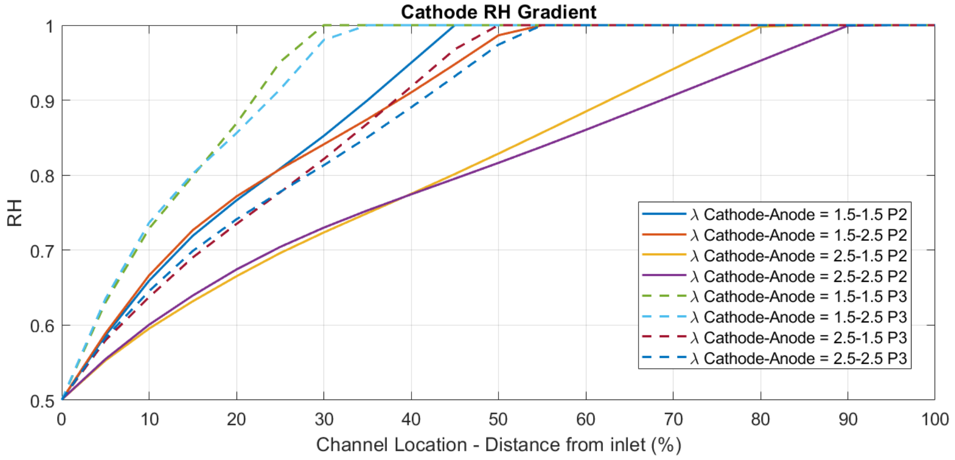

Figure 6: Relative humidity (RH) gradient across BPP for different pressure and stoichiometry conditions

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Performance Modeling of PEM fuel cells under consideration of electrochemical aging effects

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Electrochemical degradation modeling of PEM fuel cells

The amount of time and money during the development process of Proton Exchange Membrane fuel cells (PEMFCs) can be reduced by using predictive simulation tools instead of expensive long-term durability tests. A 1D Performance model using Matlab® has been developed during a PhD thesis at ZSW [1]. It works with segments along the main flow direction and calculates the anode and cathode side in co- or counterflow configuration. A cathode side contaminant model with the option of using also a filter model has already been implemented. By activating the contaminant model the impact of two of a total of four gas types (sulphur dioxide, nitrogen dioxide, ammonia and toluene) on the voltage is taken into account.

This model is now being extended to include the electrochemical degradation mechanisms in catalyst and membrane. In each of the two components, three main mechanisms were defined. In the catalyst layer platinum aging (oxidation processes, particle detachment and agglomeration, ion diffusion), carbon corrosion and the loss of hydrophobicity can occur. Consequences are the decrease of the electrochemical active surface area (ECSA) of the platinum particles and a reduced oxygen transport due to the loss of hydrophobicity and therefor water accumulation in the pores.

In the membrane, a decomposition and thinning caused by a radical attack happen. Additionally pinholes can form which leads to gas crossover (second mechanism). As a third mechanism, iron ions can occupy the free reaction places in the membrane and reduce its conductivity.

In the model, a differential equation system based on the chemical reactions and their rates is used to calculate the time dependent changes in each segment. For the catalyst degradation mechanisms, the changes in the radius size and particle size distribution of the platinum particles need to be calculated. Based on this, the model gets the new electrochemical active surface area. The ratio of the new active surface area and the initial area gives the degradation factor for the voltage calculation. Also the corroded carbon mass which causes the change in contact angle and loss of hydrophobicity will be computed every time step. In the membrane model the concentrations of hydrogen peroxide, iron, radicals and the products out of the decomposition change. The new concentrations in each time step helps to calculate the lost membrane mass and therefor the new thickness. With an assumption that with a thickness of 10% of the initial thickness the formation of pinholes starts [2], the diffusion coefficients are defined dependent on the thickness. With an assumed maximum of 6.7 $mg_{Fe2+}/g_{membrane}$ iron ion concentration in the membrane [3], another degradation factor (ratio of the calculated iron concentration and the maximum concentration) with impact on the voltage calculation is introduced.

The extended degradation model was compared with an experimental data set. Therefor a profile of about 2,500h was simulated. Especially the simulated ECSA loss shows a good agreement with the measured active surface area. The simulated polarization curves deviate a little from the experimental ones. Minor adjustments of the model are to be done to get a better match.

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Pore-Scale Investigation of Ordered Mesoporous Carbon Supported Catalyst in Proton Exchange Membrane Fuel Cells

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The state-of-the-art catalyst layer (CL) in proton exchange membrane (PEM) fuel cells consists of carbon support, ionomer and precious platinum (Pt) particles as the catalyst. The widespread commercialization of PEM fuel cells hinges on further reducing Pt loading without compromising performance or durability, and can be achieved through novel energy material design. For traditional solid carbon support, Pt particles are dispersed on the carbon surface and get covered by ionomer to ensure the transport of electrons and protons, respectively. However, the low solubility of reactant in the ionomer and the high cross-ionomer transport resistance significantly hinder overall performance [1]. Besides, Pt particles covered by ionomer also get poisoned, resulting in a substantial decrease in the oxygen reduction reaction (ORR) activity and accelerated catalyst degradation [2]. The ordered mesoporous carbon (OMC) support can optimize the catalyst by improving both mass transport and catalytic activity. OMCs aim to protect Pt particles from ionomer poisoning by allocating some of the Pt particles within accessible pores, while still enabling proton transport via water vapor, as shown in Figure 1. A pore-scale model is developed to numerically reconstruct the microstructure of OMC based catalyst and evaluate its performance by simulating the reactive transport processes within the single catalyst particle (shown in Figure 1), facilitating the optimization of design parameters including particle size, pore size, Ionomer/Carbon ratio, Pt/Carbon ratio, and catalyst distribution. This work demonstrates the significant impact of OMC microstructure and catalyst distribution on catalyst performance, highlighting the potential of the OMC to achieve a much higher performance with a reduced Pt loading.

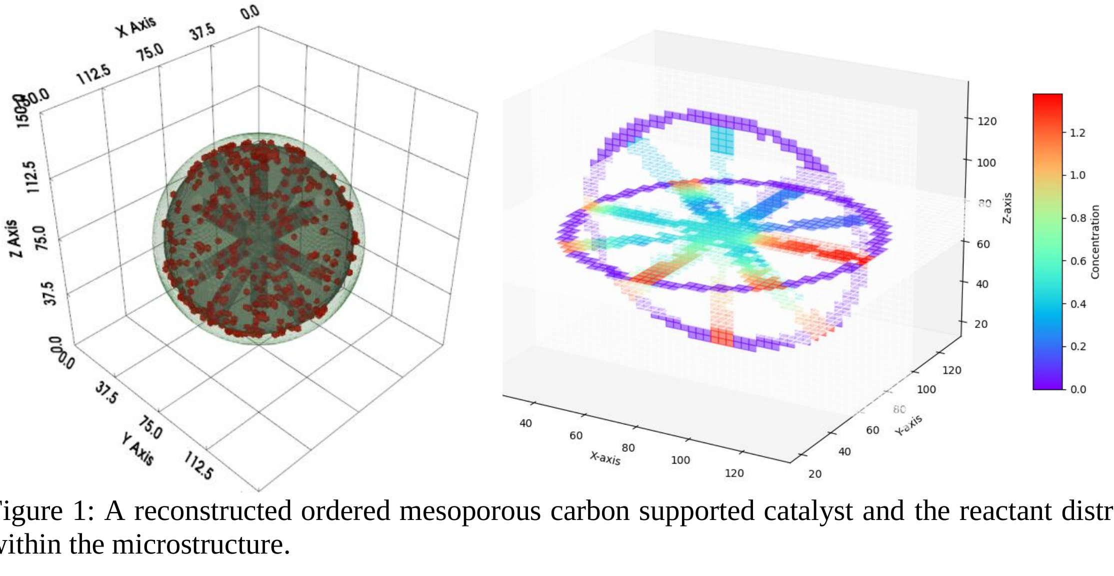

Figure 1: A reconstructed ordered mesoporous carbon supported catalyst and the reactant distribution within the microstructure.

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Mechanical Interaction Between Microporous Layer and Fiber Substrate in Gas Diffusion Layers for PEM Fuel Cells

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Gas Diffusion Layers (GDLs) play an important role in PEM fuel cells and electrolysers. The GDL is placed between the flowfield and the membrane. It enables the flow of reactants to and from the reaction sites and provides electrical contact to the electrode. During the assembly process, the cell components are pressed together to ensure good electrical contacts. The GDL is the most compressible part in the cell. Mechanically it acts as a spring that can compensate for production errors or thermal displacements during the operation of the cell. Often, GDLs consist of a carbon fiber substrate and a microporous layer (MPL). The MPL is applied via a coating process on to the substrate during production. While the mechanical properties of the fiber substrate has been subject to extensive research, the mechanical behaviour of the MPL and the MPL/fiber substrate interface is not well understood.

In [1] a theoretical model of a generated fiber substrate is given. This model is coupled to a mechanical model of the MPL and the model is solved in solids4Foam [2]. During compression an inhomogeneous stress distribution is present in the GDL due to the porous nature of the material. The stress distribution in the fiber substrate and in the MPL are evaluated in terms of potential damage to the membrane and the role of the MPL as a mechanical buffer between the inhomogeneous pore structure of the fibers and the membrane is investigated. The deformation predicted by the model is compared to CT images of real GDLs under compression.

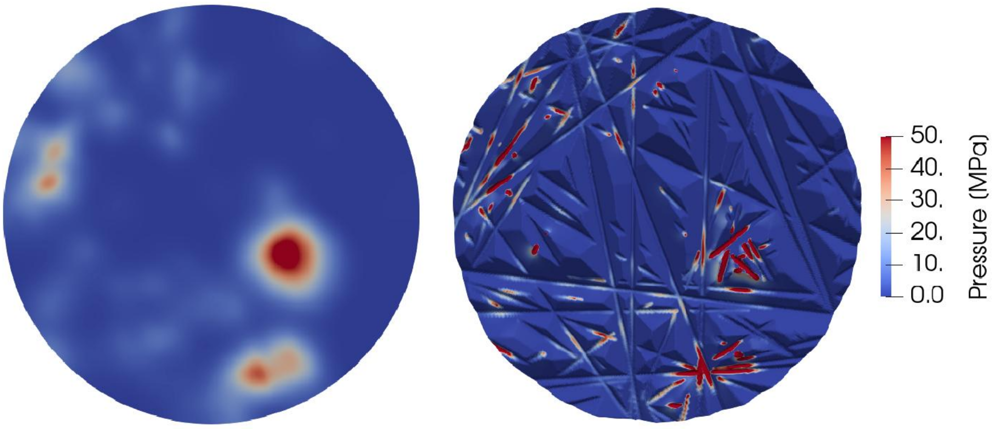

Figure 1: Mechanical stress on the MPL surface during compression of a MPL/fiber substrate composite. The outside is shown on the left; the side facing the fibers is shown on the right.

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Experimental investigation of Freeze/thaw cycle in Proton Exchange Membrane Fuel Cell

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Fuel cells, and in particular those used for mobility (PEMFC), need to operate over a wide range of operating conditions and under cycling conditions of potential, relative humidity and temperature, including freezing conditions. Today, the main causes of PEMFC system degradation are related to operation, whether in normal conditions (start-up/shut-down) or extreme conditions (freezing conditions, cold start-up). The operation of these systems involves drastic temperature cycling conditions ranging from -30°C to almost 100°C, as well as relative humidity conditions ranging from ambient to saturation. Freezing conditions can cause two major issues: (i) degradation linked to internal mechanical stress in the cell due to freeze/thaw cycling (ii) and cold starting, which is particularly problematic for automotive applications, as the aim is to ensure rapid vehicle start-up with minimum energy consumption.

The aim of this study is to understand degradation mechanisms, in particular through characterization during cold start-up. Water freezes in the bipolar plates and catalytic layers and causes delamination and degradation of the AME, drastically reducing its lifetime [1]. Kim et al. [2] reported a performance loss of around 2.4% after just 3,000 freeze/thaw cycles. During periods of freezing the proton exchange membrane loses moisture, leading to a reduction in its volume while the catalytic layer undergoes complex deformations that differ from those of the membrane. These disparities in deformation between the two components can lead to separation or irreversible delamination. The formation of ice can enlarge these openings. In addition, the deterioration of porous materials, such as the catalytic layer and the gas diffusion layer, can be significant, with the appearance of cracks and an increase in porosity. Chen et al. [3] investigated the mechanical degradation of a commercial gas diffusion layer subjected to repeated freeze–thaw thermal cycles while Yang et al. [4] highlighted that freezing-induced crack formation, Pt particle growth, and ionomer agglomeration in the catalyst layer.

In this study, Freeze/thaw cycles on PEMFC are performed between -20°C and +7°C. After the break-in phase and a first characterization, freeze/thaw cycles are repeated few hundred times before a last characterization. This protocol allows to track the main degradations induced by the Freeze/thaw cycle.

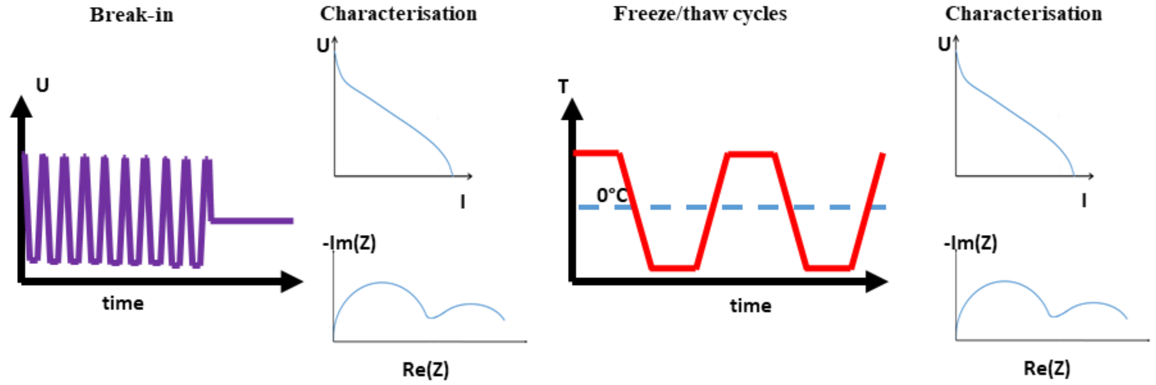

Figure 1: Aging protocol including break-in, freeze/thaw cycle and characterisation.

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Simulations on Electrode Placement for Non-Invasive Localized Impedance Measurements of Polymer Electrolyte Fuel Cells

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Insights into the spatial distribution of temperature, humidification and reactant supply are pivotal for further improvements of Polymer Electrolyte Fuel Cell (PEFC) stacks and systems [1]. An approach to collect spatially resolved impedance data of individual cells in PEFC stacks in a non-invasive way has been developed at PSI in the recent years [2]. It allows for insights into the distribution of membrane hydration during static and dynamic stack operation [3]. The high frequency resistance at 1 kHz is determined by injecting a small current on the surface of the cell and measuring the resulting voltage difference using different electrodes across the outer surface of the cell's flow field plates. The method can be also used for local Electrochemical Impedance Spectroscopy (EIS) though some challenges in signal interpretation remain [4].

The original cabling and electrode positioning intended for frequencies around 1 kHz is not ideal for low frequencies. A less induction sensitive cabling will require a different location for the voltage probing electrodes. In this work we will conduct Finite Element Modelling (FEM) based simulations to assess the optimal placement of electrodes under this new restriction [3, 5].

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Multi-scale Wettability Determination in Gas Diffusion Layers of Polymer Electrolyte Fuel Cells

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Mitigating greenhouse gas emissions from combustion engines has driven the emergence of Polymer Electrolyte Fuel Cells (PEFCs) as a promising alternative, particularly for heavy-duty applications. However, a key challenge remains water accumulation in the porous transport layers originating from the electrochemical reaction and hindering reactant transport to the catalyst layer, causing performance losses during cell operation [1]. Further enhancement of PEFC performance, particularly under high current densities or wet conditions, relies on optimizing porous transport layers (PTLs).

Besides the pore structure, the wettability of Gas Diffusion Layers (GDLs) plays a critical role in efficiently removing water from the catalyst layer. To avoid flooding of the porous structure and promote gas diffusion, GDLs are typically coated with hydrophobic agents [2].

Embedded within the DECODE (DE-centralised Cloud labs fOr the inDustrialisation of Energy materials) project [3], this work aims to lay the groundwork for a more comprehensive understanding of the wettability distribution in GDLs, which is essential for model driven optimizing hydrophobic coatings and improving PEFC performance under challenging operating conditions.

Three different methods for contact angle determination are compared and their applicability to commercial porous transport layer materials is evaluated. The determination of an external contact angle is achieved by implementing the Sessile Drop and Wilhelmy method. An internal contact angle distribution is derived from X-ray tomography data generated by a micro-CT [4, 5]. Particularly, this involves efforts in clarifying image quality requirements to achieve methodological robustness for characterizing local wettability states [6].

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Extension of an OpenFOAM CFD framework for the simulation of PEM fuel cell at the channel scale

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Polymer electrolyte membrane (PEM) fuel cells will play a crucial role in the decarbonization of the transport sector, in particular for heavy duty applications. However, performance and durability of PEM fuel cell stacks are still a concern, especially when operated under high power density conditions. In this context, the optimization of hydrogen and air distributors geometry represents a key factor to optimize both the distribution of the reactants on the active surface - to guarantee a proper water management – together with a proper electrical conductivity, which is function of the contact area. To this purpose, the adoption of computational fluid dynamic (CFD) simulation tools can provide a useful insight into transport of mass, electrical current and species, electrochemical reactions, water formation and removal, which determine the efficient operation of the fuel cell. Thus, CFD tools could represent a valuable support for the design and the optimization of the PEM device at the channel scale. In this work, the open-source simulation library *openfuelcell2* [1], based on the OpenFOAM code, is applied to evaluate both global performance and local physical quantities distributions. A specific test bench consisting of a parallel flow channel configuration installed at Politecnico di Milano is considered. The simulation methodology is based on a multi-region and multi-physics approach, where the different components of the fuel cell are modeled resorting to different computational grids defining different local domains, on which the specific governing equations are solved. Exploiting the availability of the source code, extension of the model and inclusion of different sub-models can be carried out to increase model accuracy. In this context, the library has been extended through the implementation of a specific submodule to account for the formation of Platinum oxides at the cathode side [2], which occurs especially when the fuel cell operates at low current densities, decreasing cell performance. Thus, the model is validated resorting to experimental data acquired at Politecnico di Milano showing a good agreement. Moreover, a new model for the transport of water dissolved inside the ionomer is introduced to properly represent electro-osmotic drag and diffusivity of dissolved phase together with its phase transfer with water vapor [3]. The sensitivity of dissolved phase distribution inside the ionomer is then presented, comparing the results with an alternative, well-documented approach from literature [4].

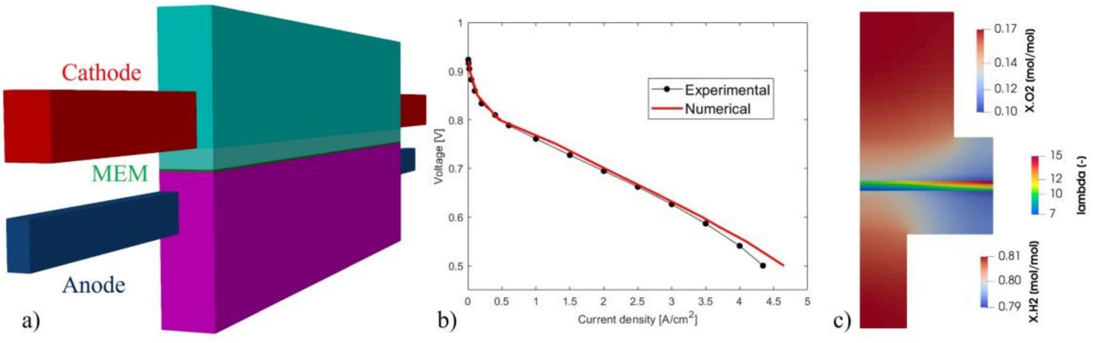

Figure 7: a) Single channel simulation model; b) Experimental and numerical computed polarization curve; c) Computed reaction concentrantions and dissolved water content at midchannel section.

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Surrogate Model-based Parameter Estimation of Physics-based Model for Vanadium Redox Flow Batteries

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A physics-based model for vanadium redox flow batteries (VRFBs) is composed of a set of partial differential equations (PDEs), which describe the electrochemical kinetics of cells and characterize the material properties. This study proposes a parameter estimation framework for the physics-based model to quantify the electrochemical properties of developed materials. To apply optimization techniques to the PDE-based model, its dimensionality must be reduced by constructing a surrogate model [1]. The surrogate model establishes a statistical relationship between the sampled parameter sets to be estimated and the voltage obtained from the PDE-based model using polynomial chaos expansion (PCE). Electrode-related parameters—reaction rate constant at the negative and positive electrodes and specific surface area—are selected to compare two VRFBs assembled with different electrode materials. The probability distributions of these parameters are obtained by repeatedly applying a genetic algorithm (GA), which optimizes the candidate parameter set to fit the surrogate model outputs to the experimental results. The specific surface area, reaction rate constants for the negative and positive electrode for the mesoporous graphite felt (mp-GF) electrode, which demonstrates superior performance [2], are estimated to be higher than those of the thermal-treated graphite felt (TGF) electrode. In addition, variance-based global sensitivities are analyzed for the voltage output for each parameter and operating condition using the constructed surrogate model and Sobol' index. The specific surface area consistently shows the highest Sobol' index in all cases, indicating that it has the highest impact on the voltage value. Moreover, internal states, such as the vanadium ion concentration and volumetric current density, are compared using the PDE-based model with the estimated parameter set. Although the mp-GF electrode exhibits more uneven state distributions than the TGF electrode, VRFBs with the mp-GF electrode can be charged to higher SOCs and discharged to lower SOCs. Consequently, higher electrode-related parameters lead to lower overpotentials and wider operating SOC range. The proposed framework helps quantify properties with restricted data and analyze the behavior of cells assembled with newly developed materials.

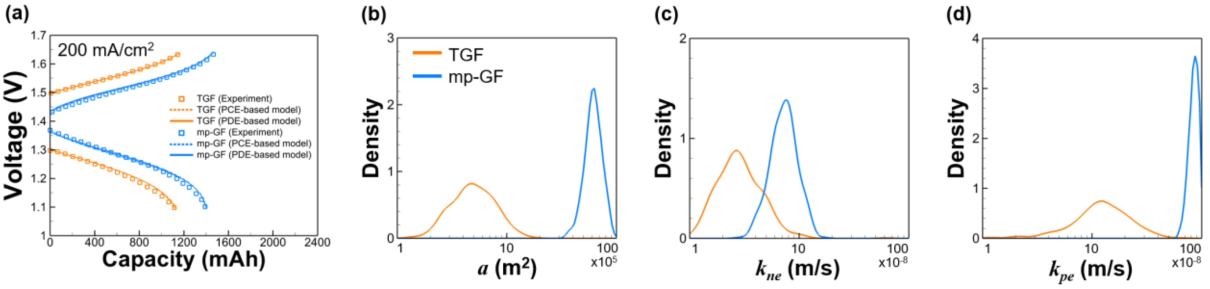

Figure 1: The voltage comparison of the VRFB cells obtained from the models using identified parameters with those from the experiments under the current density of (a) 200 mA cm^{-2}. (b-d) Distribution of estimated parameters for different materials.

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A spatially averaged pseudo-3D model for analyzing operating heterogeneities in large PEM fuel cells

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To address the performance and lifetime limitations of Proton Exchange Membrane Fuel Cells (PEMFCs), it is crucial to comprehend the operating heterogeneities at the cell scale. However, the distributions over a large PEMFC active surface area are subject to cross interactions, which renders the phenomenon of operating heterogeneities complex to understand. The study of a wide range of operating conditions is then necessary to better understand operating heterogeneities. To that end, a numerical approach is appropriate. This work is a new step towards a versatile, accurate and low time complexity model for the design of PEMFC, their understanding and improvement of performance and durability. The model presented is a spatially averaged, pseudo-3D model of a large PEMFC (~250 cm²) and developed under COMSOL Multiphysics®. It considers the cell as a superposition of layers, each layer being in-plane discretized to allow the observation of local heterogeneities over the MEA region. The transport equations are solved using a pseudo-3D approximation developed and implemented in a previous model by F. Nandjou et al. [1], integrating a semi-empirical cell voltage law for the current density prediction. Extending their work, a new approach was developed that allows significant reduction in computational time by spatially averaging the channels geometry over the active surface area [2]. Once calibrated with dedicated experimental results, the spatially averaged pseudo-3D model is used to calculate the distributions for 108 operating conditions. These simulation results give the influence of operating conditions on cell performance and on the uniformity of the current density distribution on the active surface area. Subsequently, a stack-scale experimental study substantiates the trends observed in the simulations.

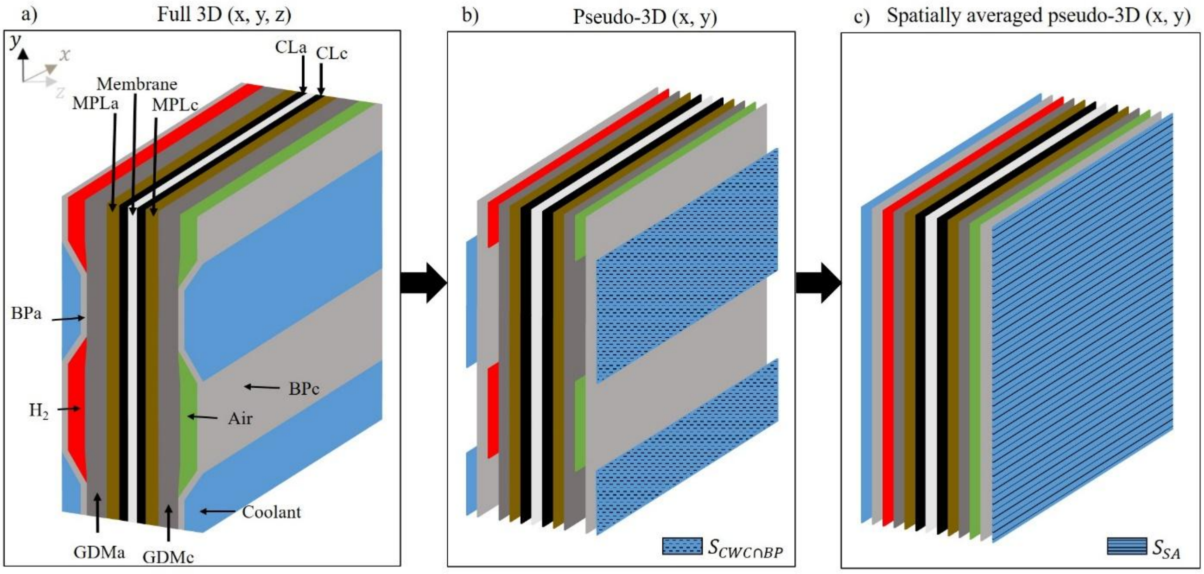

Figure 1: 3D representation (a), P3D representation (b) and spatially averaged representation (c) of the cell at rib/channel scale

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Unveiling the Deposition Dynamics in Hybrid All-Fe Redox Flow Batteries based on kinetic Monte-Carlo Simulations

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The growing demand for cost-effective, eco-friendly, and scalable stationary energy storage has driven interest in iron-based Redox Flow Batteries (RFBs) as a promising alternative to conventional systems like Vanadium and Zinc-Bromine RFBs [1]. Iron is affordable, environmentally friendly, and can be used as anolyte and catholyte in all-Fe RFBs [1]. As it only exists in oxidation states 0, +II, and +III it has the drawback that it deposits as solid metallic iron on the anode surface, leading to the term hybrid all-Fe RFB being illustrated in Figure 1a [2]. However, inhomogeneous layer deposition, hydrogen evolution reaction (HER), pH instability, and iron hydroxide precipitation hinder their practical implementation [2]. It is assumed that altered parameters and electrolyte compositions can influence the morphology of the deposited iron, but molecular-level mechanisms remain poorly understood [3].

This work employs kinetic Monte Carlo simulations based on a Lattice-gas model to investigate these molecular-level processes. A 3D BCC lattice is used to simulate adsorption, diffusion, reaction and desorption of electrolyte species on a planar glassy carbon surface as illustrated in Figure 1b. The model calculates transition probabilities for steps based on reaction rates and taking into account binding energies with neighbouring molecules. Butler-Volmer type equations govern iron plating and stripping. HER is divided into the discrete Volmer, Heyrovsky and Tafel step. Molecular diffusion on the surface is modelled as jumps between neighbouring adsorption sites. Outputs such as layer thickness, Faradaic current, open and closed porosity are analysed and compared to experimental data from rotating disc electrode tests, where effects of diffusion in the electrolyte are minimal.

Cyclic voltammetry (CV), chronoamperometry and line potential sweeps were used to parameterise and validate the model. The current resulting from the electrochemical processes was then analysed as a function of the anode potential. Individual parameters that could not be taken from the literature (e.g. activation energies) were adjusted so that the simulation results mimicked the data from the experiments. As can be seen in Figure 1c, the model is able to reproduce the main features of electrochemical experiments, i.e. peak position and shape in CV experiments. In addition, parameter variations were carried out to analyse their influence. These include temperature, pH value and binding energies.

In conclusion, the presented model provides the basis for a mechanistic understanding of iron precipitation and HER at the molecular level. Future work can build on this to achieve a knowledge-based design of electrochemical cells in all-Fe RFBs.

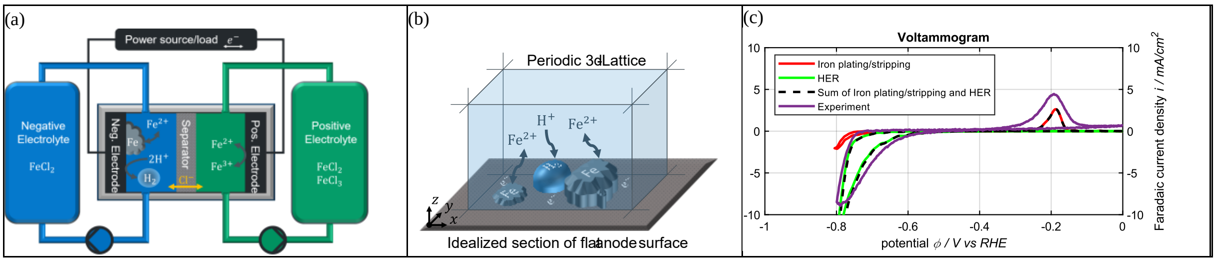

Figure 1: Schematics of a hybrid all-Fe RFB (a), illustration of 3D kinetic Monte-Carlo Model setup (b), voltammogram of simulation and reference measurement (c)

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Impact of temperature dependent kinetic parameters on overpotential distributions in solid oxide cells

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Prediction and investigation of local conditions (e.g., overpotentials and fuel depletion) that impact performance and lifetime of solid oxide cells (SOCs), requires spatially resolved models with adequate parametrization and extensive validation.

In this work a state-of-the-art SOC is characterized and kinetic parameters are determined according to an established procedure utilizing electrochemical impedance spectroscopy [1]. Characterization at three temperatures reveals temperature dependencies of multiple parameters that were previously taken as temperature-independent and improve the computation of the activation overpotentials at both electrodes. Validation of the determined parameter sets is conducted by comparison of model results with current voltage curves measured on button cells at several operating conditions.

The parameter sets determined at different temperatures are implemented in a spatially resolved 3D COMSOL cell model based on [2,3] to investigate the impact of the observed temperature dependencies of kinetic parameters on the distribution of activation overpotentials and current density. As significant temperature differences across the cell area are expected in technically relevant application, i.e. larger stacks and systems [4,5], and therefore the effect of temperature dependencies is intensified, investigation is conducted for active cell areas of 16 cm² and 121 cm².

Temperature profiles in SOCs vary significantly between fuel cell and electrolysis mode due to the different role of the reversible part of the electrochemical reaction heat, i.e. acting as a sink during electrolysis and as a source during fuel cell operation. Hence, operating points at both electrolysis and fuel cell operation are investigated.

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Electrochemical ammonia synthesis on an iron based electrode and a $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{3-\delta}$ membrane

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Electrochemical ammonia synthesis is demonstrated at ambient pressure and temperatures between 400°C and 600°C using proton-conducting ceramic cells (PCC). A suitable electrode structure was designed and iron as the electrocatalyst selected (Fig. 1). The ceramic cells are fabricated by wet chemical processes with $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{3-\delta}$ as the main ceramic component. To obtain an optimal distribution of percolating iron particles in the working electrode structure, the investigated metal catalyst is pressed into a previously sintered backbone layer by screen printing.

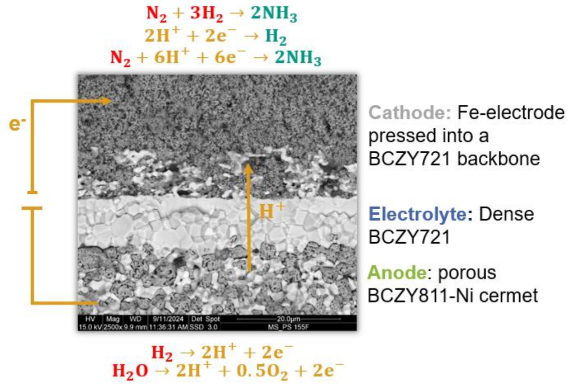

Figure 8: PCC layers and reactions at the respective electrodes.

Electrocatalytically active electrodes with an active area of 12.57cm² were evaluated under various configurations involving gas supply, temperature, and applied voltage. Experiments examining the influence of the cathode gas configuration on ammonia synthesis revealed that, the protons transported through the electrolyte to the cathode have a negligible impact. Figure 2 illustrates the ammonia synthesis rates as a function of the applied voltage for three different gas configurations, highlighting the significant role of the cathode gas composition. When only nitrogen is supplied to the cathode (blue curve), ammonia formation is minimal and the ratio between ammonia formation at -1.4V relative to OCV is less pronounced. This suggests that the protons migrating through the electrolyte do not have superior properties for activating N_2. Furthermore, this configuration is thermodynamically unfavourable, restricting ammonia formation to levels near thermodynamic equilibrium. In contrast, when hydrogen is included in the cathode gas supply (orange curve), ammonia formation is significantly enhanced. For the configuration where the anode is supplied with inert gas and the cathode with a nitrogen-hydrogen mixture (green curve), the effect of proton transport through the electrolyte becomes negligible. The data suggest that blocking the primary function of a proton-conducting ceramic cell favors ammonia synthesis.

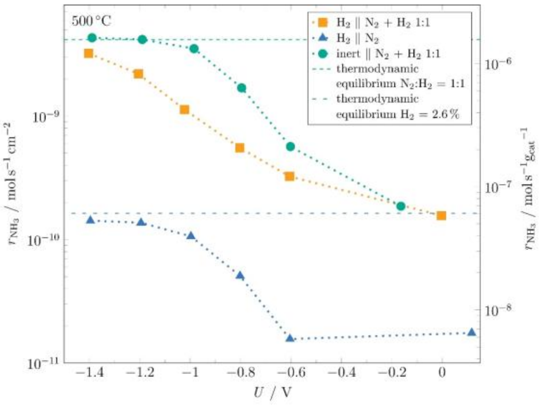

Figure 9: Ammonia formation as a function of cell voltage for 3 different gas configurations.

These findings indicate that the electrochemical promotion of catalysis (EPOC) is the dominant mechanism for nitrogen activation during ammonia synthesis. The protons transported through the electrolyte appear to interfere with the surface EPOC process, disrupting the catalytic activation and/or adsorption of nitrogen.

Multiscale Simulation of a Solid Oxide Electrolysis Cell Stack: Evaluating the Influence of a Manifold on the Performance

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Motivation

The production capabilities of Solid Oxide Cells (SOCs) are currently being scaled up around the globe and numerous commercial projects aim to leverage the unique advantages of this promising energy conversion technology. To ensure the success of such initiatives, robust SOC stack models are essential. They help in predicting the performance and durability of SOCs, allowing to optimize their design and operating conditions.

Despite the variety of available numerical models, the impact of the manifold geometry on the performance of SOC stacks is often neglected due to the significant challenge posed by adequate flow models. Herein, a fast and accurate flow model is added to the multiscale SOC modelling framework DETCHEM^{SOC} [1] in order to evaluate the influence of the manifold on the performance of an electrolysis stack of 40 Ni-YSZ/YSZ/LSM-YSZ cells.

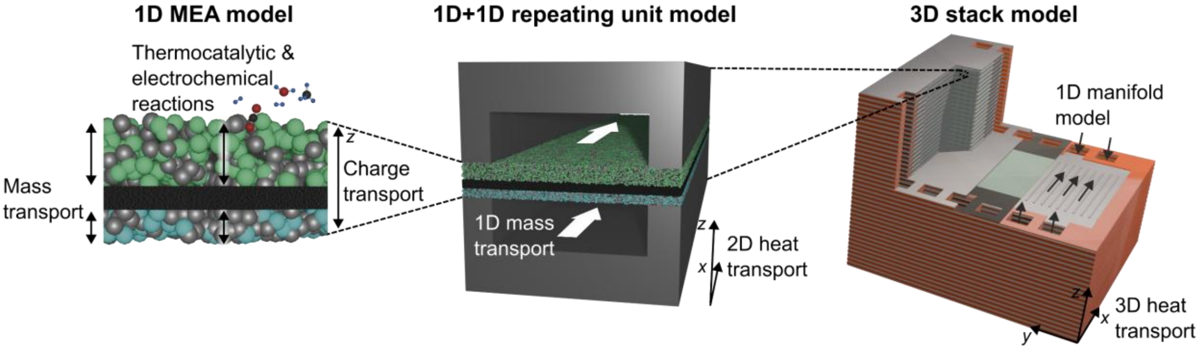

Figure 1: Hierarchical modelling approach for button cell, repeating unit and stack simulation.

Methodology

The simulations are performed using the DETCHEM^{SOC} modeling framework from the DETCHEM^{TM} detailed chemistry software package. The model is designed for the transient simulation of SOCs, including button cells, planar repeating units, and stack modules. It employs a hierarchical approach, enabling calibration with button cell experiments and subsequent application to larger systems. As depicted in Figure 1, the framework includes spatially resolved models for thermocatalytic and electrochemical reaction kinetics, charge transport, mass transport and heat transport. For this study, the stack model was expanded with an internal manifold flow model calibrated in a preceding study [2].

Results and discussion

The investigation reveals that, in an electrolysis stack of 40 cells operated at current densities of up to -2.11 A cm^{-2} over the active cell area, significant flow maldistribution close to 20% is observed over the height of the stack. Maldistribution between repeating units of the same cells, induced by changes in the fluid viscosity due to temperature gradients, is observable but comparatively small. Despite the magnitude of the flow maldistribution, the influence on the stack temperature and potential distributions is small, and the global performance remains mostly unaffected owing to compensating effects.

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2D FEM model for simulation of high temperature steam and co-electrolysis with a nickel/MIEC cermet electrode

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High-temperature electrolysers, based on oxygen conducting oxides, offer unique opportunities for the conversion of power towards higher-value chemical products. Besides the ability to operate at excellent efficiencies [1], the flexibility of different possible feedstocks that can be supplied to the electrolyser is a major advantage compared to other electrolysis technologies. The simultaneous electrolysis of steam and carbon dioxide in a single electrolyser produces tailored mixtures of synthesis gas with defined H_2/C ratios in a single step, which can then directly be used for downstream chemical processes, such as a Fischer-Tropsch synthesis. Often, unreacted educts from the downstream process, or unwanted by-products such as methane, are stripped off and resupplied to the SOEC. [2] The result is an electrode, operating under an atmosphere consisting of five or more different gas species, leading to various thermo- and electrochemical reactions. As a step towards understanding the electro- and thermo-chemical electrode-gas interactions and their influence on performance and product gas composition, an isothermal 2D FEM model of a commercial electrolyte-supported SOEC is developed in the software COMSOL Multiphysics®. The cell consists of a 3YSZ electrolyte, sandwiched between a GDC/LSCF air electrode and a Ni/GDC fuel electrode. The electrochemical kinetics are parameterized by electrochemical impedance spectroscopy measurements on 1 cm^2 button cells. [3] Further, thermochemical reaction kinetics, such as the reverse water-gas shift reaction and methane-steam reforming, are obtained by analysing 16 cm^2 electrodes in an inert environment. Gas samples are taken along the length of an alumina oxide channel over the electrode and analysed by gas chromatography to parametrize first order thermo-chemical kinetic approaches. Finally, the model is validated with 16 cm^2 single cell tests by current-voltage curves and gas chromatography along the gas channel. A very good agreement between predicted and simulated performance under steam and co-electrolysis operation is shown. Also, the model can accurately predict concentrations along the channel under operation with various H_2/C ratios, including feed gas compositions containing methane.

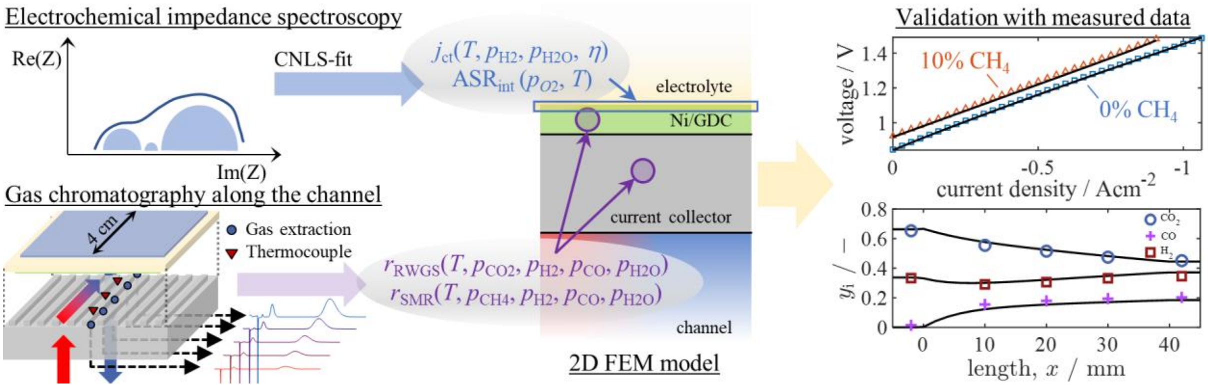

Figure 1: Schematic project overview. EIS and gas chromatography data are used to parametrize the FEM model. Validation through IV-curves and gas composition.

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Evaluation of Cell Housing Designs for Pressurized Testing of Solid Oxide Single Cells

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Pressurized operation of SOCs offers benefits in SOFC mode as it improves the performance and enables a coupling with a gas turbine. In SOEC mode efforts to pressurize produced hydrogen or syngas can be reduced.

Known facilities for pressurized operation of SOCs are based on pressure vessels enclosing the cell or stack to be operated. In a previous study the pressurized operation of SOCs without pressure vessel was presented on single cell level for electrolyte-supported cells (figure 1 (a) - (c)), which is extended for anode-supported cells (figure 1 (d)) in this work [1]. The cell is contacted with metallic flow fields similar to a stack within a metallic cell housing [2]. The application of such metallic components can be critical with respect to corrosion, chromium evaporation and subsequent poisoning of the air electrode especially for chromium oxide scale forming steel grades such as Crofer 22 H. Ideally, the cell behaviour is not affected by its testing environment as it was shown for cell housings made of Al_2O_3 [3]. Thus, a metallic cell housing made of an Al_2O_3-forming steel grade was chosen for pressurized testing and compared with a cell housing made of Crofer 22 H. The latter requires modifications in order to enable more inert testing conditions which is solved by ceramic inner parts as shown in figure 1 (e) in a Crofer 22 H shell with ceramic flow fields and ideal cell contacting with Au- and Ni-grids. Finally, all concepts are compared in this work and evaluated with respect to their readiness level for pressurized testing.

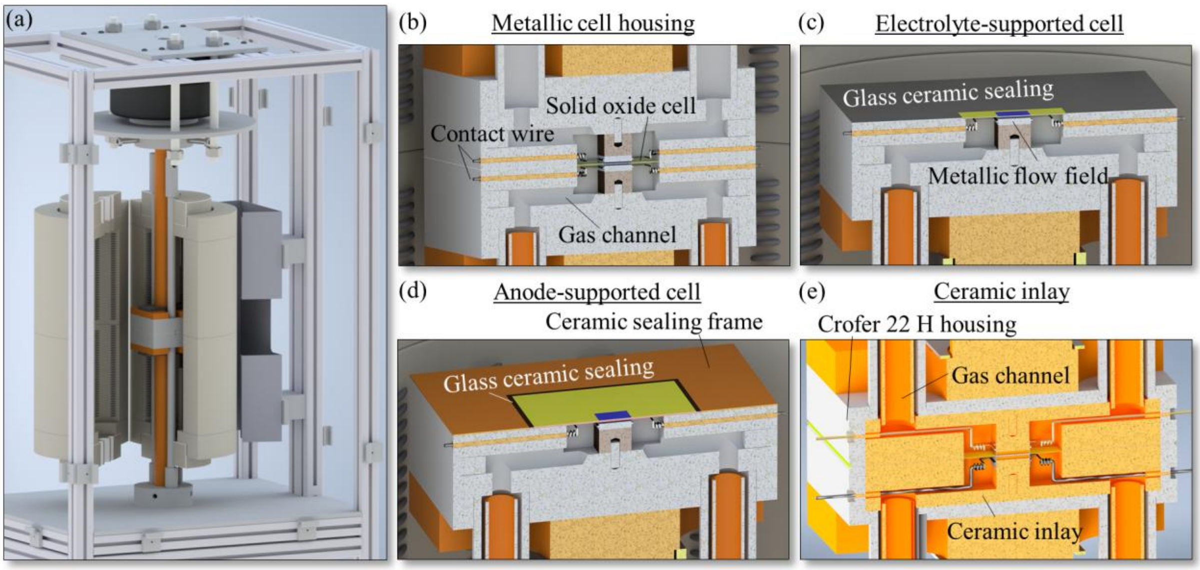

Figure 1: CAD-drawing of pressurized test bench in (a) [1] and with cross-section of metallic housing in (b) with glass ceramic sealing in (c) and (d) for an electrolyte- [1] and anode-supported cell as well as ceramic inlay in (e).

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Pressurized Testing and Modeling of Solid Oxide Single Cells

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Pressurized operation of SOCs reached a lot of interest as it improves the SOFC performance, enables a coupling with a gas turbine and reduces efforts to pressurize hydrogen or syngas produced in a SOEC. Facilities for pressurized operation of SOCs are known to be based on pressure vessels enclosing the cell or stack to be operated.

In this contribution, experiments were performed in a newly developed test bench [1] without pressure vessel as shown in figure 1 (a) and (b). In the single cell test bench fuel and air side are pressurized by a concept that minimizes the differential pressure over the cell. The cell housing is based on welded metallic components and is sealed towards the cell by a glass-ceramic sealant (figure 1 (c)). This sealant could be successfully exposed to a pressure of up to 11 bar_a during testing and was able to withstand a full thermal cycle. The cell is contacted with metallic flow fields similar to a stack (figure 1 (d)) [2].

We will show that in the pressurized mode the increase in open-circuit voltage is in good agreement with the theoretical predictions according to the Nernst-equation. IV-characteristics and impedance spectra measured at elevated pressures of up to 11 bar_a will be shown. The impact of pressurized operation on loss mechanisms will be discussed with the distribution of relaxation times. The cell performance in SOFC- and SOEC-mode will be presented and compared with predictions from our 0D electrochemical model [3].

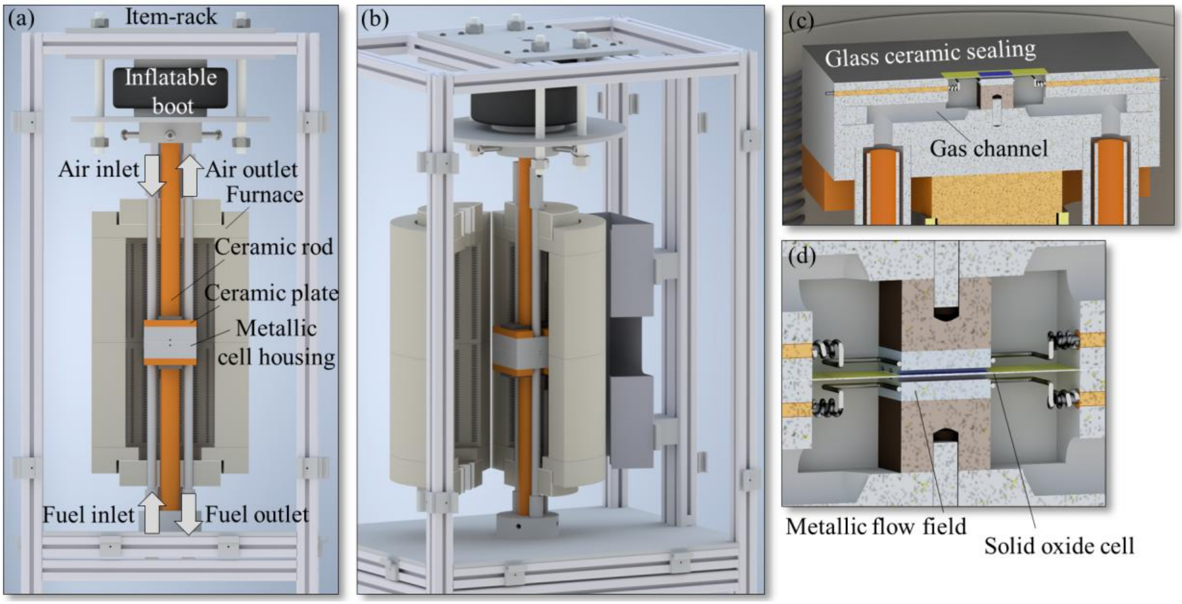

Figure 1: CAD-drawing of pressurized test bench in (a) and (b) with cross-section of glass ceramic sealing in (c) and stack-like contacting in (d). [1]

References:

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3D Segmentation and Characterization of Solid Oxide Cells

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Solid Oxide Cells (SOC) contribute to the energy transition due to their high efficiency, large fuel flexibility and reversibility between fuel cell and electrolysis operations. The SOC microstructure directly affects performance and durability, making the microstructural analysis an essential part in SOC research. The SOC is composed of three phases: wetting, non-wetting and solid. A highly efficient SOC is characterized by low phase tortuosity, high percolation and high triple phase boundary (TPB) density. During operation, the SOC microstructure evolves, and several imaging techniques can be used to observe this evolution. Advanced 3D electron microscopy techniques like Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) provide rich datasets for studying these materials, but processing and analysing these datasets require specialized tools and methodologies [1].

In this study, FIB-SEM images are obtained for an electrolyte supported cell (ESC) SOC using metallic nickel with gadolinium-doped ceria (GDC). A MATLAB code is developed to segment the FIB-SEM images, then to extract microstructural properties from these segmented images. In this study, we calculate the volume fractions of the different phases (Ni, GDC and porosity), their connectivity, particle size distribution and mean particle diameter, tortuosity, 2-phase interface surface area and triple phase boundary density [1]. The goal of the study is to compare the microstructural properties of the SOC before and after 456h of operation to discover if there is any cell degradation, and how the degradation occurs.

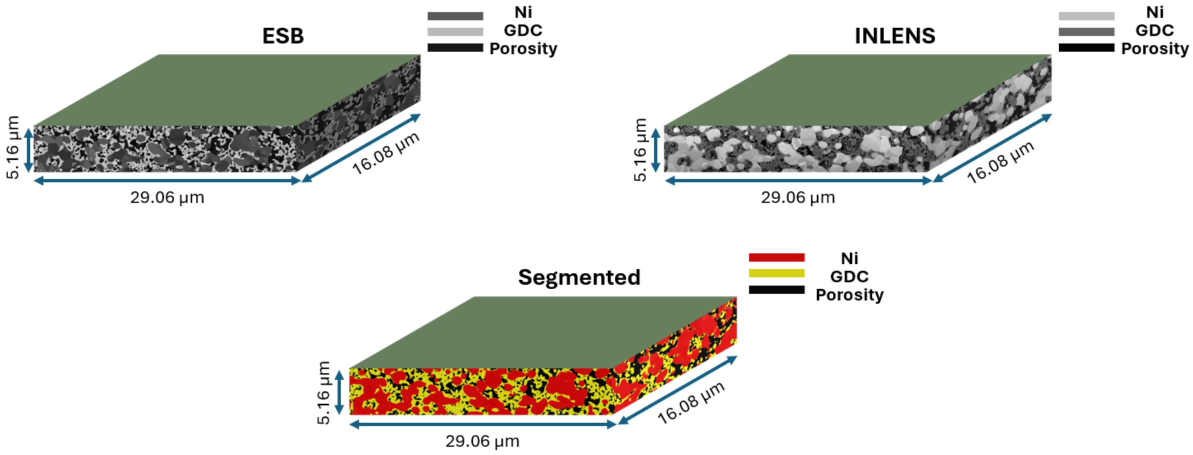

Figure 1: Imaged sample of the pristine ESC cell. The figure shows the 3D reconstruction of the FIB-SEM images, obtained using ESB and INLENS detectors, as well as the segmented sample obtained using the MATLAB code developed.

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CFD-Based Mesoscale Simulation of Triple Phase Boundary Effects on Solid Oxide Cells Performance

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This study introduces a three-dimensional multiphysics mesoscopic model to simulate gas transport and electrochemical reactions within the electrode microstructures of solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs). The model captures the intricate porous microstructure of fuel electrodes and integrates charge and species transport, with particular emphasis on the electrochemical processes occurring at the triple phase boundary (TPB) — a critical site for reactions [1]. The model is implemented using an open-source computational fluid dynamic (CFD) library, OpenFOAM.

A precise quantification of active TPBs is crucial for understanding anode degradation and performance losses [2]. This study evaluates the impact of two distinct TPB identification methods, which consider TPBs as either lines or voxels, on their distribution and the associated electrochemical performance. These methodologies produce varying TPB distributions that significantly influence performance predictions [3]. To incorporate these variations, the mesoscopic model employs localized volumetric source terms, enabling a detailed representation of electrochemical reaction dynamics.

In this work, the electrode microstructure was digitally reconstructed from focused ion beam scanning electron microscopy (FIB-SEM) images as shown in the left panel of Figure 1 [4]. The middle panel illustrates the two TPB identification methods. By applying the model, the performance is evaluated, as shown in the right panel, which displays the distributions of ionic potential, electronic potential, and hydrogen volumetric fraction. This work aims to establish a robust and accurate framework for subsequent phase-field simulations. To achieve this purpose, the differences in the electrochemical performance calculations between the two methods under electrolysis cell and fuel cell modes have been studied and compared, considering various factors such as computational domains at different scales, geometries at different positions, gas concentrations, and temperature.

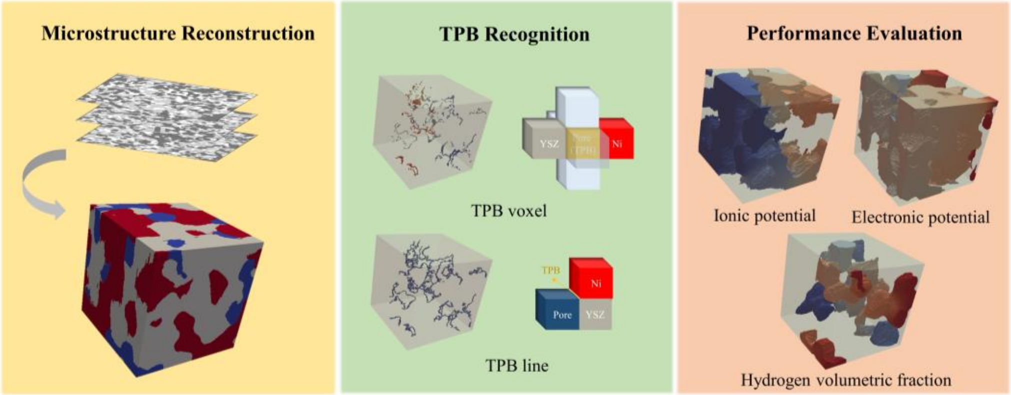

Figure 1: Mesoscale Simulation Process: Microstructure Reconstruction, TPB Recognition, and Performance Evaluation in Electrode Microstructures.

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Unraveling Performance Decay in Solid Oxide Electrolysis Cells: Laying the Groundwork for Experiment-Driven Modeling Approaches

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Solid Oxide Electrolysis Cells (SOECs) promise efficient hydrogen production but face long-term degradation limiting widespread application. This work lays the groundwork for an integrated approach using finite element method (FEM) modeling and experimental data to understand degradation mechanisms in commercial, fuel-electrode-supported Ni-YSZ SOECs. Data on performance decay and microstructural changes collected within the first 500 hours of operation via *i-V* characterization, Electrochemical Impedance Spectroscopy (EIS), and FIB-SEM tomography serves as the basis for model validation and refinement.

Initial performance analysis revealed rapid degradation during the first 100–150 hours, transitioning to a steadier decline. EIS analysis, complemented by Distribution of Relaxation Times (DRT), linked these observations to changes in the spectra's high-frequency range, indicating charge transfer and reaction limitations at triple-phase boundaries (TPBs). Initial performance loss was attributed to Si-poisoning, while Ni-related mechanisms dominated subsequent degradation, consistent with literature findings [1],[2].

The FEM model, developed in *COMSOL Multiphysics*® incorporated porosity, tortuosity, and surface-to-volume ratios derived from FIB-SEM tomography [3],[4],[5]. The parameter studies confirmed the influence of microstructural effects on cell performance. However, the model still needs to capture more parameter interdependencies to align with experimental observations. Thus, the modeling results will be discussed concerning correlation of factors that need to be included for the emulation of measurement results.

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Model-Based Analysis of Hydrogen Supply in Integrated PEM Fuel Cell/Liquid Hydrogen Tank Systems for Aviation Application

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The aviation industry is exploring sustainable alternatives to fossil fuels in order to achieve the increasingly stringent global decarbonization targets. Electrification of the main propulsion system using liquid hydrogen (LH2) powered polymer electrolyte membrane fuel cells (PEMFC) is seen as a potential solution particularly for short-range applications [1]. The scale-up and weight optimization of such systems in the megawatt range is necessary to meet the power and mass requirements for regional aircraft.

This study presents the modeling and validation of an LH2-PEMFC system with 600kW net power. The model is developed in-house in Modelica and includes the LH2 tank system, the multi-modular PEMFC system and the thermal system. Hydrogen is pre-conditioned before supplied to the PEMFC system. The integrated thermal system enables heat recovery from the fuel cells to vaporize and heat cryogenic hydrogen. The main components, PEMFC and LH2 tank, are validated by comparing with literature data. Load profiles based on realistic flight scenarios are simulated and the dynamic behaviour of hydrogen supply as well as its impact on fuel cell performance are investigated.

Key findings as shown in Figure 1 indicate that the LH2 tank pressure can be stabilized by an internal electrical heater and remains stable within 80 mbar during anode purge procedures and load variations. Additionally, the hydrogen supply temperature and the related anode inlet gas humidity variations under the current control strategy do not induce significant performance fluctuations. However, the anode inlet humidity with an average value of ~0.25 is generally low, offering the possibility for improvements of performance and durability by further humidification.

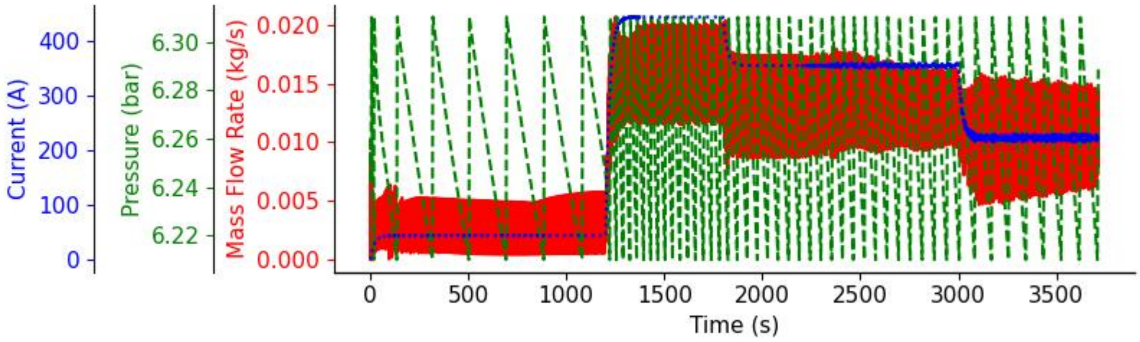

Figure 1: Current demand for a single fuel cell module (blue), variation of LH2 tank pressure (green) and LH2 mass flow rate (red) throughout the flight mission.

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Integrated Optimization of PEM Electrolyzer and BoP Dynamics: Demand-Based Hydrogen Production and Storage Using Solar, Grid, and Hybrid Energy Strategies

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Modeling electrolytic hydrogen production facilities, similar to generators in electric power systems, demands a comprehensive understanding of the underlying technology. Detailed models must incorporate cost and performance characteristics alongside sector coupling considerations specific to green hydrogen production. Integrating green hydrogen production into power system planning is increasingly recognized as critical for advancing sustainable energy systems [1]. The increasing penetration of solar photovoltaic (PV) systems has made their coupling with Proton Exchange Membrane (PEM) electrolysis a widely adopted strategy. This approach offers scalability and cost-effectiveness for hydrogen production. PEM electrolysis offers significant advantages, as demonstrated in both real-life measurements and simulations, including rapid response to fluctuations in electricity input, which enables efficient adaptation to the variable output of PV systems. However, despite the growing body of zero-dimensional mathematical models and optimization approaches for hydrogen production, many studies fail or avoid capturing critical complexities. These include the role of power electronics in the coupling, the nonlinear relationship between hydrogen production and varying electricity input fractions, and the dynamic electrical requirements of the Balance of Plant (BoP) in PEM electrolysis systems. Moreover, many published optimization models rely on linear assumptions, oversimplifying the inherently dynamic nature of hydrogen production processes, such as the non-linear response of PEM electrolyzers to fluctuating electricity inputs, temperature-dependent efficiency variations, and the transient behaviors during start-up and shut-down cycles. These models often overlook key components of the Balance of Plant (BoP), such as power electronics losses, which significantly impact overall system performance. Such simplifications can lead to inaccuracies in calculating hydrogen production and estimating the electrical requirements of the electrolysis plant, ultimately resulting in an underestimation of the levelized cost of hydrogen production.

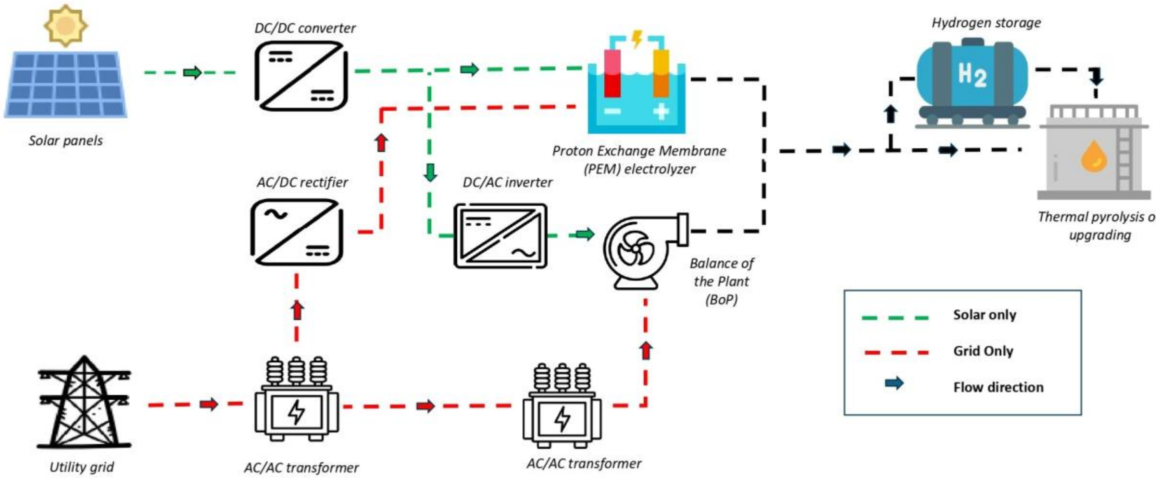

Figure 1: Operation strategies

Building on the identified challenges of linear assumptions and oversimplified models in PEM electrolysis systems, this study adopts a more comprehensive approach to improve accuracy and understanding. This study adopts information from an Aspen Plus PEM electrolysis model to address these gaps, incorporating nonlinear dynamics for hydrogen efficiency and BoP electrical requirements, including power electronics losses, to enhance optimization accuracy [2]. This research is conducted within the framework of the Circular Fuel Project, which seeks to establish a stable downstream supply of green hydrogen for Sustainable Aviation Fuel (SAF) production through solar pyrolysis. An integrated optimization model is developed to minimize operational costs while meeting a defined hydrogen production target over different time scales, such as hourly, daily, or weekly. Energy strategies — grid-only, solar-only, and hybrid — are evaluated across three European locations with varying solar availability and electricity prices. The analysis reveals that hybrid systems reduce the frequency of electrolyzer shutdowns and start-ups, driven by high electricity prices in grid-only strategies and limited solar availability in solar-only strategies. To ensure a stable hydrogen supply for downstream processes, the study integrates hydrogen storage into the optimization framework. This integration not only adds complexity but also facilitates the adjustment and validation of time scales for hydrogen production targets. By exploring various demand contract strategies, the study optimizes the size of the hydrogen storage system, ensuring a balance between the reliability of the system and cost-effectiveness. By bridging technical and economic aspects, this work delivers actionable insights and a robust framework for optimizing future electrolyzer projects.

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A homogenized modeling approach for heat transfer-flow coupling in stacked structures

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Devices with complex, repetitive stacked structures are crucial in chemical and thermal industries, and usually operate with multiple energy conversion-transport processes coupled intensively. The investigation in their design and performance is hindered by the extensive boundary layer grids and computational resources, due to the complex geometric complexity and nonlinearity of the Navier-Stokes equations. To ease such difficulty, homogenization method has been developed to simplify stacked structures into uniform porous media, however, such methods currently focus on individual field in flow or heat transfer, with limitation for fully-coupled multi-physics fields. Thus, in this paper, the homogenized method was modified by further replacing Navier-Stokes equations with Darcy's law for fully-coupled heat-flow fields, with a subsequent validation via a single repetitive unit and 5-layer plate heat exchanger. Results show that the homogenization model accurately predicts temperature, flow rate, and pressure distributions with less than 10% errors, and is robust under broad working conditions. Compared to the homogenized model with Navier-Stokes equation, the new model reduces computational time by 97% without loss of accuracy. This computational efficiency enables precise modelling of full coupling of multi-physics in complex, full-scale stacked structures, such as compact heat exchangers, fuel cell and electrolysis stacks.

CFD Simulation of Novel Spacer Designs for Membrane Humidifiers and Experimental Validation

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Water management has a crucial role in ensuring high efficiency and longevity of polymer electrolyte fuel cells. As part of water management, membrane humidifiers are a promising option to appropriately humidify the supply air stream in automotive applications. In a membrane humidifier, the humid exhaust gas stream from the fuel cell and the dry fresh air flow are brought into contact via a semi-permeable membrane to enable the water transfer to the dry side. In flat sheet membrane humidifiers, which are the focus of this talk, the gases usually flow through channels in a flow field, arranged in a cross-flow or counter-flow pattern. No additional water supply is needed since the humid exhaust stream serves as a water source. Other advantages are compact design and low parasitic losses.

To ensure sufficient humidification, the choice of membrane and flow geometry is of crucial importance. Pure Perfluorinated sulfonic acid (PFSA) polymer-based membranes or PFSA-based composite membranes are predominantly used in membrane humidifiers. Flow geometries usually consist of several channels with simple geometric cross sections such as rectangles. Alternatively, so-called spacers can be placed between individual membrane layers instead of channel geometries. This concept can enhance the mass transfer by increasing the free membrane surface area and by interrupting the formation of boundary layers. This reduces the boundary layer resistance and thus increases the water transfer. Studies on spacers can be found in other membrane applications in the literature, such as those used in energy recovery ventilators [1].

In this talk, a novel spacer geometry for membrane humidifiers is presented. The water transfer and pressure drop of a humidifier with a composite membrane in combination with the novel spacer were characterized at different operating conditions at our institute's single-layer membrane test rig [2]. The results show that the use of spacers can significantly increase the water transfer in a humidifier compared to channel geometries [3]. Furthermore, a CFD setup in ANSYS Fluent is presented. It is used to analyze the mass transfer in a membrane humidifier with complex spacer geometries and composite membranes. The model is validated with measurement data from the test rig at our institute. It is shown that the model is a suitable tool to investigate the influence of geometries on water transfer in humidifiers. In future investigations, the model will be used to systematically analyze different spacer geometries regarding their influence on humidifier performance.

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Impact of system efficiency maximization on an SOFC inside a hybrid SOFC + mGT system

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The fuel-to-electricity efficiency of a Solid Oxide Fuel Cell (SOFC) nowadays easily exceeds 60%. It can be further increased by utilizing the exergy contained in the hot outlet gases (Figure 1). Expanding these gases in a micro gas turbine (mGT), after having burned the remaining fuel, allows the recovery of a portion of the residual work. However, an optimal heat exchanger network needs to be designed to maximize the efficiency, which leads to strong interactions between system components. The maximization of the system efficiency has therefore an impact on each sub-system, especially the SOFC and the mGT. The optimal working conditions of the SOFC are not longer perfectly followed, which can have an impact on its lifetime [1] and operational safety.

The results show that the system efficiency maximization tends to influence most of the main parameters of the SOFC. The fuel utilization was varied from 77% to 86%. The optimizer tends to maximize it as the SOFC is the main contributor for electric production. The remaining energy for the mGT is however greatly reduced which leads to a degradation of the mGT efficiency. The steam to carbon ratio has almost no impact on the system efficiency between 1.8 and 2.2. The outlet gas temperature is maximized up to 780°C to reduce the air flow on the cathode side and direct more heat directly to the downstream system, the mGT, to allow for larger working conditions (especially during transient). The system optimization found an optimal system efficiency of around 66%, decreasing the optimal SOFC efficiency by around 3%.

In the simulations, the characteristics of existing components, such as the heat exchangers and the SOFC, were incorporated to achieve the most realistic results. Future work will address the dynamics of such complex system, and in a near future, experimental validation of the steady-state and dynamic simulation results will be conducted using a 10 kW demonstration setup.

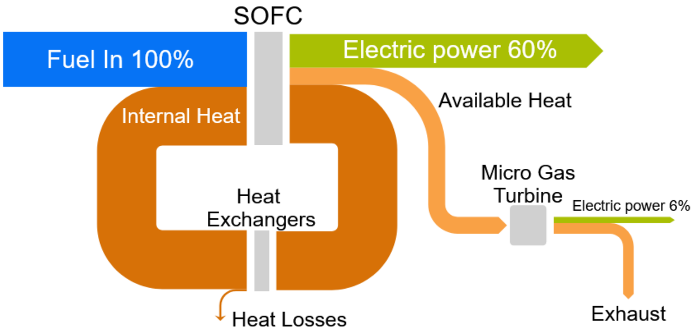

Figure 1: Energy and heat circuit from Fuel to Electricity in a SOFC + mGT system

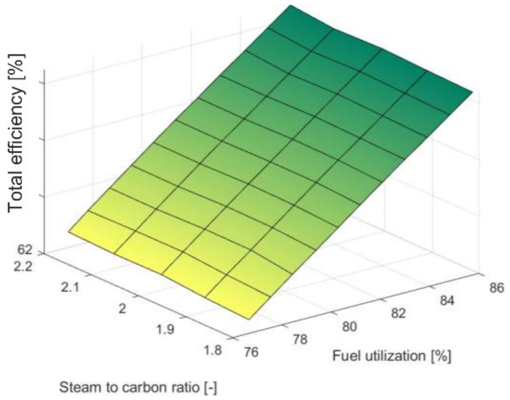

Figure 2: Impact of SOFC parameters on the system efficiency

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Abstracts for Poster Contributions

Energy Storage

Pathway towards a Validated Simulation Model for All-Solid-State Batteries

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All-solid-state batteries (ASSBs) are strong candidates for the next generation of batteries for automotive and aviation applications due to their increased energy density and improved safety achieved by eliminating flammable liquid electrolytes. The use of solid electrolytes can increase battery capacity and safety. However, solid-solid contacts between the electrolyte and the active material need to be controlled in the manufacturing process. Hence, the 3D morphology of the electrode microstructure in ASSBs has greater impact on their performance than in regular lithium-ion electrodes.

The DELFIN collaborative research project – whose results we present in this talk - seeks to develop an experimentally validated simulation model for the digital material design of ASSBs. This developed simulation platform, built on the GeoDict software of Math2Market GmbH, enables precise modeling and validation to advance ASSB design.

To accomplish this, ASSB electrodes with varied structural compositions are initially manufactured and characterized electrochemically by the Justus Liebig University Giessen. Next, RJL Micro & Analytic employs advanced multichannel µCT imaging techniques to capture detailed tomographic data of their microstructures. This 3D imaging data serves as a foundation for calibrating stochastic structure models developed by Ulm University, enabling the generation of additional virtual ASSB microstructures with varied structural characteristics. Numerical performance simulations carried out by Math2Market using the GeoDict software on these virtual structures establish key microstructure-property relationships and provide guidelines for the optimized design of the electrodes.

Furthermore, the integration of electrochemical studies with 3D µCT data aids the creation of a statistical digital twin, which is used to validate the simulation model. A parametric structure generator for ASSB cathodes is also under development for streamlining ASSB research and establishing a robust workflow for continuous ASSB innovation and design.

In the work presented here, we focus on the image processing and image segmentation, the creation of the digital twin, and the simulation of charging and discharging of ASSB based on the detailed 3D microstructure.

This approach significantly reduces the need for costly and time-consuming experimental trial-and-error methods in the design of ASSBs materials. As a result, the industrial development of high-performance ASSBs can be accelerated and made more economically competitive. The developed simulation platform serves as a tool for original equipment manufacturers (OEMs), battery producers, material suppliers, and academic researchers to better predict and evaluate future battery trends.

Optimization of multiphase electrodes in all-solid-state batteries by physicochemical impedance modeling

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A fundamental understanding of the performance limiting processes in battery cells is essential for model-based cell optimization. One of the most efficient approaches to analyze these processes is electrochemical impedance spectroscopy (EIS) followed by an investigation of the distribution of relaxation times (DRT) [1], facilitating a deconvolution of electrochemical processes differing in their relaxation frequencies.

The analysis of multiphase electrodes, in which electronic and ionic charge transport are coupled via charge transfer reactions, usually precludes a direct correlation of a peak in the DRT with a single polarization process. In this case the use of transmission line models (TLM) [2-4] is necessary. TLM parameterization by CNLS-fitting is often ambiguous, since different parameter sets can result in identical spectra [2]. Different techniques as tomography, impedance spectroscopy and conductivity measurements are required to determine the model parameters independently [4].

In this study, a physicochemically motivated impedance model based on the TLM-approach was derived and parameterized through a comprehensive analysis of an all-solid-state (ASSB) battery cell featuring a LNO coated LCO - LGPS composite cathode with a LPSBr separator and an In-Li anode [5]. Model reliability is demonstrated by validation against measured impedance spectra. With this model-based approach optimized cell design parameters as particle size, volume fraction and electrode thickness are derived by a detailed sensitivity analysis. Moreover, the limitation of the TLM approach on this type of ASSB is discussed.

Furthermore, the usage of simulated impedance spectra to build a time-domain model [3] enables the prediction of cell voltage and discharge behavior at varying C-rates, which is a crucial aspect for subsequent battery development.

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Understanding the Relationship between Microstructure and Charge Transport Properties for Sodium Solid-State Batteries: A Focus on Cathode Composite Optimization

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The growing usage of renewable energies, as well as the widespread electrification of most parts of daily life, has resulted in an increased demand for energy storage devices. At the present moment, the vast majority of this demand has been met using lithium-ion batteries (LiBs) [1-2]. However, one of the criticalities preventing a wider adoption of LiB-based technologies is Li being a strategic resource, as its extraction is limited to a small number of countries in the world, affecting the final material's cost [3]. The growing demand to apply energy storage on larger scales, then, deemed necessary the investigation of alternative ions. Among these, Sodium (Na) emerged as one of the most promising elements to reduce the reliance on Li for energy storage due to its cost-effectiveness and abundance [4]. Because of their similar chemistry, the investigation performed on Na-ion Batteries (SiBs) follows a parallel path to LiBs in many aspects, including the transition from liquid electrolytes to solid-state electrolytes, and to solid-state batteries (SSBs), consequently. These may offer higher energy density and higher thermal stability offered by the solid electrolytes [5].

The performance of Li-SSBs, however, is affected even more by the microstructure than in conventional cells. The solid electrolyte does not infiltrate pores which leads to residual pores in electrodes and separators: The distribution of pores, active interface areas and phases affect the overall performance significantly [6]. Therefore, it is of critical importance to investigate these key factors in order to properly optimize SSBs [7]. The focus of this research is to evaluate the cathode composite charge transport kinetics by studying various cathode compositions, observing how different conditions affects their electronical and ionic conductivity. The materials used for this investigation are $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ as cathode active material (CAM), Na_3PS_4 as solid electrolyte, and vapor grown carbon fibers (VGCFs) as conductive additive. The microstructure of the cathodes are studied using scanning electron microscope (SEM) and focused ion beam scanning electron microscope (FiB-SEM) techniques. Charge transport properties are investigated using 3D reconstruction and charge transport simulations are compared with experimentally determined conductivities. This investigation aims to parallel on Na-SSB other studies performed on Li-SSB [6], highlighting that, despite the similarities in their chemistry, it would be a dangerous approximation to blindly apply the knowledge obtained on LiB to Na-based cell chemistries. Apart from different particle morphologies, particle sizes, and mechanical properties which expected to influence the microstructure, the different conductivities, (electro-)chemical compatibility will distinguish the cell performance of Li- and Na-SSBs.

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A Thermodynamically Consistent Continuum Model for Ion-Selective Membranes in Aqueous Batteries

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Membranes with ion-selective properties offer great potential for the improvement of novel energy storage technologies [1]. Among these technologies, aqueous batteries such as zinc-metal batteries (ZMBs) are particularly promising due to their relatively low cost, resource availability and high theoretic specific capacity [2]. For these cells, the implementation of a filtering separator is desirable, since the crossover of certain ions has been shown to contribute significantly to the degradation of the cell [3]; e.g. $Zn(OH)_4{}^{-2}$ in alkaline zinc-manganese oxide cells (degrading the cathode) and $CO_3{}^{-2}$ in zinc-air cells (lowering the alkalinity) [4].

To gain insight for the tailored development of suitable membranes, a consistent model describing membrane transport of various species using physically meaningful parameters is required. Among the variety of available membrane models, especially the DSPM-DE model [5], the Donnan-Manning model [6, 7] and the low-T* model [8] have been proven to be applicable for some relevant membranes and certain solutes. Yet, for the intended purpose, a model with a wider applicability offering more predictive value and interpretability of the model parameters is desirable. This is achieved by combining the fundamental ideas of various models in a thermodynamically consistent manner which allows to predict qualitative trends from theory, as well as a more quantitatively accurate parameterization from experiments.

Implementation of this widely applicable membrane model into a cell scale model then allows for efficient tuning of membrane properties for the overall improvement of the battery performance.

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Understanding $LiFePO_4$ Battery Through Charging Dynamics and Electrochemical Modeling

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Lithium iron phosphate (LFP) batteries are celebrated for their safety, long cycle life, and thermal stability, but their charging behavior reveals unique electrochemical complexities, such as phase transitions, memory effects, and relaxation dynamics. Despite its critical importance, existing research on LFP modeling primarily focuses on relaxation and discharge processes [1,2], with limited attention given to the distinctive phenomena observed during charging. These characteristics are particularly pronounced in LFP batteries, where charging induces unique phase transitions and dynamic behaviors that are not adequately captured by conventional models. This study addresses this gap by developing a Multi-Particle DFN (MP-DFN) model that extends the Doyle-Fuller-Newman (DFN) framework. By incorporating a particle size distribution [3], the MP-DFN model accounts for inter-particle lithium-ion distribution while maintaining computational efficiency.

The study emphasizes the necessity of efficient solvers to manage the computational demands introduced by the multi-particle framework. A solver is developed to balance accuracy and efficiency, enabling high-fidelity simulations of LFP charging dynamics at manageable computational costs. Additionally, a comprehensive framework is proposed, encompassing solver development, parameter identifiability analysis, and parameter estimation. The validation process focuses exclusively on experimental voltage profiles during charging. Key parameters, including solid-state diffusion coefficients, reaction kinetics, and electrolyte transport properties, are optimized using a cost function that minimizes discrepancies between simulated and experimental voltage profiles. The MP-DFN model demonstrates exceptional capability in capturing critical LFP charging phenomena establishing a powerful tool for advancing the understanding and optimization of LFP batteries in high-performance applications.

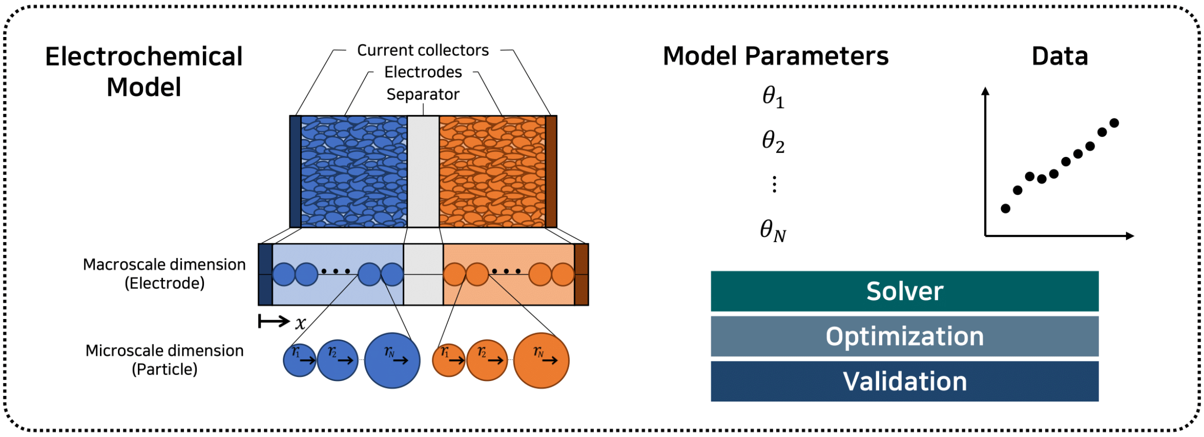

Figure 1: Schematic representation of the presented multi-particle framework.

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Physics-Based Modelling of Operando Electrical Impedance Spectroscopy for the Characterization of Lithium-Ion Batteries

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Electrochemical impedance spectroscopy (EIS) is a widely used and accessible characterization technique for investigating the dynamics of electrochemical systems of all kinds. In classical EIS, one measures a system's linear frequency-domain current-voltage transfer function in stationary conditions. In contrast, operando EIS measures the system's transfer function under operation by applying a multi-sine excitation signal during charging or discharging [1]. The obtained data is expected to contain additional information on the studied physical processes.

The analysis of EIS requires a model to link the measured impedance to the physical properties of the electrochemical system. Physics-based models are more involved and computationally expensive than the popular equivalent circuit models but allow more accurate modeling of and deeper insight into the internal physical processes of the device [2]. Here, we combine the well-established Doyle-Fuller-Newman (DFN) model for batteries [3] with the powerful numerical methods implemented in Fluxim's commercial semiconductor simulation software Setfos [4] and successfully verify the implementation with a benchmark against an established software [3]. In simulations, the impedance can be computed using a small-signal approach, that directly solves the linearized system. Combined with a transient solver, this allows for obtaining the transient impedance under different operating conditions. Short computation times provide a basis for applications such as analyzing the sensitivity of parameters, fitting measurement results, or extracting model parameters.

While these simulations sufficiently resemble operando EIS measurements with a single-frequency excitation signal, they only cover an idealized part of measurements with a multi-frequency excitation signal. It neglects both non-linearities and deviations of the best linear approximation (BLA) of the impedance from the idealized solution. To cover these effects, we perform a transient simulation using a multi-frequency excitation signal. Simulating a signal with frequencies up to tens of Hertz and a length of thousands of seconds is demanding and requires computation times of several hours. The results, however, allow us to compute the BLA of the impedance and assess its accuracy and feasibility based on a model that closely resembles the non-linear behavior of the experimental devices under investigation.

In summary, with Setfos we present a fast and robust simulation tool to model transient and frequency-domain experiments of Li-ion batteries using the physics-based DFN model and demonstrate its feasibility for reproducing measurement results and extracting parameters.

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Modelling Aging and Capacity Fade in graphite/NCA LIB: An Extended 1D Finite Element Approach with Particle Distribution Effects

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In lithium-ion batteries (LIBs), capacity fade occurs during electrochemical cycling due to various mechanisms, including irreversible lithium loss from solid electrolyte interphase (SEI) formation, particle cracking, and particle isolation, among others [1]. For cells utilizing graphite and silicon as the anode material, substantial amounts of cyclable lithium are consumed in the formation of the SEI layer on the electrode surface. Ekström et al. proposed an aging model that accounts for this phenomenon through a linear combination of two current contributions: one from regions of graphite particles covered by an intact microporous SEI layer, and another from areas where the SEI layer has developed cracks [2]. Thus, the performance of a LIB cell is influenced significantly by the microstructural properties of its electrodes. To simulate these aging processes, the Newman model in its pseudo-two-dimensional (P2D) form is commonly used, while fully resolved models including the three-dimensional (3D) microstructure of both porous electrodes are less frequently used due to their high computational cost [3,4].

We have developed an extended 1D finite element model that is computational effective and accurate in describing the effect of cycle-aging on commercial Graphite/NCA LIB cells. The model incorporates the particle size distribution (PSD) histogram of electrode particles, derived from microscopy data instead of resolving the full 3D electrode microstructure. The extended PSD homogenized model, implemented in COMSOL Multiphysics, is utilized to simulate the cell's cycling behaviour and compared with experimental data.

Figure 1 illustrates the simulation results for discharge cycles at a 0.5C rate, comparing two models: one that includes PSD (left) and another without PSD (right). Experimental data for the first cycle are also shown with asterisk markers. The inclusion of PSD yields a model that more accurately represents the cycling performance. The potential drop across the SEI layer is greater in the non-PSD model, highlighting the influence of particle distribution on the electrochemical response. This model can be further applied to study aging behaviour in different electrode materials with varying PSDs by optimizing the micro- and macroscopic parameters introduced in the model.

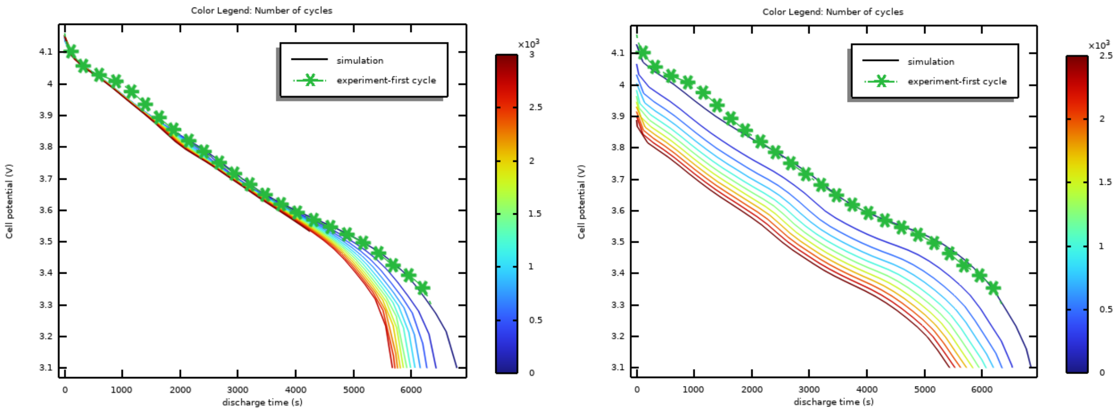

Figure 1. Simulated discharging cycles for 0.5C current representing the anode SEI aging effect (solid lines) and experimental first cycle data (green asterisk) with(left) and without (right) particle size distribution.

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Modeling and Simulation of Lithiation-Induced Cracks in Battery Active Particles

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Short overview about the key modeling aspects

The poster is going to present a comprehensive study of lithiation-induced cracking behaviors at the anode side, a critical phenomenon in battery performance and durability. A robust modeling approach is introduced, supported by an overview of the advanced numerical tools employed in the analysis. Through illustrative numerical examples, the potential and versatility of the proposed method are demonstrated, offering valuable insights into the mechanics of cracking and its mitigation.

The cracking model is based on [1] which is a widely accepted modeling approach and has been used by several authors. Some further details concerning the energy density split are based on [2].

Mechanically, the theory of small deformations is used and the mechanical influence of lithiated lithium is incorporated by using an additive decomposition of the total strain into chemical and mechanical parts based on [3].

The arising equations are solved using the Finite-Element-Method and the resulting nonlinear equations require Newton-Raphson-type solvers. The presented implementations have been done using the C++ based library *deal.ii*.

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A Novel Design of Physics-Informed Neural Networks for Modeling Mechanical Degradation in Active Materials with Phase Separation

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The aging of lithium-ion batteries is a critical factor influencing their performance and longevity. This complex process arises from the interplay of electrochemical reactions and mechanical changes within the electrodes. A key aspect of battery aging involves the degradation of electrode materials, which is driven by mechanical stresses generated during ion insertion and extraction in active material particles.

Ion intercalation, which governs the charge-discharge behaviour of lithium-ion batteries, leads to concentration gradients within active material particles. These gradients, shaped by transport and reaction kinetics, cause mechanical stresses due to the spatial confinement of ions. Over time, these stresses can induce fractures in the particles, ultimately compromising the structural integrity and functionality of the electrodes.

Understanding these degradation mechanisms requires detailed analysis of the phase transitions in commonly used cathode materials, such as Lithium Cobalt Oxide (LCO) and Lithium Iron Phosphate (LFP) [1,2]. During intercalation, transitions between lithium-rich and lithium-poor phases can create significant mechanical stresses, particularly in the transition zone. These stresses may exceed the material's tolerance, leading to fractures and accelerated aging of the electrodes.

The computational challenges associated with simulating these complex processes have motivated the adoption of alternative modeling approaches. Physics-informed neural networks (PINNs) offer a promising solution by integrating the transport equation into their training algorithms, enabling accurate predictions of concentration profiles within active material particles. By integrating the transport equation into the training algorithm, PINNs can predict concentration profiles in active material particles with improved accuracy and reduced computational demand. A novel PINN design has been developed to address the moving boundary Stefan problem associated with phase transitions in active materials.

Additionally, artificial neural networks (ANNs) are employed to model the electrical potential of active material particles. These networks utilize data from microstructural simulations to capture electrochemical-mechanical interactions within the battery system.

Furthermore, to understand the extent of particle fracture and its impact on electrode performance, a phase-field-like damage model is integrated into the grey-box model. The governing equations are derived from the stationary point of the potential energy functional of the active particle system.

The objective of this research is to develop a comprehensive framework that encompasses the chemical diffusion process, mechanical equilibrium, and fracture mechanics in a unified model. Such an approach aims to provide deeper insights into the mechanical degradation of battery materials and support the advancement of durable lithium-ion battery technologies.

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Diagnosis and Data Analysis of Aging Patterns for Second Life Applications of Electric Vehicle Batteries

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Rapid and accurate diagnosis of the state of health of electric vehicle batteries with a view to their second-life applications still remains a difficult problem that needs to be resolved. In a context of upcoming pressure for the battery market, driven by economic, environmental or practical issues, batteries second life applications emerge as a solution [1], [2], [3]. From modules having undergone a first life as an electric vehicle, we simulated three different possible second life applications (Figure 1). Two batches of aged prismatic modules (50 Ah) with different first lives were considered, characterized, and randomly spread into three aging groups. Solar-type profile simulates renewable energy storage, with a charge during day and discharge during night. UPS (Uninterruptible Power Supply) protocol consists of applying constant voltage at 100 % state of charge. Lastly, classical storage protocol simulates calendar aging. Check-ups are made on a regular basis by cycling at low C-rate and making Electrochemical Impedance Spectroscopy (EIS) measurements at different state of charge. Different tools are used for data analysis such as Equivalent Circuit Models, Incremental Capacity Analysis (ICA), or projection algorithms.

Figure 1: Three applications for second-life batteries after their first life, following a diagnostic evaluation

Primary check-ups of aging protocols point out three different behaviours independent from first life. Concerning the solar-type profile: although signs of aging are observable in ICA data, most cells showed a stabilization in terms of performance, and even a resistance decrease with a gain of capacity for some of them. As regards the UPS protocol, cells showed an expected behaviour: resistance increase and capacity loss. The same behaviour occurs for the classical storage protocol, but in a slower manner. For each protocol, advanced data analysis of ICA and EIS highlight different degradation modes and identify defective cells. These promising results could provide a better insight into the remaining useful life of a battery (RUL) in the context of a given second-life application. Further work will be the continuation of aging tests, the exploitation of dimensionality reduction and descriptive statistical analysis for diagnostic purposes.

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Comparing Common Zero-dimensional SEI Models Under Varied Conditions

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Recent studies have identified state of charge (SOC) as a primary driver of solid electrolyte interphase (SEI) growth in lithium-ion batteries, while C-rate and temperature play secondary roles [1]. Zero-dimensional SEI models, broadly categorized into solvent-limited and electron-limited mechanisms, are commonly used to model and understand SEI growth [2]. Using the PyBaMM framework, this work explores how different types of SEI models respond to varying operating conditions. Our analysis compares these model categories under different charging protocols, revealing variations in their predicted degradation patterns. While higher initial SOC leads to increased SEI growth at the same C-rate due to longer discharge times, the relationship becomes more complex when discharge rates are adjusted to achieve uniform discharge duration, as demonstrated in Figure 1. These findings provide insights to guide optimization of battery formation and cycling protocols, suggesting that total exposure time and SOC distribution may be more critical factors than specific C-rate patterns in determining SEI evolution.

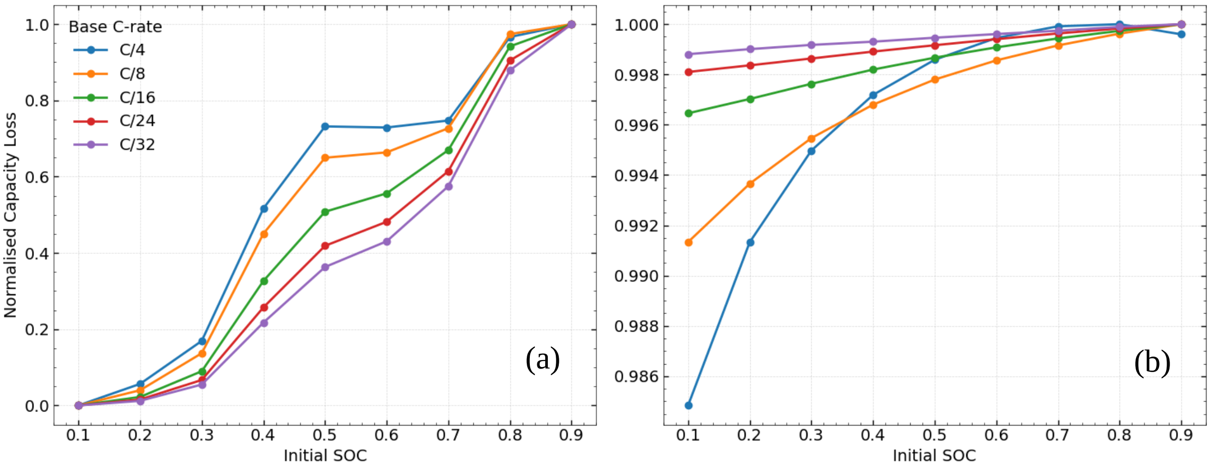

Figure 1: Comparison of capacity loss as a function of initial state of charge (SOC) when C-rates are adjusted to maintain constant discharge duration: (a) Interstitial Diffusion Limited model and (b) Solvent Diffusion Limited model.

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Diagnostic protocol development for rapid SOH assessment for LFP/LMFP battery chemistries

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Accurately estimating the state of health (SoH) of lithium iron phosphate (LFP) batteries remains a significant challenge due to their flat voltage profile, high stability, and complex impedance behavior, which complicate the tracking of subtle degradation markers. Traditional diagnostic and validation protocols often require lengthy check-ups spanning several days, making them inefficient for rapid assessments [1]. This study investigates the potential of the novel Intermittent Current Interruption (ICI) method [2], as a faster replacement for conventional protocols, emphasizing its time efficiency when implemented in a check-up protocol, offering shorter test durations, while maintaining accuracy suitable for validation purposes.

ICI is utilized to track key resistance and diffusion parameters that serve as indicators of battery performance and aging. To validate ICI, its results are systematically compared with Electrochemical Impedance Spectroscopy (EIS) across both new and aged commercial same-manufacturer 18650 LFP cells. Additionally, further validation of ICI is being explored through comparisons with methods such as Differential Voltage Analysis (DVA) and Incremental Capacity Analysis (ICA). To gain deeper insights into degradation mechanisms, post-mortem analysis of tested cells will be conducted. Additionally, the protocol is set to be extended to various cell formats and sizes supporting its development as a universal diagnostic tool.

Beyond LFP, this study also seeks to establish a foundation for effective diagnostic and check-up protocols for emerging lithium manganese iron phosphate (LMFP) batteries, which share LFP's olivine structure but offer higher working potential and energy density. However, these benefits come with trade-offs, including reduced stability and potential challenges like the Jahn-Teller effect. This research aims to establish robust diagnostic protocols to address the unique demands of both LFP and LMFP technologies.

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Predictive Analysis and Data-Driven Modeling for Electrochemical Degradation of Li-ion Batteries

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Lithium-ion (Li-ion) batteries are widely used across various industries, ranging from portable electronics and electromobility to battery energy storage systems. Stationary energy storage systems, in particular, play a crucial role in stabilizing power grids, integrating renewable energy sources and providing reliable energy supply. Li-ion batteries are characterized primarily for their exceptional energy density, low self-discharge rate, and long lifespan. Despite their longevity, Li-ion batteries are prone to capacity degradation, reflected in their State of Health (SOH), which is a crucial metric for assessing their remaining capacity and overall reliability, during both calendar and cyclic aging, leading to a decline in performance and reliability. These batteries represent complex electrochemical systems, characterized by numerous degradation phenomena. Consequently, various approaches are employed, including physics-based models [1], empirical models, equivalent circuit models, or data-driven models leveraging machine learning techniques [2, 3].

In this experiment, 14 Li-ion pouch cells of the lithium-nickel-manganese-cobalt oxide (NMC) type were tested. The testing was conducted at temperatures of 5, 25, and 45 °C and Depth of Discharge (DoD) levels of 70%, 90%, and 100%, as Li-ion batteries exhibit varying degradation mechanisms and rates under different conditions, as described by Ch. Birkl et al. [4]. The batteries were charged using a Constant Current Constant Voltage (CCCV) protocol and discharged using a Constant Current (CC) method, with each battery undergoing a total of 500 cycles.

The experiment focuses especially on developing a data-driven model based on machine learning, utilizing 12 Li-ion batteries as training dataset while dedicating the remaining 2 for validation by estimating their SOH. While battery state prediction using such a dataset may require processing time, the primary aim of this research is to enable real-time analysis through a Reduced-Order Model (ROM). This model selectively incorporates key data points rather than the full dataset, ensuring accurate estimation of the battery's condition based on specific input parameters.

The work contributes to evaluating battery performance during cycles not included in the training data, reducing costs associated with testing batteries of similar composition. Moreover, this work will provide a solid foundation for a digital twin designed to monitor stationary battery system conditions in real-time, enabling strategies to minimize degradation and enhance reliability.

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Simulation of NMC cathode particle fracture based on the multiphase-field method

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Intergranular cracking is considered a major cause of capacity fading in layered battery cathodes [2]. During intercalation and deintercalation of Li-ions, the highly anisotropic chemo-mechanical expansion of $LiNi_{0.1}Mn_{0.1}Co_{0.8}O_2$ (NMC811) primary grains within the agglomerate causes complex mechanical stress fields, triggering crack formation particularly during the initial cell charge cycle (cathode discharge) [2] [3, p.14] [4] [5, p.9]. A promising approach in grain engineering is correlated primary grain structures called *rod-shaped* morphologies, to which researchers [5, p.17] [6] allocate reduced anisotropic stress and cracking compared to common *gravel-shaped* morphologies. Building on previous work by Daubner et al. [1], this study examines spherical agglomerates in a 2D framework with a diameter of 10 µm. Using the multiphase-field method, it simulates chemo-mechanical lattice expansion and resulting cracking, beginning with an idealized, spatially homogeneous lithiation. This enables to analyze the effects of primary grain orientation and grain boundaries. Subsequently, Li-ion diffusion is modeled through a Potentiostatic Intermittent Titration Technique (PITT), with mechanical simulations conducted at times of interest. It is shown that strong grain misorientation causes tensile stress peaks in grain boundaries, while approximately parallel grain orientations instead lead to a local stress-reduction. This confirms the hypothesis of the above mentioned research and is reflected as well in the crack results, wherein cracking primarily occurs between unaligned grains. As a result, these regions have high intergranular crack densities, causing shattering into many fragments of the gravel-shaped agglomerate, while radially-aligned grains mostly stay coherent with lower crack densities.

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The importance of degradation mode analysis in parametrising lifetime prediction models

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Predicting lithium-ion battery lifetime remains one of the biggest challenges in the battery field. Accurate enough lifetime prediction was shown to require large amounts of diverse and correctly curated data taken under carefully controlled conditions, models that capture the correct mechanisms, their coupling and the effect of inhomogeneity across the cell, computational tools able to run models for hundreds/thousands of cycles, and thus tools to analyse large amounts of data, both experimental and obtained from model predictions, as well as accurate characterisation tools for validation.

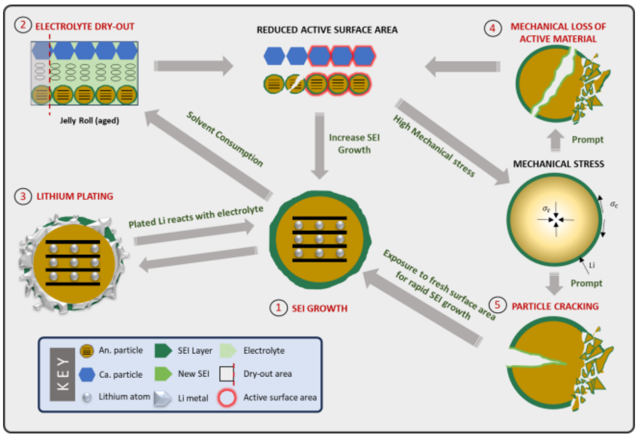

Figure 1: Schematic of the five degradation mechanisms considered in the Multiphysics PyBaMM model and their coupling.

A recent surge in lifetime prediction efforts using physics-based, empirical, or data-driven models, has been focussed on validation against capacity fade and power fade. However, using a physics-based multiphysics model (in PyBaMM) with coupled degradation mechanisms (Figure 1), we show that there are multiple combinations of degradation mechanisms that result in the same prediction of capacity and power fade [1]. Model predictions are analysed in comparison with experimental data from 21700 LGM50 cylindrical cells degraded at three different ambient temperatures [2]. This allows incorrect conclusions regarding the relevant dominating degradation mechanisms, and could lead to erroneous predictions of significant features, such as the knee point. Experimentally, degradation mode analysis involving the loss of lithium inventory and loss of active material emerges as a state-of-the-art tool for cell degradation studies. We show that the degradation modes (DMs), complemented by information from the cell resistance increase, are an informative intermediate layer for improving model accuracy and identification of the relevant degradation mechanisms and their coupling. For this reason, we propose that any trustworthy model for degradation prediction must include the relationships between degradation mechanisms and degradation modes.

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Your Charge Transfer Coefficient is not simply 0.5: Insights into Kinetics of Lithium-Ion-Batteries

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Electrochemical reaction kinetics is a challenging field with a bunch of open questions. For Lithium-Ion-Batteries, there is still an ongoing discussion, whether concentrations or activities should be used to describe the state of charge (SOC) dependence of the exchange current density [1]. Frequently, a concentration-dependent formulation [2] is used in battery modelling, while assuming charge transfer coefficients to be 0.5 and constant with respect to SOC. Here, we show, that these dependences are more complex, which significantly changes the view on battery kinetics.

The preferred method to determine the exchange current density is Electrochemical Impedance Spectroscopy. It is very powerful in discriminating reaction processes from transport phenomena.
However, due to its linearization it is not suitable to determine charge transfer coefficients [3]. Nonlinear Frequency Response Analysis (NFRA) [4] is equally powerful in frequency-based discrimination of reactions and transport while maintaining the nonlinear information in the signal and thus enabling a highly sensitive parameterization of charge transfer coefficients.

We performed impedance analysis and NFRA on two NMC622 half cells over the whole SOC range. The cells had different thicknesses to show our method works independently of the cells' microstructure. For parameterization, a Doyle-Fulle-Newman model was developed in frequency-domain, which enables the formulation of the original partial differential equations as a boundary value problem of a differential-algebraic system of equations, leveraging the model performance.

Using the model, at first the exchange current density was parameterized on the EIS data for each SOC. Subsequently also the charge transfer coefficients were parameterized with the NFR data.
The results show a strong dependence of both exchange current density and charge transfer coefficients on the state of charge, proving that advancing theories for the concentration-dependence of kinetics are key for better understanding of LIBs and enhanced model accuracy.

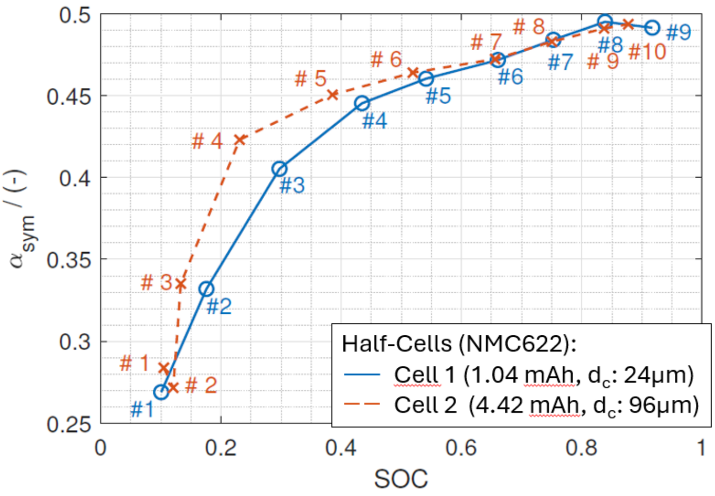

Figure 1: Charge transfer coefficient over SOC from two cells with different cathode thicknesses d_c.

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KMC Simulation Study of SEI Formation from LiFSI/DME electrolyte in Li-Metal Battery

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Rechargeable lithium metal batteries are of great interest due to their high theoretic energy density [1] and the electrochemical potential of lithium metal. However, their practical realization has not yet been feasible due to poor cyclability and the safety hazards arising from the highly reactive nature of lithium metal. The highly reactive nature of the lithium metal electrode with liquid electrolytes can result in a continuously growing Solid Electrolyte Interphase (SEI), which can cause irreversible capacity loss leading to poor cyclability. Also, dendritic deposition of lithium at the electrode surface poses the risk of causing short circuits and thus thermal runaway events. A robust, stable SEI can help in mitigating these issues. Ideally, an SEI would have high ionic conductivity while limiting electronic conductivity, facilitating the easy transfer of ions while preventing side reactions.

In this study, we focus on the SEI formation process using 3D Kinetic Monte Carlo (KMC) simulations, which are parameterized using Density Functional Theory (DFT) calculations. Building on the simulation framework developed by Wagner-Henke et al. [2], it has been adapted to study the LiFSI(salt) / DME (solvent) electrolyte system. The electrolyte was chosen based on experimental studies that have reported that highly concentrated LiFSI/DME systems exhibit very good cycling stability and coulombic efficiency [3], and therefore are promising candidates for stabilizing the lithium metal anode in liquid electrolyte systems. In this contribution, I will outline the simulation methodology, the electrolyte choice basis, the reaction network, and discuss results on the SEI formation. Both the SEI species, LiF and Li_2O exhibit a relatively even distribution along the SEI thickness and show a steady growing profile even after 100 ns. At 100ns, thickness of 1.76nm is observed for the SEI.

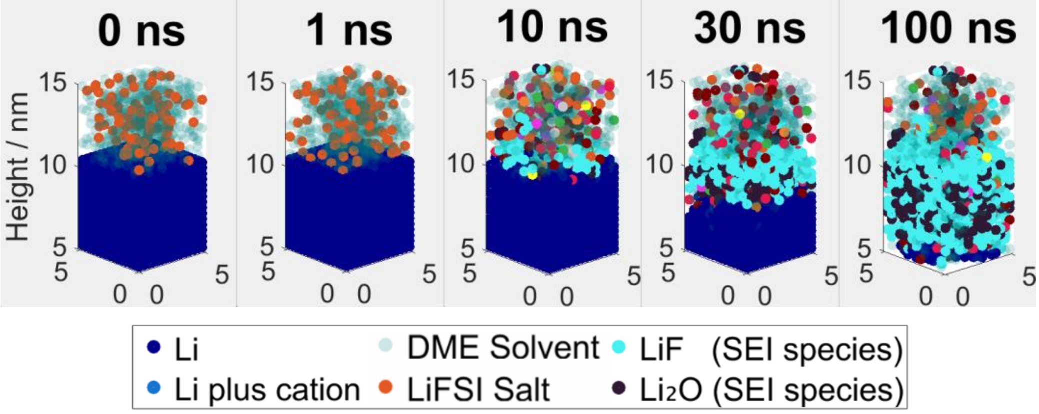

Figure 1: Results of SEI formed in the first 100ns for LiFSI/DME reactions

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Unravelling Reaction Mechanisms in Liquid Electrolytes of Lithium-Ion Batteries to Calculate Thermochemical-Kinetic Parameters

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We developed a reaction network for a simulation-based safety analysis of a thermal runaway in Li-ion battery cells using experimental and modelling techniques. The simulations require reliable kinetic parameters of key reactions that lead to the electrochemical degradation and thermally induced thermal decomposition, respectively, of all battery cell components such as current collectors, electrodes, the electrolyte, and the separator [2-4]. Our contribution in this project is to assist in generating a fundamental understanding of the overall reaction network and to identify elementary key reaction steps using calculations on the atomic scale that employ quantum chemical methods. For identified elementary key reaction steps we calculate temperature dependent reaction rates using molecular dynamics simulations and machine-learning techniques.

In the presentation we will unravel the detailed mechanism of the thermal degradation of a liquid electrolyte that consists of $LiPF_6$, a mixture of organic carbonates and traces of water which leads to HF. The presence of HF initiates an autocatalytic degradation of the organic carbonates which leads to organophosphates and CO_2 [5].

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LiquidElectrolytes.jl - A Generalized Poisson-Nernst-Planck solver written in Julia

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LiquidElectrolytes.jl [1] is a solver for generalized Poisson-Nernst-Planck models taking into account finite ion size, solvation and electroosmotic pressure based on the formulations developed in [2,3]. It utilizes a thermodynamically consistent finite volume space discretization approach which uses the sum of the electrotstatic potential and the excess chemical potential as convective terms [4,5]. It is realized on top of the solver kernel VoronoiFVM.jl [6] for coupled nonlinear PDE systems which takes advantage of Julia's automatic differentiation capabilities [7] to generate the full linearization of the coupled nonlinear system as a basis for a robust Newton solver for the discrete nonlinear system.

Recent additions to the package include handling of electroosmotic flows based on the coupling with a FEM Stokes solver based on ExtendableFEM.jl [8] and handling of rotating electrodes. An Interface to the CatMAP Python package [9] is work in progress.

The poster introduces the general features of the package. In order to showcase its capabilities, we present simulation results for the effect of the double layer on electrochemical reactions.

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Thermal Modelling in Cylindrical and Prismatic Cells

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Overcoming challenges in model architecture, characterisation and validation

Creation and validation of thermal models for cylindrical and prismatic cells presents unique challenges due to their form factor and design complexities. Unlike pouch cells, where established methodologies exist to independently determine anisotropic thermal properties [1], the external can acts as a thermal distributor, masking the inherent anisotropic thermal behaviour of the jellyroll. This raises a critical question: how can we validate thermal models for these cell form factors with confidence, ensuring parameters are not overfitted to compensate for inaccuracies elsewhere?

In thermal modelling, temperature response measurements are often used to validate models, but this approach inherently couples multiple thermal properties (anisotropic thermal conductivities and specific heat capacity) with heat generation rates. Without independent determination of the thermal properties, a singular solution for the thermal state of the overall thermal model cannot be ascertained. This will lead to erroneous predictions of cell performance and forces engineers to overcompensate using additional safety protocol in cell and battery pack design. Here, methods to mitigate this risk by decoupling these parameters through careful model design and experimental processes are explored.

For pouch cells, independent experiments allow for accurate determination of anisotropic thermal properties. Through-plane conductivity can be robustly measured using heat flux sensors, as demonstrated by Gavin White et al. [1], while in-plane conductivity can be calculated with high confidence using the constituent parts method. Once these properties are independently validated, heat generation rates can be fitted to measured temperature response with high confidence of a singular solution for a given thermal state.

The pouch method is not directly transferable to cylindrical and prismatic cells due to the thermal distribution effects of the external can and the anisotropic complexity of the jellyroll. To address this, we are developing a methodology that encompasses the following steps:

1. Heat generation determination: Heat generation is derived from electrical data, ensuring:
    - Elimination of reversible heating through pulsing at a constant SOC [2], or through entropy characterisation [3].
    - Assumption of uniform heat generation within the electrode stack.
    - Consideration of "hot spots" such as the cell cap or external welds.
2. Thermal property decoupling:
    - The thermal properties of the can, cap, and connecting tabs are determined independently, considering their geometry and material characteristics.
    - These properties are integrated into the full thermal model, thus decoupling the thermal behaviour of the electrode stack from the rest of the cell.

Implementation of these steps ensures that the anisotropic thermal properties and heat generation rates can be characterised independently. As a result, empirical measurements of temperature change during an experiment can be used to validate, not fit, the model. In doing so, an effective model is predicting a temperature via the fundamentals that have driven temperature rise, a reverse of the incumbent curve fitting process, previously described.

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Thermochemical-Kinetic Insights into the Thermal Degradation Mechanisms of Lithium-Ion Batteries through Gas Analysis Modeling

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Understanding the role of chemical composition in lithium-ion battery (LIB) safety, particularly under thermal abuse, is essential because elevated temperatures accelerate degradation triggering further exothermal reactions which may ultimately lead to a Thermal Runaway Event. This study employs a thermochemical-kinetic model validated with High-Temperature Online Electrochemical Mass Spectrometry (HT-OEMS) gas analysis data to examine the reactions responsible for gas evolution and their interconnections during thermal abuse.

The findings reveal that the hydrolysis of the conductive salt $LiPF_6$, driven by impurities such as water, is a key degradation pathway, even though these impurities are typically present in low concentrations. A notable product of this hydrolysis, POF_3, reacts with linear carbonate solvents like DMC, forming organophosphates that can further generate POF_3, perpetuating the degradation cycle. The electrolyte's composition, which often includes linear and cyclic carbonates, plays a crucial role in modulating these reactions. While cyclic carbonates such as EC inhibit the degradation of linear carbonates, they promote other mechanisms, such as EC polymerization, which increases CO_2 generation.

Moreover, the presence of EC suppresses solvent evaporation, resulting in higher concentrations of reactants in the liquid phase and favouring further degradation reactions. The strong interactions among the chemical components, mainly when EC and $LiPF_6$ are present, limit significant pressure increases in the system. These interactions reduce the solubility of gases in the electrolyte, further influencing the degradation pathways. These insights underscore the intricate and complex interplay between chemical composition and system dynamics in the degradation process.

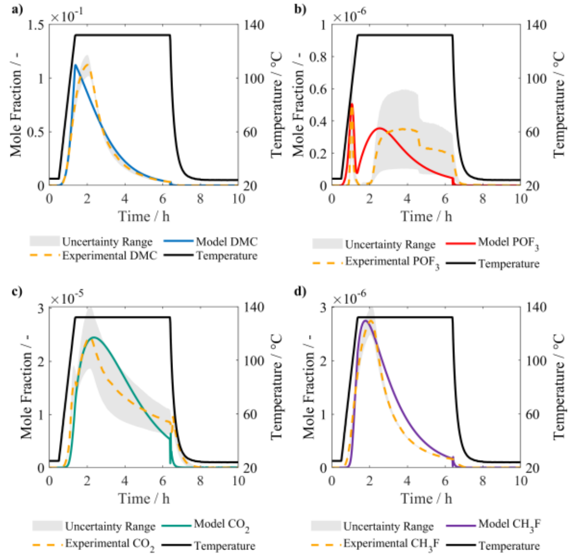

Figure 1: Gas profiles from the thermal degradation of EC/DMC/$LiPF_6$. (a) DMC, (b) POF_3, (c) CO_2, and CH_3F. Dashed lines represent the average experimental data, while solid blue, red, green, and purple lines show the model outputs for the mole fraction profiles of DMC, POF_3, CO_2, and CH_3F, respectively. The grey area indicates the uncertainty range from repeated experiments, and the black solid line represents the temperature profile.

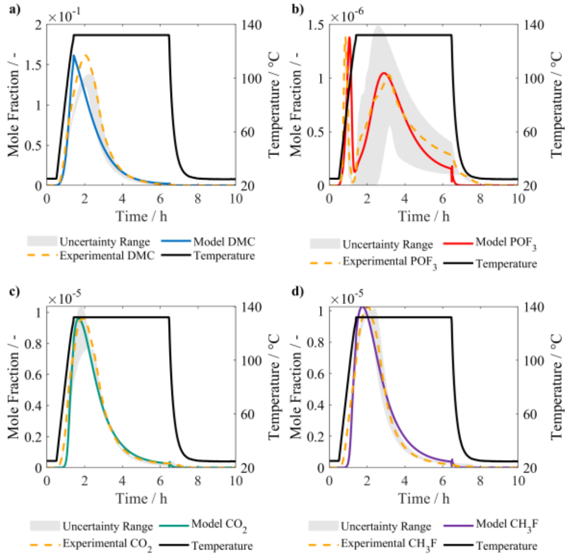

Figure 2: Gas profiles from the thermal degradation of DMC/$LiPF_6$. (a) DMC, (b) POF_3, (c) CO_2, and CH_3F. Dashed lines represent the average experimental data, while solid blue, red, green, and purple lines show the model outputs for the mole fraction profiles of DMC, POF_3, CO_2, and CH_3F, respectively. The grey area indicates the uncertainty range from repeated experiments, and the black solid line represents the temperature profile.

Quantum algorithms to solve partial differential equations in battery modelling

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Mathematical models of electrochemical systems such as batteries or fuel cells consist of sets of coupled nonlinear partial differential equations. We describe how variational quantum algorithms (VQAs) can be used to solve these equations on a quantum computer [1]. VQAs are hybrid quantum-classical algorithms, where a cost function is calculated on a quantum computer and its parameters are optimised classically. We present a spacetime representation, inspired by the Feynman–Kitaev Hamiltonian [2], where the solution to a PDE at all times is obtained by minimising just one function.

We describe how quantum nonlinear processing units [3] can be used to evaluate the required cost function efficiently. We propose an adaptive strategy to mitigate the barren plateau problem, which means that gradients vanish exponentially with the number of qubits.

The approach is illustrated for the nonlinear Burgers equation. We optimise the problem on a noiseless simulator and run the circuits containing the result on IBM Q System One and Quantinuum Model H1, demonstrating that current quantum computers are capable of accurately reproducing the exact results.

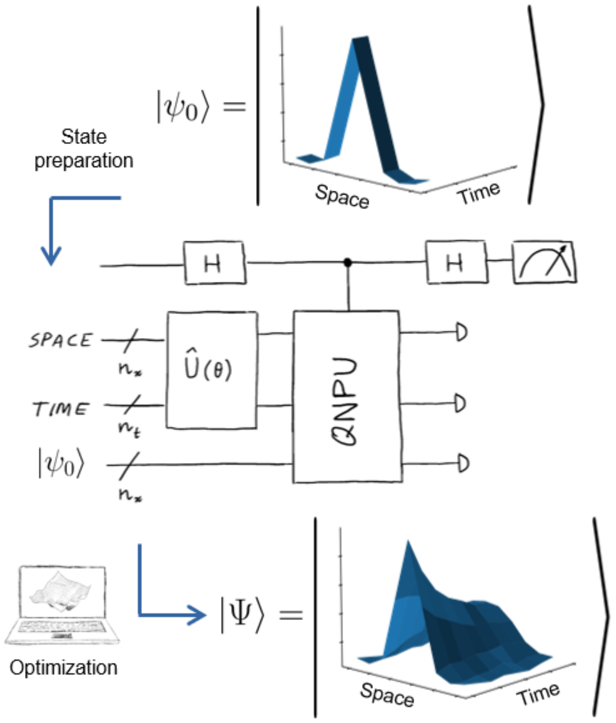

Figure 1: Schematic summarising the proposed method.

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Investigation of the influence of different thermal aging conditions on the thermal transport properties and porosity of lithium-ion battery electrodes

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A thermal management system is required to ensure the safe and optimized operation as well as a long lifetime of lithium-ion batteries in electric vehicles. The design of these systems is thereby commonly based on the respective cell behavior at the Begin of Life (BoL). During operation, various aging mechanisms occur on both the anode and cathode side, depending on the cell chemistry as well as operation conditions like current load, temperature and pressure. These mechanisms change the properties of the battery cells significantly. For a more profound understanding and design of thermal management systems, the dependency of the thermal cell behavior on the State of Health (SoH) until the End of Life (EoL) is crucial.

The different aging mechanisms are depending not only on the temperature level but also on temperature distributions and changes during the aging process. Various aging induced changes of the microstructure at the electrode level lead to altered effective thermal material properties, resulting in reduced heat transfer among other changes. For an optimized thermal management throughout the whole lifetime of the electric vehicle, the information about these changes is necessary. Additionally, the alterations of the thermal cell behavior will also directly impact the electrical and electrochemical performance of the battery system. To assign the occurring aging mechanisms to the effects on the heat transfer, it is crucial to measure the electrodes individually because of the different aging mechanisms within anode and cathode.

Therefore, in this work, the influence of different thermal aging conditions on the heat transfer of cathode and anode stacks is investigated on electrode level to gain more insight on the individual underlying mechanisms. With an inhouse experimental methodology for the thermal characterization at electrode level (electrode stack, current collector and coating) the effective thermal conductivity can be determined by measuring the specific heat capacity with differential scanning calorimetry, the density with a gas pycnometer and the temperature diffusivity with laser flash analysis, taking the heterogenous microstructure into account.

The main focus of this contribution is the influence of homogenous and inhomogeneous temperature distributions during cyclic aging on the effective thermal conductivity and the comparison of the EoL to the BoL. The thermal aging conditions for the investigated cells were chosen over a wide temperature range to trigger different aging mechanisms within the cells. The investigated cells consist thereby of graphite anodes and blend metal oxide cathodes. Multiple samples were taken from different positions of the aged electrode material at EoL and the corresponding local effective thermal transport properties were determined. The effective thermal conductivity of several cells with different thermal aging conditions as well as the impact of the porosity and its aging induced changes are investigated and presented.

A Combined Experimental and Modeling Approach to Transfer Experimental Test Cell to Automotive Pouch Cell Behavior

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The dynamic performance of lithium-ion battery cells strongly depends on the underlying loss processes such as contact resistances, charge transfer and diffusive processes. These combined effects determine the frequency-dependent impedance behavior of the cell. A widely used technique for characterizing the impedance of electrochemical systems, including lithium-ion cells, is electrochemical impedance spectroscopy (EIS). When paired with equivalent circuit modeling, EIS enables the quantification of various processes as functions of temperature and state-of-charge (SoC). In further combination with open-circuit voltage measurements, models, describing the full cell behavior, can be derived. In commercial cells, however, only the full cell behavior in terms of impedance and performance can be studied and characterized whereby information about the individual behavior of anode and cathode are not directly accessible.

Understanding the local electrode potentials within a battery cell is crucial to ensure a safe and optimal operating window, as well as to develop innovative fast-charging strategies for lithium-ion batteries. Three-electrode test cells allow the desired measurement of the individual electrode behavior during operation. Nevertheless, transferring the results from these test cells to large-scale commercial (pouch) cells is not straightforward.

In this work we investigate the comparison of an automotive 60 Ah pouch cell with three-electrode cells built out of extracted electrodes from the pouch cell and standard components for the separator and electrolyte, using a commercial test cell housing. The measurements from the experimental setup, using a standard separator and electrolyte, show excellent agreement with automotive pouch cells in terms of impedance behavior at medium SoCs and temperatures, as well as performance at medium C-rates. However, discrepancies at higher C-rates and rapidly changing current loads hinder the direct transfer of test cell data to large pouch cells.

To address this challenge, we propose an equivalent circuit model that incorporates an ohmic correction factor, bridging the gap between experimental data and pouch cell behavior. The model's parameters are derived from half-cell impedance data, allowing for the investigation of local potentials at both the anode and cathode within the simulation.

The proposed methodology offers significant potential for efficient and accurate parametrization of simulation models by utilizing the extracted electrode materials from pouch cells, along with readily available standard separators and electrolytes, all while ensuring high reproducibility. Including the electrodes in the model represents a notable advancement over a simulation model that is parameterized solely at the pouch cell level, which neglects the individual processes occurring at the anode and cathode.

Investigation of crucial effective transport parameters of Li-ion cells based on experimental impedance spectroscopy by a hybrid simulation model

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The performance and aging behavior of a lithium-ion battery (LIB) are strongly influenced by the inner multiphysical processes as well as outer influence factors like the thermal boundary conditions. However, the inner physical processes, the quantification of those and their changes during operation and aging aren't easily accessible and requires a high level of characterization effort. To gain insights into those multiphysical processes, simulation models have been a well-established and useful tool to resolve the complex interaction of charge, heat and mass transport as well as electrochemical reactions. Combining experimental measurement data of integral variables, such as impedance and voltage behavior, with simulation models enables to evaluate and determine inner physical transport parameters. However, such an inverse parameterization approach requires in-depth knowledge of the interaction of inner cell parameters and integral cell behavior.

In this work, a model consisting of the combination of an equivalent circuit model (ECM) and a physical pseudo-2D (p2D) model according to Doyle-Fuller-Newman (DFN) [1] was developed and implemented in COMSOL Multiphysics. With the help of this model, impedance spectra based on the multiphysical processes can be predicted and the underlying parameters can be systematically analyzed. By comparison of the impedance spectra from simulation with experimental data, the physical parameters determining the overall cell behavior can be identified. This inverse-parameterization approach was accelerated by the implementation of a least square optimization tool, fitting the simulated impedance spectra to an experimental data set [2,3] by automatically optimizing the values of the physical parameters. Additionally, the voltage behavior of the cell is analyzed to gain further information about parameters which are sensitive in the time domain.

A challenging task by applying a DFN modeling approach combined with an optimization algorithm is to identify the value range of the crucial effective transport parameters, which are influenced by the microstructure of an electrode. Based on previous works on the sensitivity influence of each model parameter and the usage of an established heterogeneous 3D microstructure model, the range of the effective transport parameters can be narrowed down. The 3D microstructure based on spherical and non-spherical particles is thereby generated with a drop and roll-algorithm, in which crucial parameters like particle size can be adjusted to replicate the particle distribution of real battery electrodes. The developed microstructure simulation model is then applied to analyze the impedance and voltage behavior as well as to derive crucial effective transport parameters like the tortuosity of the porous electrodes. In this contribution the results of variations of the microstructural parameters like particle shape and size distribution are shown and the transfer from a heterogeneous 3D microstructure to a homogenized p2D model is evaluated.

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Modeling of Local Pressure Inhomogeneities in Large Format Lithium-Ion Batteries Using a Thermal-Mechanical Multi-Scale-Multi-Domain Model

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The intercalation reaction in lithium-ion batteries causes significant volume change in the active material. Due to spatial limitations in common battery applications, this entails mechanical stresses on the electrode layers and thereby influences the performance and lifetime of the battery. Mechanical effects are closely linked to electrochemical and thermal processes in the cell, giving rise to complex interactions that are difficult to predict. Moreover, large cell dimensions, which become ever so common in today's battery industry, further increase complexity due to local variations of state variables. Therefore, modeling is essential to enhance understanding of the governing- and limiting processes. In this contribution we present a fully coupled multi-scale-multi-domain model including a P2D electrochemical model on the electrode scale, a 3D thermal model on the cell scale and a distributed 0D mechanical model, that describes the cell expansion, compression and the consequent porosity change of the electrodes over the whole cell area. The multi-scale-multi-domain approach [1,2] allows to model the physical processes on all relevant length scales from the active material particles up to the full cell level, while resolving local inhomogeneities on the full cell level in a computationally efficient manner. This allows to investigate operating strategies that not only account for thermal gradients in the cell but also gradients of mechanical pressure that can be induced by different housing or clamping conditions. The model is parametrized and validated to a commercial 20 Ah large format pouch cell. The characterization of the electrochemical properties is done on the electrode level by FIB-SEM microstructure characterization and electrochemical impedance spectroscopy. The mechanical properties are determined separately for each single cell layer by stress-strain measurements. Also, the effective thermal properties are determined separately for all cell components. The model, its parameterization and validation as well as selected simulation results, including representative mechanical and thermal boundary conditions, will be presented.

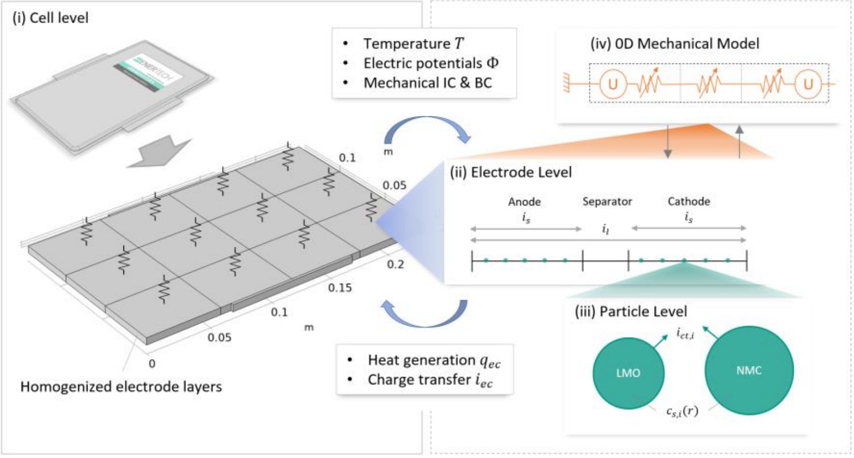

Figure 1: Overview of the multi-scale-multi-domain model including electrochemical-, thermal-, and mechanical processes on all relevant length scales.

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Development of a Physics-Based Electrochemical and Thermal Model of Li-Ion Batteries for Microcontroller Applications

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Enabling fast-charging procedures is one of the key challenges of Li-ion battery applications, from automotive to power tools. At high charging rates, the cell's aging behavior changes significantly, primarily due to internal temperature increases and the heightened risk of lithium plating caused by substantial overpotentials. A combination of physicochemical and thermal models can be used to accurately predict cell behavior even at high C-rates. Utilizing this approach to simulate cells during charging reduces the risk of plating, thereby enhancing safety as well as cycle stability.

However, achieving accurate model predictions requires substantial computational effort and extensive parameterization, making onboard application on a simple battery management system (BMS) challenging. To address this gap, we developed a reduced physicochemical and thermal model capable of running on a basic microcontroller (MCU). This model resolves the electrochemical processes, including the anode potential, which enables the detection of lithium plating. Combined with the thermal model, it also considers the cell's thermal behavior and temperature-driven parameter changes. By utilizing the model's output information, real-time control of the charging process becomes feasible.

The results of the reduced model are compared with those from the commercial software PyBaMM, implemented as a pseudo-two-dimensional (P2D) model [1], using the same parameter set as in [2]. Initial data indicate that the developed model and the PyBaMM implementation show good agreement for charging rates up to 2C. In the next step, it is planned to parameterize a commercially available Li-ion cell for higher charging rates and investigate the model's hardware and computational requirements.

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Analysis of DEM-calendered anode microstructure for electronic and ionic conductivity

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Within lithium-ion battery production, dedicating attention to all process steps along the fabrication chain and understanding their influence on the batteries' performance indicators is crucial for enhancing battery operation. Such key indicators include the electrode's electronic and ionic conductivity, which are both determined by its chemical and structural composition.

The calendering process primarily determines the final structural composition of the electrode, as this process step is the last to influence the electrode's microstructure before the electrode is incorporated into the battery. By compacting the electrode-current collector composite, calendering contributes to the mechanical integrity of the cell, ensuring that the electrodes remain intact and securely bound to the current collectors [1]. The calendering process reduces the microstructure's porosity so that electronically conductive agents form contiguous networks, which improve the electronic conductivity of the electrodes. However, lower electrode porosity also diminishes the accessibility of lithium ions to the active materials during charge and discharge cycles. An optimal calendering degree achieves enhanced electrical conductivity and mechanical stability at the same time as high ion mobility, making it a critical factor for later battery performance. [2]

In this work, the calendering process of anode microstructures from irregular-shaped graphite is simulated via the Discrete Element Method, and the resulting microstructures are analysed for electronic and ionic conductivity. Analysis shows that the chosen shape for the simulated active material particles significantly influences the results of the calendering simulation: stresses experienced by the electrode during the simulation increase by nearly 85 % if the simulations employ spherical instead of flat particles to represent the graphite active material. This shows that the typically employed spherical particles cannot capture experimental results for graphite anode calendering accurately. Thus, non-spherical particles, representing the actual shape of graphite, are used in the calendering simulations and the subsequent structural analyses, yielding realistic results. A correlation between the degree of densification and final performance parameters is established, and all simulated results are compared with experimental values. Intrinsic resistances of the materials used in the simulations are determined by means of laboratory tests. The mechanical and structural simulations offer a good representation of the experimental results.

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Fully coupled three-dimensional electrochemical and thermal simulation of cylindrical lithium-ion battery cells

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During battery operation it is essential to know the cell temperature accurately to improve performance, aging and safety. The battery management system, for example, utilizes this information to control the cooling system appropriately and prevent damage, e.g. from thermal runaway. Further, the electrochemical behaviour is affected by the local temperature since material parameters like the ionic conductivity and current exchange density are highly temperature dependent. The electrochemical behaviour is often modelled with the P2D Newman model which neglects cell format details like voltage drop over the current collector [1]. Existing methods to determine the internal cell temperature often rely on specific operation modes like EIS or pulse resistance [2].

In this work we present a new method for cylindrical cells by coupling a P4D electrochemical simulation on a cartesian grid with a thermal simulation on a cylindrical grid. This allows quantifying the local temperature distribution within the cell for arbitrary boundary conditions and its implications on the electrochemical behaviour.

Our method (see Fig. 1) starts with unrolling the winded sheet consisting of electrodes, separator and current collectors. The smallest periodic layer-stack is used for the electrochemical simulation domain in through-direction. In the electrochemical simulation part of a timestep, the local temperatures are fixed, and the local thermal powers are computed from resulting concentrations and potentials. These local thermal powers are passed to the thermal simulation part conducted on a cylindrical grid where each winding is approximated as concentric circle. Here, the heat equation with the previously computed local thermal powers as source terms is solved. The resulting temperature field is passed back to the electrochemical simulation in the next timestep.

A simulation study is conducted where cell dimensions and boundary conditions are varied and analysed with respect to the resulting temperature gradient within the cell and its implications on the cell performance.

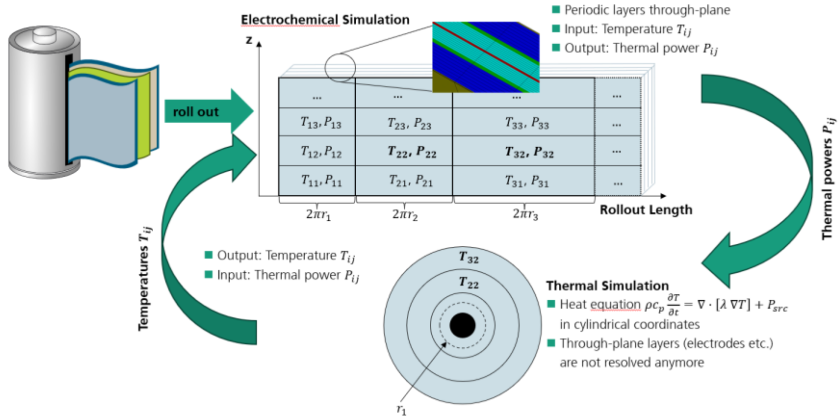

Figure 1: Scheme of simulation algorithm

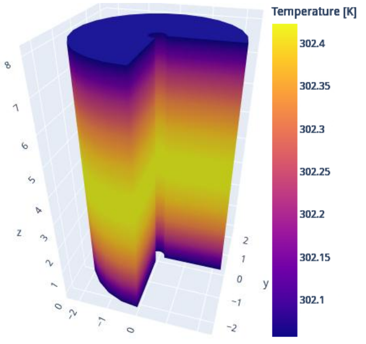

Figure 2: Representative temperature field

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Modelling Voltage Hysteresis in Silicon-Based Anodes and LFP Cathodes Using PyBaMM

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Voltage hysteresis is a significant challenge in lithium-ion batteries, affecting efficiency, energy density, and state-of-charge estimation, particularly in materials like silicon-based anodes and lithium iron phosphate (LFP) cathodes. Silicon anodes, while offering high theoretical capacity, experience pronounced hysteresis primarily due to phase changes during lithiation-delithiation and plastic deformation in the solid-electrolyte interphase (SEI). LFP, on the other hand, is a cost-effective cathode material known for its excellent safety profile and long lifespan, making it ideal for applications requiring high load currents and endurance. However, LFP also exhibits voltage hysteresis due to solid-solution behaviour and phase transition. Addressing these sources of hysteresis is essential for optimizing charge/discharge efficiency, estimating state of charge, predicting charge-discharge energy and extending cycle life.

Despite the importance of accurate hysteresis modelling, current approaches often rely on empirical fits, such as sigmoid-based profiles, which lack precision and physical insight into underlying electrochemical processes. This limitation underscores the need for a physics-based approach that can be integrated with sub-models—such as degradation and thermal effects—for better predictive accuracy. PyBaMM provides a promising platform for this, enabling flexible integration of detailed hysteresis mechanisms within an open-source framework.

This study employs a multi-step modelling approach in PyBaMM to capture the thermodynamic hysteresis effects in both materials, focusing specifically on phase-change-induced hysteresis in silicon. For silicon anodes, we begin with a 0D model adapted from literature and validated against experimental data [1,2] capturing the core reaction mechanisms and phase transitions. This model is extended to a pseudo 1D framework incorporating spatial diffusion within the electrolyte, enabling a detailed analysis of effects of mass transport limitations in electrolyte.

For LFP cathodes, a current MATLAB-based model developed in DandeLiion is being adapted into PyBaMM, facilitating testing with coupled degradation sub-models and supporting an open-source approach to analysing hysteresis.

Together, these models provide a foundation for understanding and managing voltage hysteresis in silicon and LFP electrodes, advancing the understanding of performance limitations of highly relevant commercial Li-ion battery chemistries.

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Investigation of LTO anodes as a reference for EIS and NFRA measurements

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To enhance the energy and power density of Li-ion battery electrodes, detailed insights into their behavior are essential. Electrochemical reaction kinetics are among the key factors influencing performance, and precise measurement data are critical for developing highly accurate models. To thoroughly investigate electrode kinetics, Electrochemical Impedance Spectroscopy (EIS) [1] and Nonlinear Frequency Response Analysis (NFRA) [2] are powerful and complementary techniques. Obtaining sufficient data to parameterize a reaction kinetics model requires conducting EIS and NFRA measurements across various temperatures and states of charge (SoC). Furthermore, isolating the contributions of the anode and cathode necessitates performing these measurements on each electrode individually.

This experimental characterization is conventionally achieved using symmetric cells. However, obtaining reliable results for SoC variability in symmetric cells is challenging because each SoC requires constructing a new cell. Furthermore, symmetric cells often exhibit poor time stability in their impedance spectra.

This study presents a more efficient approach using experimental cells with a $Li_4Ti_5O_{12}$ (LTO) anode as the counter electrode. LTO displays an almost constant exchange current density across a wide SoC range (10–90%). As demonstrated in this work, this property results in SoC-independent anode spectra within the frequency range of interest. Provided that the charge transfer coefficients are also SoC-independent, the same applies to the nonlinear frequency response (NFR). Moreover, due to differences in microstructure, LTO electrodes exhibit frequency responses in ranges distinct from those of common NMC cathodes. Consequently, to obtain the frequency response of a single electrode at varying SoCs, it suffices to perform measurements on a full cell with an LTO counter electrode and subtract the SoC-independent anode response.

To validate this novel method, an LTO electrode was first characterized. The SoC-independence of LTO spectra and NFR was then verified experimentally and supported theoretically. Finally, the method was demonstrated through a series of EIS and NFR measurements on LTO–NMC83 full cells, enabling the determination of SoC-dependent linear and nonlinear frequency responses of the NMC83 electrode.

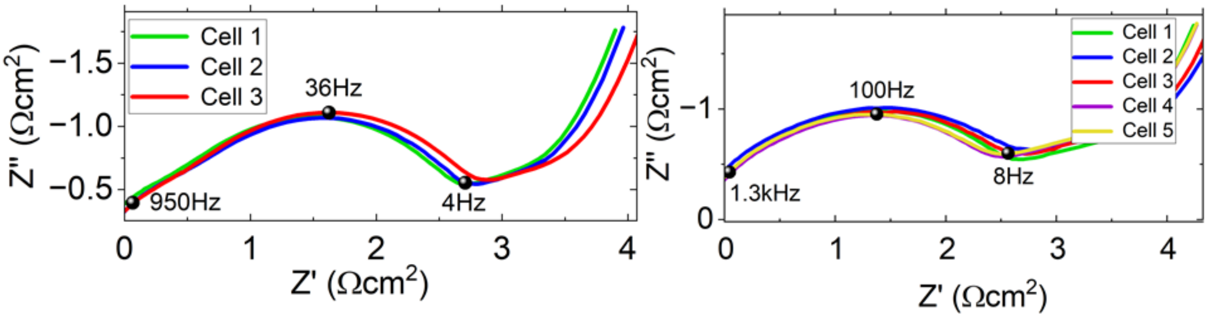

Figure 1: Cathode EIS response at SoC 50 obtained after removing the LTO contribution from the measurement data on a) LTO-NMC83 full cell, b) LTO-NMC811 full cell.

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Fast Inference of Physics-Based Models with Surrogate Neural Networks

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Despite significant advancements in state-of-the-art numerical solvers, solving physics-based battery models remains computationally demanding. Reducing computational costs is highly desirable for: (i) enabling deployment on modest on-board hardware and (ii) addressing tasks like optimal design, parameter identification from data, and optimal control. The latter tasks often require a large number of model solutions, exacerbating the computational challenges associated with slow solvers.

A contemporary solution is the development of model "surrogates," i.e. approximate models that map inputs and parameters (e.g. currents and diffusivities) to observable outputs (e.g. cell voltage). This approach is gaining traction within the battery modelling community.

We present a novel supervised method for constructing neural network (NN) surrogates, offering enhanced flexibility in handling diverse input structures. Notably, our surrogate can accommodate arbitrary time-dependent current inputs and infer state-dependent functional parameters. To the best of our knowledge, this is the first surrogate model to achieve these capabilities. This advancement is of significant practical importance, as it enables the application of our surrogates on deployed devices where the demands on the battery can be highly inhomogeneous.

As a proof of concept, we construct a surrogate for a Single Particle Model with Electrolyte (SPMe) that predicts concentration profiles under arbitrary current inputs and non-linear diffusivities within a defined range. This highlights the potential of our method to address complex scenarios. A preliminary example, shown in the accompanying figure, demonstrates a 10^4-fold speedup compared to classical solvers. These fast and flexible surrogates enable real-time updates to posterior parameter distributions and facilitate online inference, offering a practical alternative to battery teardowns.

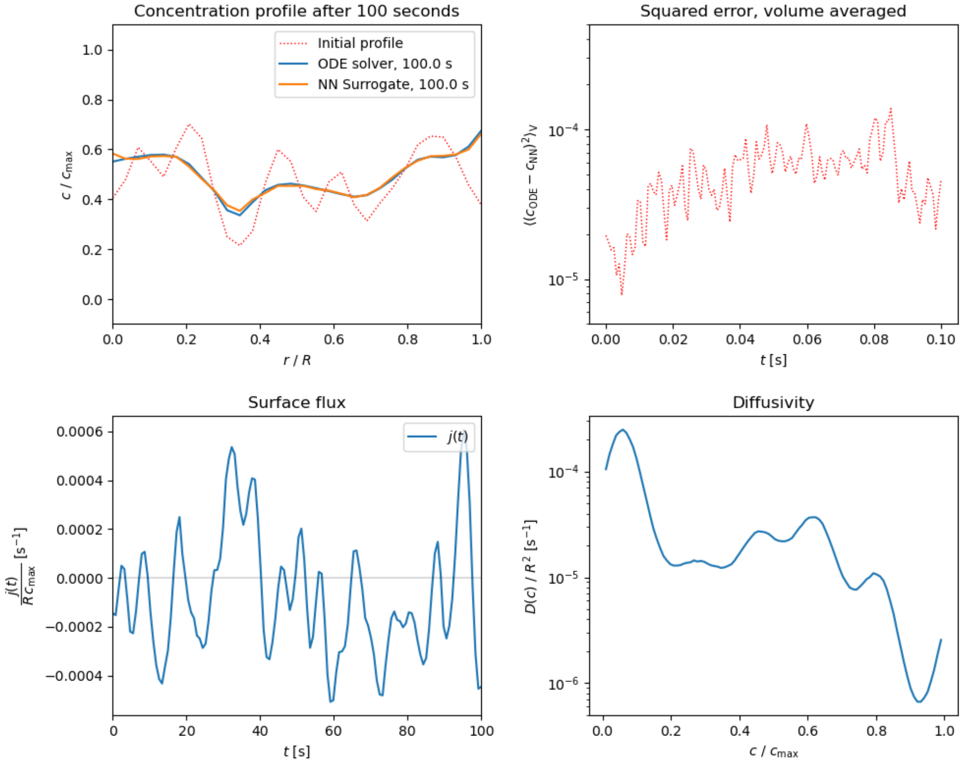

Figure: Comparison between the neural network (NN) surrogate and the traditional ordinary differential equation (ODE) solver for a randomly sampled surface flux (bottom left) and diffusivity function (bottom right). The top left panel displays the concentration profile after 100 seconds of evolution, while the top right panel shows the evolution of the mean squared error over time.

Investigating Image Processing for Determining Geometrical Parameters of P2D Battery Models and Its Influence on Model Validity

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The particle size distribution (PSD) of electrode materials is critical to the performance of lithium-ion batteries. The PSD of both positive and negative electrodes depends on the materials used and the manufacturing process, but can also change during battery operation. The size and number of active particles have a significant effect on the capacity and kinetic behaviour of the electrodes. However, actual electrodes contain particles of different sizes and shapes, making it difficult to measure the PSD and define a single representative radius for modelling purposes [1,2]. There are several possible imaging techniques to analyse particle sizes in 2D, such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM), or in 3D, such as focused ion beam scanning electron microscopy (FIB-SEM) or X-ray Computed Tomography (X-ray CT) [3]. However, they have the disadvantage of being expensive and demanding in terms of sample preparation. In this work, we explore the use of top-view images from conventional digital microscopy in combination with automated image analysis as an alternative and investigate the impact on model validity within P2D model parameterization workflows.

In this study, we explore image processing strategies to determine the particle size of lithium-ion battery electrodes for an efficient parameterisation process. Segmentation techniques are used to identify the induced particles and derive the PSD as shown in Figure 1. The results of this analysis are presented for electrodes harvested from large format pouch cells. The particle size assessment is part of a heuristic parameterisation workflow that aims to determine the full set of parameters of a P2D battery model through a direct measurement strategy. As this requires a stepwise parameterisation, parameter interdependencies have to be considered. In particular, particle size influences the solid diffusion coefficients measured by galvanostatic intermittent titration (GITT) and exchange current densities determined by electrochemical impedance spectroscopy (EIS), and consequently the tortuosity and effective electrode conductivity estimated by C-rate tests. We discuss the uncertainty in particle size assessment and how it propagates through such parameterisation workflows.

Using this analysis within the parameterisation workflow will enable researchers to improve their understanding and optimisation of electrode materials. In particular, this becomes critical once ageing models are integrated and is therefore relevant to advancing the accurate prediction of battery life using mechanistic models.

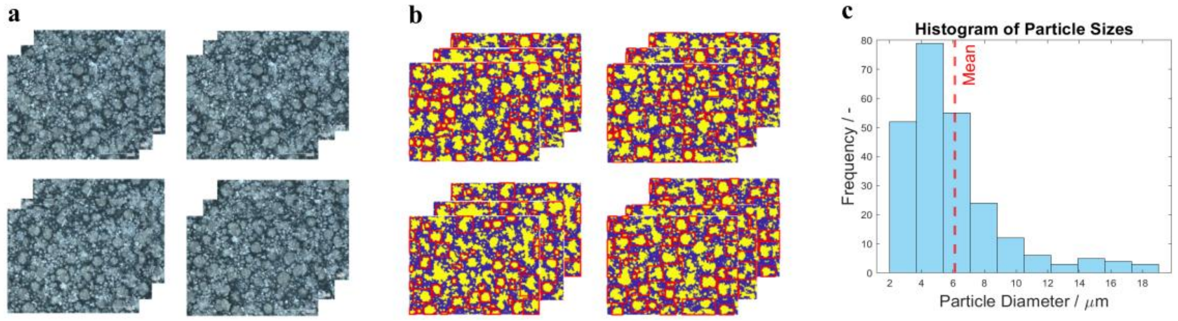

Figure 1: a) Top-view images from digital microscopy, b) processed images, c) particle size distribution

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Enhanced Virtual Upscaling - From Battery Cell to Module With Smart Sensor Measurements

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Virtual twins show great potential to accelerate the development of battery modules at a stage where only A- or B-samples of the physical cells are available. This means that parametrized models only exist on the scale of individual cells and that the module is nothing but a virtual assembly of the cells and a thermoregulation system. To raise the acceptance of virtual module design, the underlying cell models must be sufficiently accurate and computationally performant. The accuracy relies on robust parameterization procedures and even more so on novel measurement techniques as data source for parametrization. Computational performance can be raised by the application of order reduction techniques that allow keeping the physical essence of the genuine cell model which is assembled many times in a module.

Optical fiber Bragg grating (FBG) sensors are capable of tracking internal temperature, pressure and strain of a cell while it is cycled and subject to different boundary conditions [1]. These measurements provide insights into the cell's thermal properties and related chemical observables, enabling the pinpointing of different heat sources, such as irreversible power losses and reversible (entropic) heat. Due to the micron size of the FBG sensors and possibility of using FBG sensor arrays, multiple sensors can be positioned even within small format cells, allowing spatial temperature distributions to be monitored. This is demonstrated for a 21700 cylindrical cell which uses beyond state-of-the-art cell chemistry, i.e., a NMC cathode and high-Si anode.

Based on experimental data, a multi-scale multi-domain (MSMD) model is developed and parametrized with the system modelling platform AVL CRUISE™ M. The model of the 21700 cell comprises a 3D thermal domain, a 2D electrical domain, representing the collectors, and a domain which describes the electrochemical processes within the cell based on the P2D approach [2]. The highly resolved and parameterized MSMD model of the single cell serves as a reference for a virtual upscaling procedure to the module level. Based on thermal simulations which are linked to dedicated measurements from FBG sensors, two reduced order models are developed which are individually tailored to two module thermoregulation concepts representing stationary storage and automotive application.

The reduced and computationally accelerated cell models are embedded into dedicated battery module models (also developed in CRUISE M), following commercially available designs and cooling concepts using bottom and air convection cooling, respectively. The thermal behavior under various loads is simulated, focusing on the requirements for each specific use case. These learnings allow to adapt and improve cooling designs. The tailored reduced models still contain the full functional scope of the P2D model, providing access to physical states relevant to address battery degradation. This opens up the possibility to virtually assess how different degradation scenarios impact the module design compared to pristine cells.

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Modelling the discharge behaviour of battery cells with phase-separating active materials on the example of LFP

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LiFePO4 (LFP) is a wide-spread used cathode material for rechargeable batteries. It is known for its phase-separating characteristics during charging and discharging. Furthermore, the shape of the active material particles is platelet-like with large ac-facets. Modeling helps understanding batteries behaviour during charging and discharging better. One popular model to electrochemically model battery cells is the classical P2D model for Lithium-ion-batteries [1,2]. This model describes the behaviour of batteries consisting of spherical active material particles that form a solid solution, where diffusion is represented by the classical Fickian equations. On the other hand, phase-separation can be modelled with the help of the Cahn-Hilliard model for diffusion [3]. The goal of this work is to develop a physically consistent half-cell model for LFP based on the P2D model and the Cahn-Hilliard-equation to describe diffusion for his phase separating material.

In this study, we present a half-cell model consisting of LFP platelets as the cathode active material particles. These platelets feature a large ac-facet. Lithium intercalation occurs exclusively through the ac-facets. By assuming infinitely fast diffusion within the diffusion tunnels perpendicular to the ac-facets and symmetry across the platelet width, a step-wise dimensional reduction to a one-dimensional system is achieved [4]. Due to these assumptions the intercalation surface term can be interpreted as a volumetric source. These adaptions are used for the mass conservation equation of the half-cell models. The equations describing the electrode level are kept like in the classical P2D model. In this contribution, we present and discuss the discharge behaviour as obtained by this model.

The resulting discharge curve for 1C can be seen in Figure 1. The curve shows a plateau at a height of 3.375V which is plausible because the typical value of 3.41 V can only be reached for low C-rates. The drop in voltage before the plateau is reached could be explained by a nucleation barrier of the LFP/FP phase boundaries.

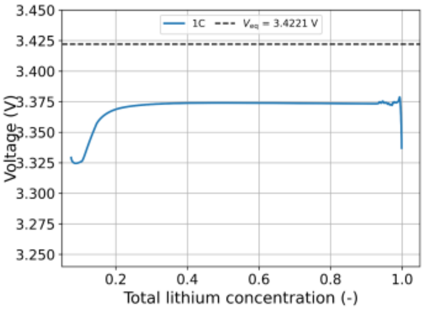

Figure 1: Discharge curve of LFP half-cell at 1C.

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Electrochemical and mechanical behavior of a lithium-ion cell with a silicon-graphite negative blend electrode

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Combining silicon and graphite in a blend negative electrode in lithium-ion batteries allows to take advantage of both, high capacity of silicon, and high lifetime of graphite [1]. In this study, a multiphysics pseudo-three-dimensional (P3D) model was used to investigate the electrochemical and mechanical behavior of silicon in silicon-graphite blend electrodes. The model builds on a thermo-electrochemical and mechanical framework and incorporates fictitious silicon particles into an existing model of a 350 mAh lithium-ion pouch cell with an LCO/NCA positive electrode and a graphite negative electrode. The base model has been previously parameterized and validated by Schmider et al. [2]. Key parameters, such as the lithium diffusion coefficient in silicon, were extracted from literature, and a novel thermodynamic approach was introduced to capture the voltage hysteresis of silicon. The hysteresis model was validated against published experimental half-cell data for silicon against Li/Li$^+$.

We show systematic simulations that explore the influence of varying anode thickness, silicon volume fractions, and particle sizes on electrochemical performance and mechanical expansion. Results indicate that thinner anodes increase the degree of lithiation due to the fact that less silicon is available but also lead to higher mechanical stresses despite improved gravimetric energy density. Particle size variations revealed that smaller particles exhibit higher degrees of lithiation due to a larger surface-to-volume ratio, while larger particles induce pronounced voltage hysteresis and higher stress. Additionally, microscale lithium stoichiometry gradients within graphite and silicon phases were visualized, showing gradient-free behavior in silicon at smaller particle sizes.

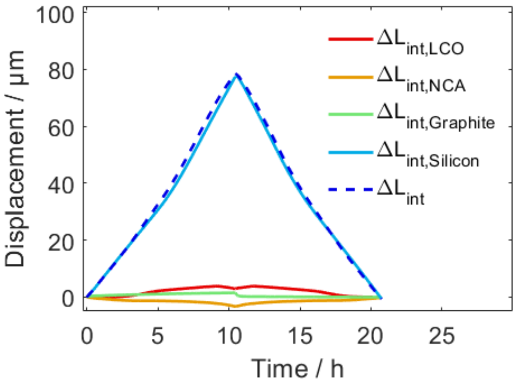

Figure 1: Simulated intercalaction-induced displacement of each active material in the cell consisting of a Si/Graphite blend at the negative and an LCO/NCA blend at the positive electrode.

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Dual Particle Model with Electrolyte for Lithium-ion Batteries with Silicon/Graphite Negative Electrodes

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Silicon-graphite composite anodes for Lithium-ion batteries (LIBs) are increasingly being adopted to enhance the energy density compared to traditional LIBs with graphite anodes. In traditional LIBs, the Dolye-Fuller-Newmann model is solved in a pseudo-2-dimensional (P2D) framework to examine the electrochemical behaviour. However, due to differences in the reacting voltage window and material characteristics during reactions between silicon and graphite, the traditional P2D model has limitations to describe the complex behaviour of composite electrodes. Recently, a P2D-based composite electrode model (CEM) has been developed that considers the interactions between both materials [1]. Although the proposed model precisely describes these interactions, solving the coupled nonlinear governing equations makes it computationally expensive. In this work, we propose a dual particle model with electrolyte (DPMe), which is based on the single particle model with electrolyte (SPMe) and CEM. The DPMe shares the basic structure of the SPMe, which solves for a single particle and electrolyte, but assumes the particle is composed of both silicon and graphite. This approach reduces the dimensionality of the CEM while still capturing the essential electrochemical dynamics. To construct the proposed model, the following assumptions and steps are applied: 1) The sum of the reaction amounts of silicon and graphite equals the total reaction amount; 2) The potential of silicon and graphite are assumed to be the same. By satisfying these assumptions, the DPMe accurately describes the varying reaction amounts of each material and their stoichiometric profiles during operation. Compared to the CEM, the DPMe effectively analyzes the individual dynamics of silicon and graphite. In addition, a genetic algorithm (GA), an optimization technique, is applied to estimate the parameters of the DPMe. By utilizing the estimated parameter set, both the DPMe and CEM reproduce both charging and discharging data obtained by the experiment. Therefore, it can be concluded that the developed model not only represents the electrochemical behavior of the composite anode but also accurately predicts the output voltage. The proposed DPMe model provides a computationally efficient framework to quantify properties and analyze the behavior of LIBs with composite electrodes.

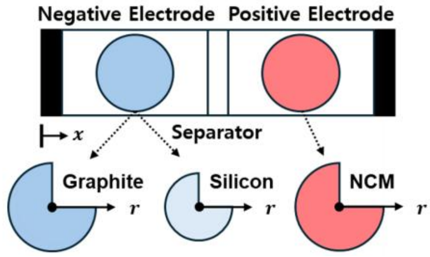

Figure 1: Schematics of the proposed DPMe.

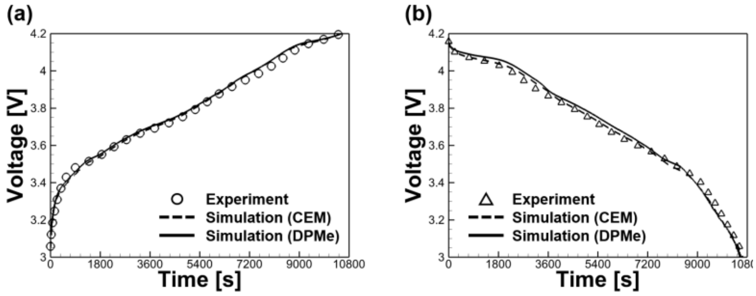

Figure 2: Comparison of the voltage during (a) charge and (b) discharge obtained from the experiment and simulation of CEM and the proposed DPMe.

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Integration of lithium-ion batteries in a micro-photovoltaic system: Demonstration of an active charging system

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Micro-photovoltaic systems allow a simple and decentralized contribution of all citizens to the energy transition [1]. Consequently, they show high growth rates. At the same time, batteries of electric bicycles or gardening tools are today available in many households, where they are usually used only temporarily (for example, only on weekends). We have developed an active charging system with three different operating modes (PV operation, battery charging and battery discharging) to integrate such lithium-ion batteries into a micro-photovoltaic system. The charging system has two advantages for the owners: Firstly, the self-consumption is increased, which reduces the purchase of electricity and saves money. Secondly, the batteries are charged with one hundred percent renewable, self-produced electricity, which is a direct contribution to climate protection. For the power grids, the buffering by the battery additionally reduces feed-in peaks.

Following the successful development of the active charging system, the development of adequate water-proof housing for the power electronics, and the construction of a test field, long-term tests with five micro-photovoltaic systems are currently underway. The field tests include four systems with an active charge controller with various batteries, as well as a reference system without a charge controller and battery. The long-term field tests will be used to test the newly-developed charging system. In addition, energy flows are measured during these field tests and evaluated afterwards. This allows a comparison of the performance of all five micro-photovoltaic systems (for example, self-consumption). Furthermore, our newly developed algorithm for SOC diagnostics with voltage-controlled models [2,3] is integrated into the active charging system.

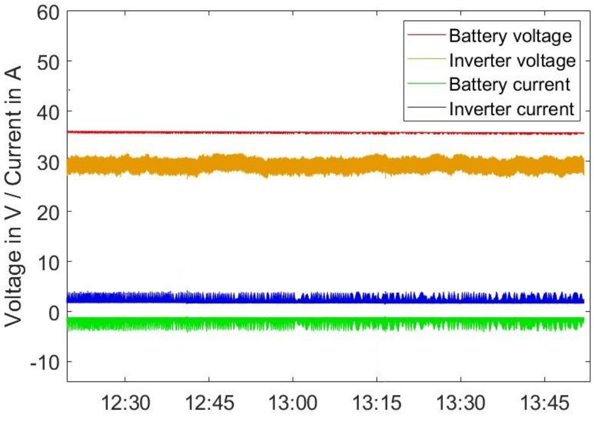

Figure 1: First measurements of a micro-photovoltaic system with the newly-developed charge controller and an electric bicycle battery. The battery is discharged with predefined power (80 W).

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Growth Mechanisms of Lithium Metal Dendrites Revisited

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Operando observations of growth using high resolution light microscopy

Metals such as lithium and sodium are considered ideal anodes compared to carbon-based materials for the development of future high energy batteries. However, alkali metals have a tendency for dendritic growth, which can lead to short cycle life and poses the risk of short circuits, raising safety concerns.

Various concepts and mechanisms of metal deposition and dissolution and dendritic growth are described in the literature. Although most growth models assume growth at the tip, experimental observations indicate that lithium can grow from the root. Besides these well-known growth locations, metal can be inserted within the growing structures. Our *operando* light microscopy observations indicate that this insertion mechanism appears to be active in a wide range of deposition rates (the rate was varied by a factor of 1000).[1] Such large rate variations lead to different large-scale morphologies (needles, loops, bushes) of which the local building blocks are the same. The building blocks consist of kinked lithium filaments and their growth involves the diffusion of lithium atoms into crystalline defects of the metal around the kinks (i.e. grain boundaries) [2]. In these observations metal insertion far away from the protruding tips is predominant. Particularly at extremely high rates this is surprising, given the kinetic enhancement that is expected to be present at the tips. Bai *et al.* performed microscopic measurements and report a transition from mossy lithium to tip-growing dendritic lithium which is believed to be correlated with the decreasing salt concentration near the surface after Sand's time.[3] Data on the relevance of different growth mechanisms are limited in literature but are important in order to control metal deposition in real cells.

To examine transitions between different growth mechanisms, symmetrical cells consisting of two lithium metal electrodes were built and *operando* light microscopy measurements were conducted. At the highest rates, we achieve electrolyte depletion as indicated by the rising cell voltage and can trigger a transition in growth mechanism from mossy to filament lithium growth. In contrast to Bai *et al.*, we found that both growth modes can be simultaneously active, and growth away from the tip is possible for both growth modes. On the poster, examples of different growth modes will be shown and the transition induced by electrolyte depletion at the highest rates will be illustrated. Our data demonstrates that metal deposition and dissolution are influenced by numerous factors, whose extent and correlation with the growth mechanism still need to be investigated in order to enable batteries with alkali metal anodes.

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Time-Dependent Global Sensitivity Analysis of the Doyle-Fuller-Newman Model

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The Doyle-Fuller-Newman model is arguably the most ubiquitous electrochemical model in lithium-ion battery research. It is used in academic battery research as well as industry to investigate the evolution of experimentally inaccessible internal quantities and tackle numerous research questions. However, as it is a highly nonlinear model, its input-output relations are still poorly understood. Researchers therefore often employ sensitivity analyses to elucidate relative parametric importance, e.g., preparatory to the data-driven parametrization of battery models [1]. However, some sensitivity analysis methods, for example the one-at-a-time method, are ill-suited for the complexity of the model, as pointed out by Saltelli et al. [2]. This necessitates the use of global sensitivity analysis. Yet, most available global sensitivity analysis methods are only applicable to scalar quantities of interest, limiting or even hindering their use to explore the parametric sensitivity with regard to time-dependent states of the Doyle-Fuller-Newman model.

We therefore implement a novel framework for global sensitivity analysis of time-dependent model outputs based on the work of Alexanderian et al. [3] and apply it to a drive cycle simulation using the open-source framework PyBaMM [4]. We conduct a sensitivity analysis on the full parameter vector of 24 considered parameters, with parameter ranges obtained from the LiionDB [5], and on subgroups thereof to resolve lowly sensitive parameters. Additionally, we explore the model error when insensitive parameters are set to arbitrary values. By doing so, we show that the method consistently identifies insensitive parameters, whose variations cause only small deviations in the time-dependent voltage response of the model. While the obtained results are not necessarily universally transferable to other applications, our implementation of algorithms for time-dependent global sensitivity analysis along with the presented findings enables a new and versatile approach to investigate, optimize, and parametrize battery models.

We hope that by providing the methodology, research questions related to parametric sensitivity for time-dependent quantities of interest, such as voltage responses, can be addressed more easily and adequately in simulative battery research and beyond.

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A Reduced Order Model of Physics-Based Hysteresis in Lithium Iron Phosphate Electrodes

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Lithium iron phosphate (LFP) and its derivatives are of sudden and critical commercial interest as electrode materials for Li-ion batteries. These materials exhibit lithiation-induced phase change, leading to phenomena such as voltage hysteresis. However, the 'gold-standard' Newman model, based on a microscopic description of lithium diffusion within electrode particles, is incapable of predicting phase change phenomena, leaving a gap in the modelling of these materials. The recently introduced 'composite phase change model' [1] has addressed this gap through systematic minimisation of the Gibbs energy to arrive at a physics-based model of an ensemble of phase changing particles, out of which voltage hysteresis arises naturally. Despite its success at replicating phase change phenomena, this model is limited by computational cost to a small number of particles, used as representatives for the larger population and, as a result, solutions feature jagged numerical artefacts. In this work we present a reduced order variant of the composite phase change model, termed the continuum composite phase change model (CCPM)**.** This reduced order model is derived from the many-particle limit of the composite model for particles of similar geometry, avoiding the pitfalls associated with finite populations encountered by the latter. Rather than modelling a finite ensemble of particles individually, the CCPM instead deals in probability density functions for the lithiation state of an infinite population of particles. As a result, phase change becomes a continuum process, eliminating the numerical stiffness and jagged solutions associated with the instantaneous phase change of each particle. This in turn reduces the computational cost associated with solving the model, in addition to allowing easier parameterisation due to a reduction in the number of parameters. Like the composite model, the reduced order model naturally predicts a range of hysteretic phenomena, including major loops, minor loops, and temporary enhancement effects, and can easily be embedded within a classical Newman framework to account for the effects of electrode conductivity and electrolyte transport.

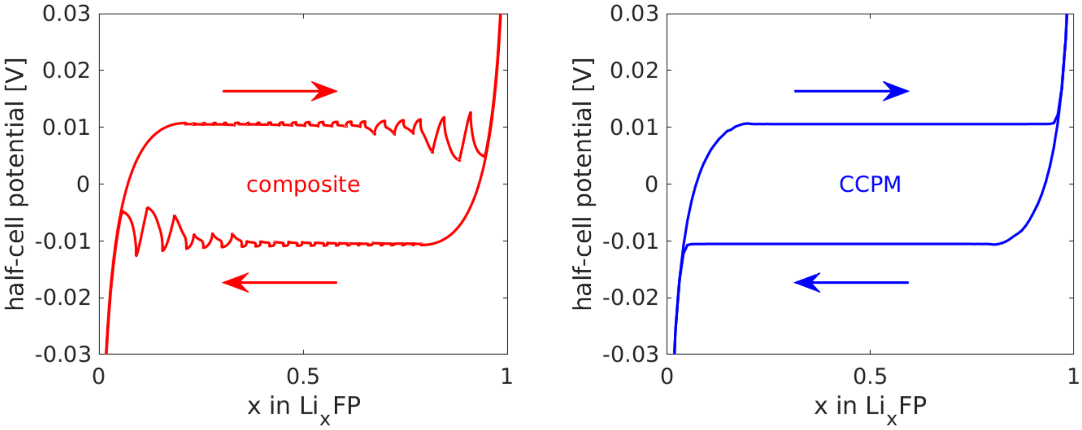

Figure 1: Comparison of major loops for a thin electrode half-cell, as predicted by the composite model (left) and the new CCPM (right). Note the unphysical jagged features present in the composite model in comparison to the smooth solutions of the CCPM that match experimental measurements. Computation time was roughly equal between the two simulations.

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A Novel Energy-Based High-Fidelity Multiphysical Model for Robust Simulations Across a Wide Range of Electrolyte Concentrations

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The employment of lithium-ion batteries in contexts demanding extreme operational parameters, such as ultrafast charging at high C-rates (>3C) or operation with ultra-dilute electrolytes (<0.1 M), is increasing. In these applications, simulations—especially those utilizing high-fidelity models—are crucial for accurately predicting battery performance and safety, as they allow for a detailed understanding of the complex electrochemical processes that occur under such demanding conditions. However, simulating ultra-dilute electrolytes poses significant challenges, including numerical instability due to sharp concentration gradients and difficulties in accurately representing ionic transport phenomena at low concentrations.

To address these challenges, a multiphysical model was developed that effectively addresses these issues. This porous electrode model integrates key phenomena such as ion pair formation and the formation of the electric double layer (EDL), which includes a diffuse double layer (DDL) extending into the electrolyte [1], as well as the adsorption of charged species at the interface. This comprehensive representation accurately captures the electrochemical processes occurring within the battery. The numerical challenges are addressed by converting concentrations into energies according to the Nernst equation, which delineates a quantitative relationship between the electrochemical potential and the concentrations of the ionic species implicated in the electrochemical reaction. This exponential representation guarantees that the values remain positive, thus effectively mitigating issues that may emerge in finite element method (FEM) simulations when the numerical solution of concentrations approaches zero or becomes negative.

The approach is demonstrated for a one-dimensional lithium-ion cell design utilizing an ultra-dilute electrolyte of lithium hexafluorophosphate ($LiPF_6$) at a concentration below 0.1 M, implemented using COMSOL Multiphysics. The cell features a porous electrode architecture with a graphite anode and nickel manganese cobalt (NMC) cathode, reflecting the composition typical of conventional lithium-ion battery systems.

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Collaborative experimental-computational workflows for accelerated parameterization of battery models

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Traditionally, parameterizing physical battery models involves extensive characterization and measurements that often use specialized equipment, destructive methods and requires significant domain knowledge. The rapid emergence and diversification of new battery chemistries increases the challenge due to the lack of literature data to complement extracted parameters from measurements. In case of commercial cells, the parameterization process further includes time-consuming cell teardown and costly characterization at the material and component levels, resulting in high expenses and prolonged testing timelines. All of this generally limit the use of physics-based models in application. Evidently, there is an increasing demand for more efficient parameterization workflows and tools that minimize time and cost while guaranteeing reproducibility and desired levels of accuracy.

In this work, we present a collaborative experimental-computational workflow to efficiently parameterize physical models from electrochemical data that, when fully implemented, allow a completely automated pipeline from execution of the experiments to the parameterized model. Central to this approach is the use of a standardized, unambiguous and machine-readable data description based on the Battery Interface Ontology (BattINFO) which ensure that data and parameters are described with clear, unambiguous meanings and consistent units [1]. This allows automated processing of the data with the use of advanced digital tools. Herein, we employ the two inverse-modelling frameworks *PyBOP* developed by University of Oxford [2] and *EP-BOLFI* from DLR [3] as well as the data storage platform *Kadi4Mat* to document the workflows and links between the data. In an exemplary study case to demonstrate the approach, we start from synthetic data generated by a parameterized model in *PyBaMM* to establish the data workflows and study the effect of data quality by addition of different levels of noise. Switching to experimental data extracted from commercial graphite electrodes, we investigate the effect and robustness towards variation of the test parameters used in the experimental procedure. Furthermore, we start to evaluate identifiability of the parameters and optimize the experimental sequence to improve the outcome.

The shown approach can significantly reduce the quantity of measurements required for battery model parameterization, paving the way for a more cost-effective and efficient development pathway. Importantly, as experimentalists who invested a lot of efforts on conventional parameterization activities in the past, the main authors want to put an emphasis on the benefits of digitalization and automation and encourage more collaboration between the experimentalists and theoreticians starting at an early stage of research.

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Continuum Modeling of Ca-based Batteries

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Among the various post-lithium battery materials, calcium is a promising anode material due to its high natural abundance and improved safety compared to lithium, while having only a slightly lower electrochemical potential than lithium. [1] We focus on a Ca-S cell and a battery with an anode mainly made of Ca-Sn alloys and a 1,4-polyanthraquinone cathode [2].

We model these Ca-based batteries to gain a better understanding of the processes inside the batteries. Our model considers concentrated solutions and porous electrodes. It describes the one-dimensional transport of ions from the anode to the cathode on a macroscopic scale by means of a system of differential and algebraic equations. The charge transfer reactions are modeled using Butler-Volmer kinetics. [3] We adapted this model to the battery cell with the Ca-Sn alloy anode and the 1,4-polyanthraquinone cathode [2] and parametrized it.

The difficulty in adapting the model to the Ca-S cell lies in the different sulfides which occur in the polysulfide shuttle. For each sulfide a transport equation is added, and the concentration of that sulfide or the porosity is described, respectively. [4] Compared to the Li-S cell, there are more unknows related to speciation in the electrolyte and the thermodynamics of the precipitates. We aim to parametrize the model with data from our project partners in the BMBF CaSino project.

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Influence of intragranular cracks on effective transport properties of granular cathode material using homogenization

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Given the growing need for specialized energy storage systems, it is essential to elucidate the relationship between battery electrode microstructure and physical properties. To this end we focus on the microstructure of porous cathodes and its effect on electronic and ionic transport. These physical properties influence an energy storage cell's electrochemical behaviour and therefore its area of application. To calculate these transport properties for an assembly of particles, we utilize the computationally inexpensive resistor network method instead of a spatially resolved method [1]. While the resistor network method approximates the microstructure of the active material at electrode level using discrete particles, the internal makeup of those particles is also highly salient for the overall transport properties.

To investigate the influence of intragranular cracks in active material particles on the transport inside of them, we on the one hand considered two and three dimensional FEM simulations of single cracks in a rectangular or cuboidal domain. The cracks where approximated by ellipses and spheroids, respectively. It was possible to construct a predictive analytical function based on the key geometrical crack properties: volume, aspect ratio and angle of rotation. The main obstruction to the transport is hereby given by the area the crack is shading in transport direction.

On the other hand, to investigate a more generalised case of periodically distributed cracks within a particle, a known homogenisation method for porous media was utilized [2]. Calculating the effective material properties requires solving a specific cell problem that is again solved using a finite element based software. It is again possible to construct an analytical function for predicting the effective transport properties.

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The change of Na storage mechanism from Soft Carbon to Hard Carbon

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Sodium ion batteries (NIB) are a potential alternatively for Lithium ion batteries (LIB) because of low cost and more abundant. Unfortunately, graphite anode in LIB is not suitable for NIB due to low capacity and high volume expansion. Other Carbon materials, such as: Soft Carbon (SC) and Hard Carbon (HC), are applied for NIB anodes. In previous theoretical studies, DFT calculation can clarify Na storage mechanism in Carbon materials, but they are unable to describe microstructure effect due to simulation cost [1]; while Machine Learning can summarize effect of microstructure but the Na storage mechanism in Carbon materials is neglected [2]. In this work, we continue develop our previous effective model [3] to study both Na storage mechanism in Carbon materials and the effect of microstructure of Carbon materials. Especially, we clarify how Na storage mechanism depends on microstructure when Carbon materials change from SC to HC [4], figure 1.

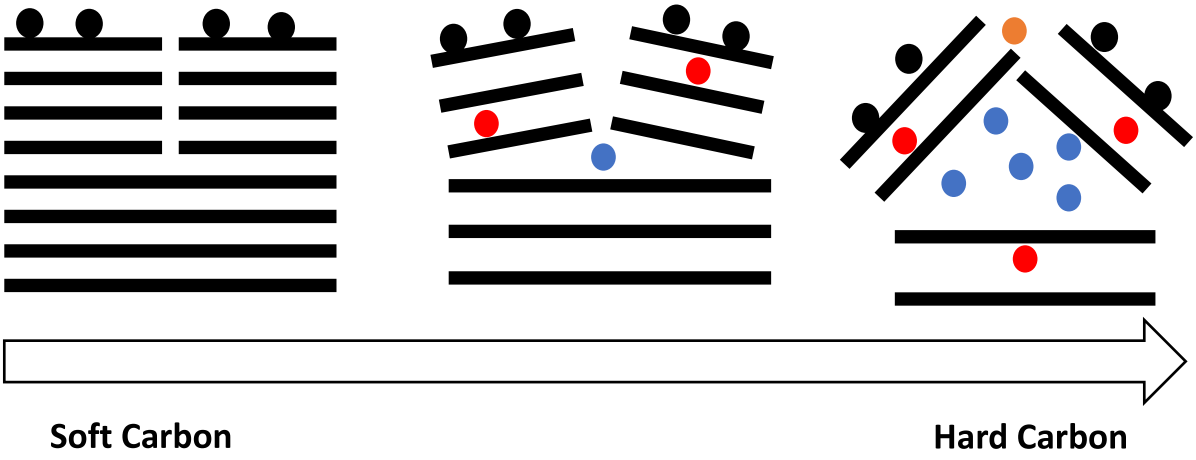

Figure 1: Change of Na storage mechanism from Soft Carbon to Hard Carbon. The black, red, blue, and orange circles are: adsorption Na on the graphite surfaces, layer Na in between 2 graphite layers, pore Na inside the pore, and defect Na at the (corner) defect sites of graphite layers respectively.

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Model-based Characterization of Aging in Sodium-Ion Batteries

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Linking Experimental Observations and Model-based Analysis
Sodium-ion batteries are emerging as a cost-effective and resource-abundant alternative to lithium-ion batteries due to lower material cost and greater resource availability [1]. However, a more detailed understanding of the mechanisms of their aging and degradation, including the effects of different cycling conditions such as fast charging, is essential to advance their commercial viability [2].

This work investigates the effects of cycle aging and fast charging/discharging of sodium-ion batteries, combining experimental insights with model-based analysis. Experimental analysis, including galvanostatic cycling, impedance measurements in full and symmetric cells, and scanning electron microscopy analysis of electrodes, were performed to capture the aging behaviour of the batteries. These experimental results laid the foundation for the subsequent modelling.

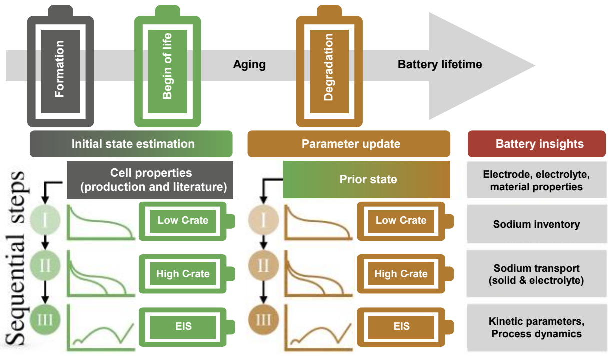

Figure 1: Schematic depiction of the model parameterization strategy, adapted from [3]. The insights from different parameter values as model output are summarized on the right.

A pseudo-2D physicochemical model including the solid electrolyte interphase (SEI), originally developed for lithium-ion batteries [3], was adjusted to sodium-ion batteries, incorporating the MSMR (Multi-Species, Multi-Reaction) method [4, 5] to describe electrode open-circuit potentials and detailed (de-)intercalation reaction kinetics at both electrodes. Parameter sets for three key stages - after formation, after 50 aging cycles, and after 100 aging cycles - were obtained and analyzed, as depicted in figure 1, to correlate experimentally observed aging phenomena, such as capacity fading, with underlying degradation mechanisms.

Experimental results showed a significant and irreversible capacity loss at fast charging rates (≥3C). The identified parameter evolution suggests that the capacity loss occurs due to depletion of the anode sodium inventory due to increased side reactions, such as SEI growth, during fast charging. SEM analysis of the electrodes supported these findings. Other parameter values that can be extracted from the model parameterization include solid and liquid phase mass transport parameters and kinetic parameters such as reaction rate constants. Conductivities and double layer capacitances can also be obtained. This work demonstrates the value of combining experiments and modelling in the investigation of degradation mechanisms and highlights the role of SEI dynamics in capacity loss during fast charging.

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Extending multi-scale simulations of sodium-ion batteries

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Sodium-ion batteries (SIBs) promise an appealing pathway towards a more sustainable and green energy storage technology compared to state-of-the-art Lithium-ion batteries (LIBs). Although there has been a remarkable progress in the development of SIBs in recent years, energy and power density have not yet reached the level of LIBs. In order to improve SIBs in this respect, advanced modeling and simulation techniques are a powerful tool accelerating material development and electrode design.

One of the major challenges in modeling batteries is the wide range of physical and chemical processes on varying length scales, that can limit the performance of the overall cell. Over the last decades, many simulation techniques have been developed on all relevant length scales. However, even with the usage of modern supercomputers it is still impossible to run simulations, that resolve an entire battery at its smallest length scale. Therefore, finding ways to combine multiple models in a single simulation is not straight forward, but yields the chance to better understand the interplay of different effects such as transport processes or surface reactions.

Microstructural resolved simulations provide an accurate description of the processes on the electrode scale and distinguish between different materials, which allows for locally imposing material specific models. In this contribution, we present relevant examples and applications of our latest developments for microstructural resolved simulations of SIBs with local models to efficiently capture the transport in and on active material particles. In particular, we developed a model for NVP ($Na_3V_2(PO_4)_3$). NVP is a promising intercalation material which has shown superior performance when synthesized with a hierarchical pore structure [1]. More specifically, the NVP particles are synthesized to form a nano-porous NVP/C composite material [2]. In our simulations we use a local homogenization technique with representative nanostructured active material particles, while still resolving the electrode structure on the micro-scale. Doing so, we capture the dynamics during discharge and provide ideas for improvements of the electrode structure.

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DoE Supported Parameterization of a Five Equation Pseudo Chemical Battery Thermal Runaway Model

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Parhizi et. al. [1] offers an Arrhenius reaction rate model to predict battery thermal runaway (TR) via 3D CFD simulation. This model describes heat production from the decomposition of solid electrolyte interphase (SEI), cathode, anode and electrolyte and the exothermal heat coming from the electrochemical processes due to battery internal short circuit (ISC). Typically, the reaction rate parameter of such models are determined via accelerated rate calorimetry (ARC) and differential scanning calorimeter (DSC) analysis of anode, cathode and electrolyte material, see Peng [2] and Abada [3]. Commercial battery testing applies ARC test of assembled battery cells to record cell skin temperatures during thermal runaway. The emphasis of this report is to determine the reaction rate parameter for the SEI, cathode, anode and electrolyte decomposition together with ISC for a commercial 66 Ah pouch Li-Ion battery from available cell skin temperature using design of experiment (DoE). The design space is spanned via S-optimal and Latin hypercube methods. Polynomial fits and recursive neural networks (RNN) are used to determine the optimum parameter. The model is used in a 3D CFD thermal propagation (TP) analysis of a 4s4p battery module. The model performance is compared to the empirical TR model of Citarella [4]. A variation of battery state of charge (SoC) and cell spacer material is used to demonstrate no TP development target.

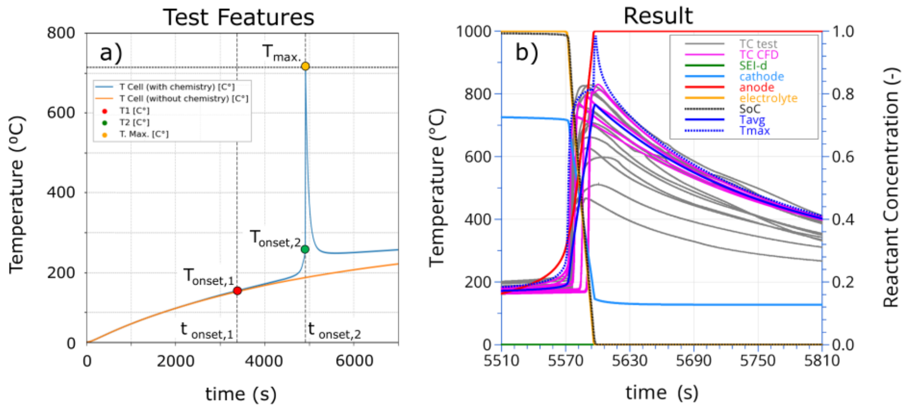

Figure 10, a) test features used for DoE optimized, b) CFD result of DoE optimization

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A Review of Coupled Numerical Modelling of Heat Transfer and Flame Propagation in Batteries

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The growing demand for sustainable energy storage technologies, particularly batteries, has driven significant research on their safety and performance [1]. The occurrence of thermal runaway (TR) events occur when exothermic reactions rapidly release heat and flammable gases, potentially leading to fires, ignitions, and explosions [2]. These events demonstrate how crucial sophisticated numerical simulations are for anticipating and reducing TR-related risks. Recent studies have explored the complex dynamics of flame propagation in confined and semi-confined environments [3,4,5,6]. Illacanchi et al. [3] highlighted that wall-induced pressure waves can reduce flame propagation speed, while Liberman et al. [4] demonstrated that rarefaction waves generated during flame deceleration create reverse flows and vortices, further disrupting the flame structure in confined channels. Meanwhile, Veiga-López et al. [5] noticed oscillatory instabilities in a Hele-Shaw cell, where acoustic waves induced pulsating, finger-like flame patterns.

These results demonstrate how environmental limitations can change flame dynamics. Although Computational Fluid Dynamics (CFD) simulations, especially Large Eddy Simulations (LES), have enhanced our understanding of TR events, challenges remain. Most existing models focus on module-level phenomena, simplifying the representation of spatial temperature gradients and interactions between heat conduction, convection, and radiation [7]. Furthermore, while studies like [8] have examined hydrogen jet flames and their interaction with surfaces, they do not fully address the unique conditions of wall-bounded fires in battery cells. Experimental data reveal that the cathode material composition influences gas release and ignition characteristics during TR [2].

The design and placement of ventilation systems also play a crucial role in controlling flame spread between adjacent cells [1]. Nevertheless, there is still a gap in high-fidelity simulations that capture the complex coupling of conduction, convection, and radiation at the cell level. Note that small-scale radiation models are scarce despite their importance in predicting heat transfer to neighboring cells and preventing cascading TR events. This study proposes a simulation framework using LES combined with reduced chemical kinetic schemes and experimental validation to model critical cell-level phenomena such as unstable flame fronts, anisotropic heat dissipation, and pressure gradients during venting.

This model helps the analysis of how small design changes—such as electrode composition, vent hole placement, or sensor positioning—can affect TR evolution and containment. By concentrating on detailed cell-level analyses, this research aims to identify specific failure patterns and propose improvements in thermal management and battery pack design. Our approach seeks to contribute to the prevention of critical TR scenarios in large-scale energy storage systems, providing a foundation for more effective containment and safety strategies.

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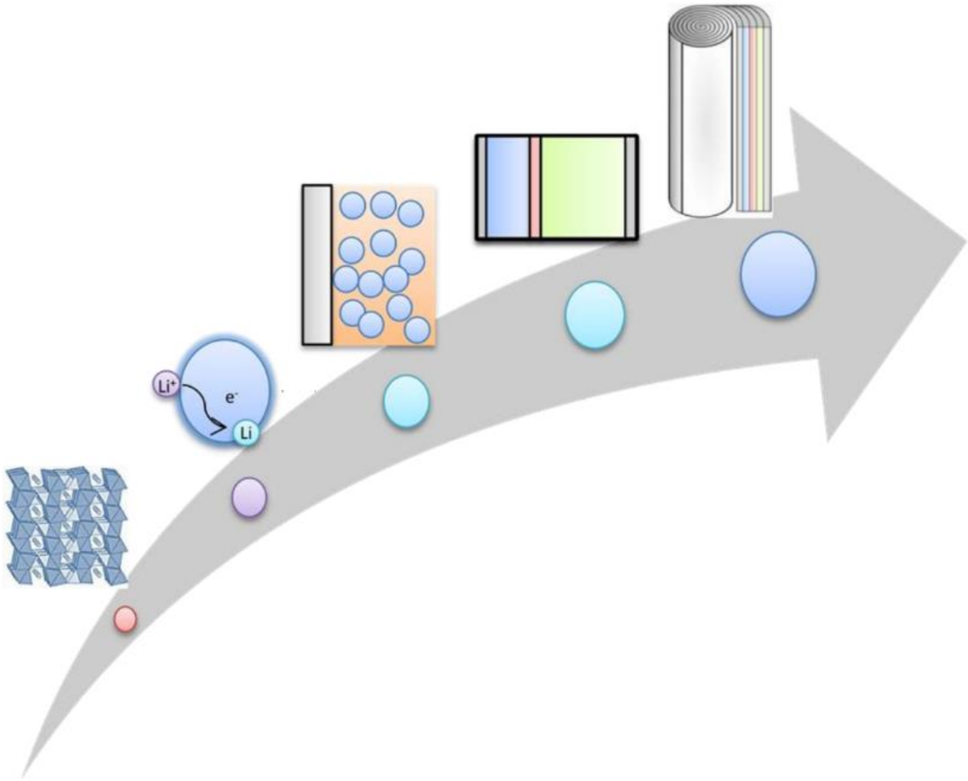

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