15th Symposium on Modeling and Validation of Electrochemical Energy Devices. ModVal 2018

Book of Abstracts

Conference Proceedings

Publication date:
2018

Permanent link:
https://doi.org/10.3929/ethz-b-000240521

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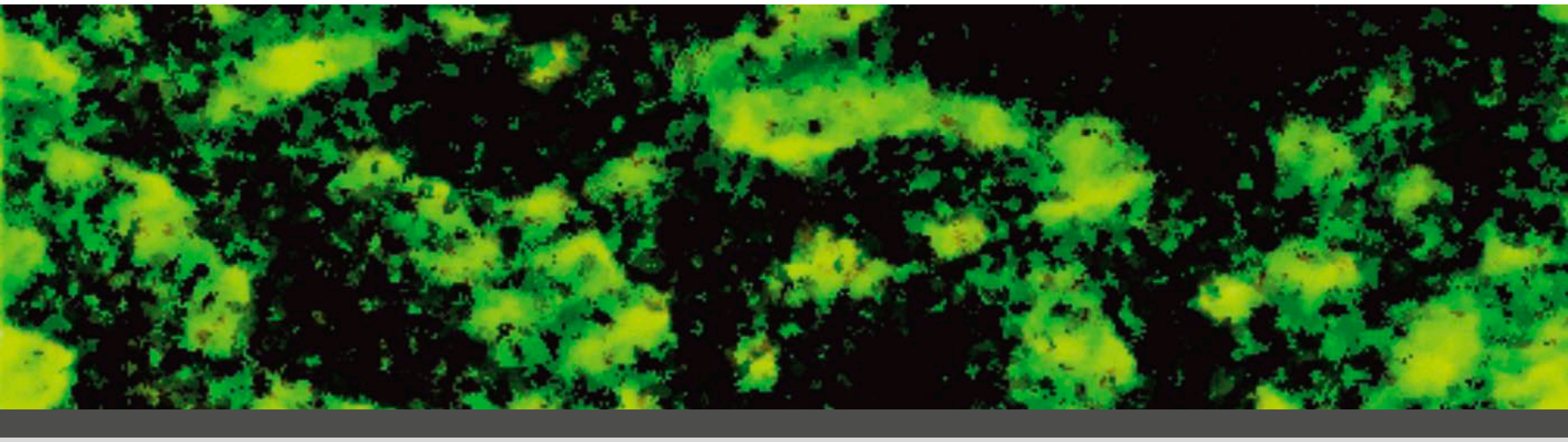
15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices

ModVal 2018



Book of Abstracts

April 12–13, 2018
Aarau, Switzerland

www.modval2018.ch

Publisher
Electrochemistry Laboratory
Paul Scherrer Institut
5232 Villigen PSI

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Printing
Paul Scherrer Institut
ModVal 2018 Book of Abstracts

Version
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Elemental mapping of the surface of a proton conducting fuel cell membrane prepared by swift heavy ion beam irradiation and grafting. Green areas (sulfur) indicate ion conducting domains (diameter around 1 micron), black areas (fluorine) the insulating matrix. Related article: J. Mater. Chem. A 5 (2017) 24826 (DOI: 10.1039/c7ta07323b)

Book of Abstracts

15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices (ModVal 2018)

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Table of Contents

Page

Welcome to ModVal 2018

The ModVal symposia were initiated in 2004 by the Swiss Federal Office of Energy and have since then taken place annually in locations alternating between Switzerland and Germany, initially focusing on pertinent topics in the development of fuel cells, in particular the polymer electrolyte fuel cell (PEFC) and the solid oxide fuel cell (SOFC). Over the years, the scope of the symposium has expanded to rechargeable batteries and now also includes electrolyzers and flow batteries. All of these are clustered under the general term ‘electrochemical energy devices’, highlighting their intended use as energy storage and conversion devices for a range of applications, such as electromobility, decentralized power generation, and stationary energy storage.

ModVal aims at disseminating new results in research, fostering the exchange of ideas, notably between experimentally oriented and simulation centered research, promoting personal contacts, and stimulating new collaborations. It is targeted at colleagues from academic and governmental institutions as well as industry.

We wish to thank all the plenary and invited speakers, oral and poster presenters for contributing to ModVal 2018 and all the participants for making this a stimulating and memorable event. Furthermore, we gratefully acknowledge the sponsors for financial support, and thank the colleagues of the Electrochemistry Laboratory of PSI for assistance in organizational matters.

The ModVal 2018 Organizing Committee

March 2018

How to cite contributions:
{Author list}, “{Title}”, Proc. 15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices (ModVal 2018), E.J. Berg, F.N. Büchi, J. Eller, L. Gubler (Eds.), Aarau, Switzerland, April 12-13, 2018, {pages} (DOI: 10.3929/ethz-b-000240521)

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Program

Thursday April 12th, Morning

	Session A (*Flow Batteries*) Saal 2	Plenary & Session B (*Batteries*) Saal 1
8:45	Welcome	
9:00	Plenary 1, Chair: F. Büchi **A. Kucernak** Mass transport free electrocatalysis of the oxygen and hydrogen reactions – effect of surface sites and spectator species	
9:50	Coffe Break & Poster Mounting	
	Session A1 Redox Flow Batteries Chair: L. Gubler	Session B1 Microstructure I Chair: E.J. Berg
10:20	Invited A1 **J. Noack** Current development trends and challenges for redox-flow batteries	Invited B1 **V. Wood** Understanding the Impact of Separators on Lithium Ion Battery Performance
10:50	**F. Oldenburg** Balancing Transport with Amphoteric Membranes in All-Vanadium Redox-Flow Batteries at Different Current Densities	**J. Landesfeind** Critical Analysis of Tortuosity Values obtained from Impedance Spectroscopy and X-Ray Tomographic Data
11:10	**R. Banerjee** Characterization of Carbon Felts for Vanadium Redox Flow Batteries – A Pore Network Modelling Approach	**Y. Kerdja** 3D Imaging and Multi-Scale Modeling For Positive Electrode Materials Of Lithium-Ion Batteries
11:30	**G. Shukla** A Kinetic Monte Carlo Framework for a Discrete Multiphysics Description of Semi-Solid Redox Flow Batteries	**O. Birkholz** Influence of the electrode microstructure on the effective electronic and ionic conductivity of Lithium Ion Batteries using discrete element methods
11:50	**L. Feierabend** Model Development and Simulation of Flowing Slurry Electrodes for Zinc-Air Batteries	**S. Müller** Heterogeneity of Lithium Ion Battery Electrodes and its Influence on Electrochemical Performance
12:10	Lunch & Poster Session (Foyer)	

Thursday April 12th, Afternoon 1

	Session A (*Conversion Devices*) Saal 2	Plenary & Session B (*Batteries*) Saal 1
13:20	Plenary 2, Chair: E.J. Berg **A. Van der Veen** Linking electrode behavior at the macro and meso scale to electronic structure	
	Session A2 Electrolysis Chair: R. Hanke-Rauschenbach	Session B2 Microstructure II Chair: V. Wood
14:20	Invited A2 **M. Carmo** Perspectives on the Research and Development of Low Temperature Water Electrolyzers	Invited B2 **V. Schmidt** Stochastic microstructure modelling of aggregate particle systems in hierarchically structured electrodes
14:50	**I. Zenyuk** *Operando* X-ray tomography and sub-second radiography for characterizing transport in polymer electrolyte membrane electrolyzer	**T. Hofmann** Electro-chemo-mechanical simulation of 3D-microstructures for lithium-ion batteries
15:10	**P. Trinke** Modelling of the supersaturation of dissolved gas in PEM electrolysis cells	**R. Morasch** Experimental Validation of Simulated Ionic Resistances in Laser-Structured Electrodes
15:30	**G. Serre** PEM water electrolysis modelling: Upscaling strategies	**T. Danner** Microstructure-Resolved Impedance Simulations for the Characterization of Li-Ion Battery Electrodes
15:50	**G. Futter** Modeling of SOECs –Physics-based Impedance Analysis of MIEC electrodes	**S. Cernak** Influence of non-spherical active material particles on the macroscopic cell performance of three-dimensional battery simulations on the microscale
16:10	Coffee Break & Poster Session (Foyer)	

Thursday April 12th, Afternoon 2

	Session A (*Conversion Devices*) Saal 2	Session B (*Batteries*) Saal 1
	Session A3 PEFC Modeling Chair: Y. Bultel	Session B3 Beyond Li-ion Chair: A. Van der Veen
16:40	**J. Fuhrmann** Robust quality preserving numerical methods for electroosmotic flows	**M. Ebadi** Modelling Lithium/Electrolyte Interfaces for Li-Metal Batteries
17:00	**J. Schumacher** An open implementation of a two-phase PEMFC model in MATLAB	**M. Bayer** Electrochemical modeling and its influence on Na-MCl_2 cell design
17:20	**M. Siegwart** Time-of-flight neutron imaging for the localization of freezing events during PEFC cold starts	**G. Bauer** Multi-scale and multi-physics simulation of all solid-state batteries
17:40	**S. Zhang** Simulation of a high temperature polymer electrolyte fuel cell short stack with OpenFuelCell	**G. Li** Modelling Space Charging in Multi-carrier Solid Electrolytes
19:30	Conference Dinner (Sorell Hotel Aarauerhof)	

Friday April 13th, Morning 1

	Session A (*Conversion Devices*) Saal 2	Plenary & Session B (*Batteries*) Saal 1
8:30	Plenary 3, Chair: L. Gubler **R. Hanke-Rauschenbach** Modeling of PEM water electrolysis: A review	
	Session A4 Catalysis Chair: J. Eller	Session B4 System & Parameter Validation Chair: P. Novák
9:30	Invited A4 **E. Fabbri** Insights into Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water	Invited B4 **W. Bessler** End-of-life prediction of lithium-ion battery cells based on mechanistic ageing models of the graphite electrode
10:00	**R. Alink** Modeling of Cathode Catalyst Degradation in PEM Fuel Cells	**D. Howey** Parametrisation of the Single Particle Model for Lithium-ion Cells
10:20	**T. Haisch** Origin of the hysteresis between forward and reverse peak in cyclic voltammograms of the alkaline methanol electrooxidation	**S. Kosch** An efficient two-dimensional cell model for lithium-ion cells based on pseudo-spectral collocation method
10:40	**M. Lin** An integrated concentrated solar fuel generator concept utilizing a tubular solid oxide electrolysis cell as the solar absorber	**V. Laue** Is parameter estimation with a pseudo-2-dimensional battery model more than curve fitting?
11:00	Coffee Break & Poster Session (Foyer)	

Friday April 13th, Morning 2

	Session A (*Conversion Devices*) Saal 2	Session B (*Batteries*) Saal 1
	Session A5 Microstructures Chair: I. Zenyuk	Session B5 Ageing & Degradation Chair: W. Bessler
11:30	**N. Prasianakis** High performance full resolution modelling of mass transport and phase change phenomena in anode and cathode sides of PEFCs	**J. Reniers** Battery degradation modelling for optimal control of grid-connected lithium-ion batteries
11:50	**J. Yu** Simulation of Water Transport in the Stochastic Micro-structure of Polymer Electrolyte Fuel Cell Using the Lattice Boltzmann Method	**K. Darcovich** Fast mode switching effects on battery degradation
12:10	**A. Mularczyk** Convection driven droplet detachment from gas diffusion layers	**B.-X. Xu** Phase-field Modeling on Li-ion Batteries
12:30	**C. Evangelisti** New porous Nickel-doped Materials for alkaline water electrolysis	**T. Danner** Local Inhomogeneities and their Impact on Lithium Plating in Lithium-Ion Batteries
12:50	Lunch & Poster Session (Foyer)	

Friday April 13th, Afternoon

	Session A (*Conversion Devices*) Saal 2	Session B (*Batteries*) Saal 1
	Session A6 Cell Level Modeling Chair: J. Schumacher	Session B6 Ion Transport & Interfaces Chair: D. Howey
14:00	**Y. Bultel** Investigation of liquid water heterogeneities in large area PEM fuel cells using a pseudo-3D multiphysics model	**T. Zhang** A Nonlocal Species Concentration Theory: Application to Phase-separating Lithium ion Battery Cathode Particles
14:20	**C. Fink** 3D Modeling of Chemical Degradation Mechanisms in PEM Fuel Cells	**L. Blume** Non-linear Lithium-Solid Polymer Electrolyte Interface Kinetics Investigated by Millisecond Current Pulses
14:40	**A. Niroumand** Electrochemical detection of electric shorts in PEM fuel cell stacks	**J.Y. Ko** Electrochemical modeling of intercalation electrode NMC(1/3): Determination of transport and kinetic properties
15:00	**H. Grimler** Understanding limiting processes in anion-exchange membrane fuel cells	**M. El Kazzi** The Controversial Surface Reactivity of $Li_4Ti_5O_{12}$ in the Aprotic Electrolyte Disclosed with XPEEM
15:20	ModVal 2019 Announcement and Closing	

Oral Contributions

Nr.	**Authors**	**Title**	**Page**

Plenary Lectures

1	A. Kucernak, L. Lin, K. Fahy, M. Laitz	Mass transport free electrocatalysis of the oxygen and hydrogen reactions – effect of surface sites and spectator species	26
2	A. Van der Veen	Linking electrode behavior at the macro and meso scale to electronic structure	28
3	B. Bensmann, M. Suermann R. Hanke-Rauschenbach	Modeling of PEM water electrolysis: A review	29

Invited Talks

A1	J. Noack	Current development trends and challenges for redox-flow batteries	30
A2	M. Carmo, M. Müller	Perspectives on the Research and Development of Low Temperature Water Electrolyzers	31
A4	E. Fabbri, B.-J. Kim, M. Nachtegaal, X. Cheng, M. Borlaf, I.E. Castelli, T. Graule, T.J. Schmidt	Insights into Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water	32
B1	M.F. Lagadec, R.Zahn, V. Wood	Understanding the Impact of Separators on Lithium Ion Battery Performance	34
B2	V. Schmidt M. Neumann, S.E. Wetterauer, T. Carraro, M. Osenberg, A. Hilger, I. Manke, A. Wagner, N. Bohn, J.R. Binder	Stochastic microstructure modeling of aggregated particle systems in hierarchically structured electrodes	35
B4	W.G. Bessler	End-of-life prediction of lithium-ion battery cells based on mechanistic ageing models of the graphite electrode	37

Contributed Talks

A1.1	F. J. Oldenburg, T.J. Schmidt, L. Gubler	Balancing Transport with Amphoteric Membranes in All-Vanadium Redox-Flow Batteries at Different Current Densities	38

---

[1] presented by R. Alink with title “Modeling of Cathode Catalyst Degradation in PEM Fuel Cells”

B5.4[2]	S. Hein, A. Latz	Local Inhomogeneities and their Impact on Lithium Plating in Lithium-Ion Batteries	97
B6.1	T. Zhang, M. Kamlah	A Nonlocal Species Concentration Theory: Application to Phase-separating Lithium ion Battery Cathode Particles	98
B6.2	L. Blume, U. Sauter, T. Jacob	Non-linear Lithium-Solid Polymer Electrolyte Interface Kinetics Investigated by Millisecond Current Pulses	99
B6.3	J.Y. Ko, M. Varini, M. Klett, H. Ekström, G. Lindbergh	Electrochemical modeling of intercalation electrode $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$: Determination of transport and kinetic properties	101
B6.4	D. Leanza, C.A.F. Vaz, I. Czekaj, P. Novák, M. El Kazzi	The Controversial Surface Reactivity of $Li_4Ti_5O_{12}$ in the Aprotic Electrolyte Disclosed with XPEEM	102

---

[2] presented by T. Danner

Poster Contributions

Nr.	Authors	Title	Page
P1	S. Gößling, V. Peinecke	2-D + 1-D PEM fuel cell simulation and validation	104
P2	E.A. Astafev, A.E. Ukche, Y.A. Dobrovolsky	PEM Fuel Cell Electrochemical Noise Measurement, Analysis and Modeling	105
P3	R. Richter, J. Häcker, T. Danner, N. Wagner, K.A. Friedrich, A. Latz	A common framework for the simulation of next-generation metal-sulfur batteries	107
P4	D. Froning, J. Yu, U. Reimer, W. Lehnert	Transport Simulation in Gas Diffusion Layers of High-Temperature Polymer Electrolyte Fuel Cells and Analysis of Surface Characteristics	108
P5	F. Biebl, I. Glatt	Digital Battery Development with GeoDict	109
P6	M. Landstorfer	Modelling and Simulation of Porous Electrodes with Multi-Scale Homogenisation techniques	110
P7	E. Asylbekov, H. Nirschl	CFD-DEM Simulation of the Carbon Black Distribution during the Mixing Process	111
P8	L. Ifrek, Y. Bultel, S. Rosini, G. Cauffet, O. Chadebec, L. Rouveyre	Local faults identification on a PEM fuel cell by external magnetic field measurement	112
P9	B. Suthar, J. Landesfeind, A. Eldiven, H.A. Gasteiger	Method to Determine In-Plane Tortuosity	114
P10	J. Sturm, H. Ennifar, S.V. Erhard, A. Rheinfeld, S. Kosch, A. Jossen	State Estimation of Lithium-Ion Cells using a Physicochemical Model based Extended Kalman Filter	115
P11	M. Zlobinski, T.J. Schmidt, P. Boillat	Operando in-plane neutron imaging study of water/gas distribution in PEM water electrolyser under various operating conditions	117
P12	(withdrawn)		
P13	A. Rajan, A. McGordon, J. Marco	Prediction of cyclic ageing and storage ageing in a lithium ion battery using an electrochemical model	119
P14	H. Xu, M. Bührer, F. Marone, T.J. Schmidt, F.N. Büchi, J. Eller	Studies of Water Distribution in the Gas Diffusion Layer of Polymer Electrolyte Fuel Cells using X-ray Tomographic Microscopy	121
P15	(reallocated to oral contrituion B1.3)		

P45	N. Kulkarni, R. Jervis, F. Iacoviello, Q. Meyer, P.R. Shearing, D.J.L. Brett	An X-ray tomography investigation and modelling the effect of non-uniform cell compression of polymer electrolyte membrane fuel cell membrane electrode assemblies	160
P46	O. Hodjati-Pugh, A. Dhir, R. Steinberger-Wilkens	Multiphysics Modelling and Experimental Validation of a Segmented Microtubular SOFC: A Study of Interconnect Configuration	162

Abstracts for Oral Presentations

Mass transport free electrocatalysis of the oxygen and hydrogen reactions – effect of surface sites and spectator species

Anthony Kucernak, Lyra Lin, Kieran Fahy, Madeleine Laitz
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The vacuum deposited catalyst method is an approach which allows development of ultra low loading electrodes (<1 μg_{pt} cm^{-2}) with very high mass transport performance (k_{MT} > 10 cm s^{-1} c.f for rotating disk electrode k_{MT} <0.005 cm s^{-1}) optimised for gaseous reactant transport. This new approach has allowed a range of observations of the hydrogen and oxygen reactions hitherto unseen, as it allows access to ***specific*** current densities much higher than achievable in electrolysers or fuel cells (~A cm^{-2}). In this presentation we consider the effect of spectator species on the electrocatalytic performance of the above reactions and also consider the application of the approach to produce ultra-low loading fuel cell electrodes.

Production of electrodes

The catalyst layer was prepared as described by Zalitis *et al* [1]. Porous polycarbonate track etched (PCTE) membranes (Sterlitech, PCTF0447100) with a pore size of 400 nm and a porosity of 0.125 were coated with a 100 nm gold layer by sputter deposition (Emitech K575X). After extensive cleaning, these gold coated PCTE membranes then had a range of commercial Pt/C vacuum filtrated onto 2 mm diameter spots utilising a suitable Nafion containing ink. After deposition of the catalyst layer, a hydrophobic coating of an amorphous fluoropolymer (AF) (DuPont DeNemours, a copolymer of 2,2-bistrifluoromethyl-4,5,difluoro-1,3-dioxile and tetrafluoroethylene with the trade name Teflon AF 2400, 2.1 $\mu g.cm^{-2}{}_{Geo}$) dissolved in Fluorinert FC-40 (Sigma, F9755) was applied to the unmodified side of the gold coated PCTE membrane. The thin membranes are then floated (catalyst side down) on the electrolyte surface. An example of the deposition of a catalyst particle at the neck of a 400 nm pore is provided in Figure 1(a), and the entire 2mm diameter catalyst layer shown in Figure 1(b). The electrode is then floated on the surface of the static electrolyte at the gas/liquid interface, Figure 1(c)

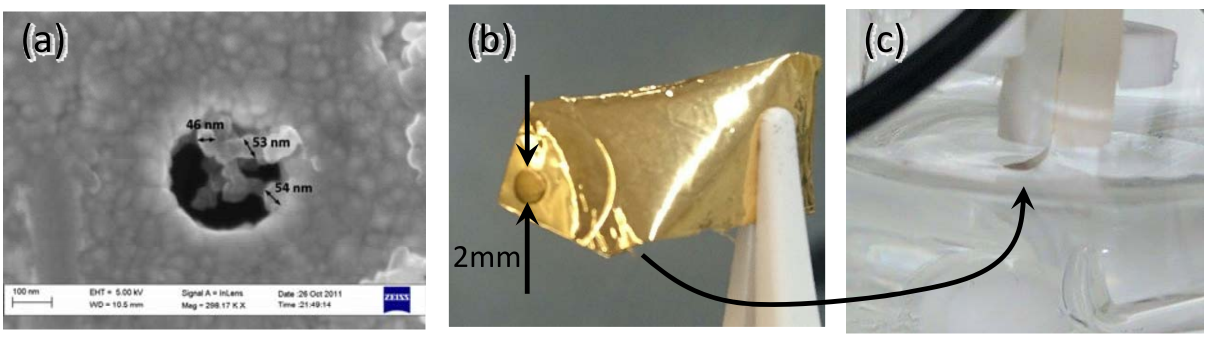

Figure 1: (a) Catalyst particle deposited at neck of 300 nm gas pore; (b) Example of vacuum filtered catalyst layer produced on gold sputtered polycarbonate membrane; (c) Catalyst coated polycarbonate membrane floating at liquid/gas interface in an electrochemical cell.

Effect of spectator species and site specific activity

By considering the performance of the hydrogen reactions as a function of platinum particle size (2.1 – 15 nm) using a set of well characterised catalysts, we find that the activity is composed of two components which vary in a defined way with particle size, Figure 2(a). Geometrical considerations and electrokinetic modelling suggest that those two components correspond to (a) the response of edges/vertices, and (b) the response of facets (Pt(100) and Pt(111)), Figure 2(b). Edges and vertices are much more active towards the hydrogen reaction close to the equilibrium potential than facets, Figure 2. This suggests that for the hydrogen reaction, the ideal catalysts are highly defective with few facets. Furthermore, it is seen that the performance of both edges and facets are adversely affected by spectator species, and in specific anions. We find that above the point of zero total charge, (E(pztc)) the current decays away, and this effect is associated with blocking of reaction sites by anions. The edge sites are much more susceptible to blocking by spectator species, and thus although they are more active below the E(pztc), they quickly become inactive at higher potentials. Facet sites appear to be less susceptible to blocking than edge sites.

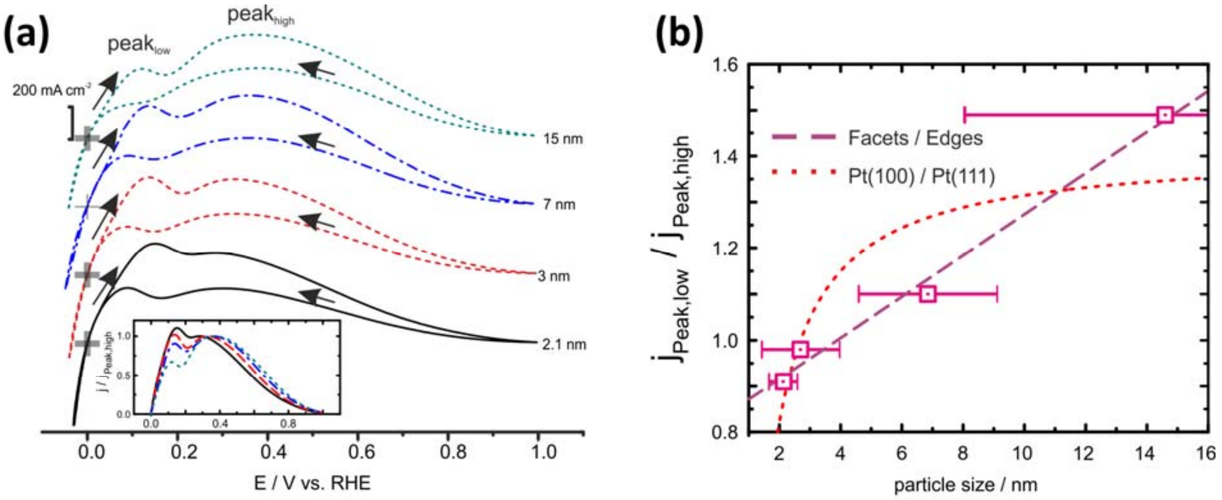

Figure 2. (a) Voltammograms (corrected to surface specific current density) of the HOR for Pt/C of different particles sizes with targeted loading to give a roughness factor in the range 0.7 – 1. Loading of electrodes for the different particle size are 15 nm (7.8 μg$_{Pt}$ cm^{-2}); 7 nm (2.5 μg$_{Pt}$ cm^{-2}), 3 nm (1.2 μg$_{Pt}$ cm^{-2}) and 2.1 nm (0.7 μg$_{Pt}$ cm^{-2}. Inset: Anodic scan in normalised to the height of the second peak. (b) Plot of ratio of peak current densities for the low and high peaks as a function of platinum particle size along with best fit curves for the response expected if the peaks are due to facets and edges or just different facets (Pt100 vs Pt111). The CVs were run in 4 mol dm^{-3} $HClO_4$ at 10 mV s^{-1} at 298 K. 1 bar hydrogen.

By modelling the individual performance of each of the two different sites, we obtain parameters for the exchange current densities on both sites. We find that the edge sites have an exchange current density which is about two orders of magnitude greater than the facet sites, but that the performance of the facet sites are still reasonable considering the results on single crystal electrodes.

Extension of approach to producing catalyst coated membranes

Recent results have shown how catalyst coated membrane using Nafion 212 membrane may be produced using the vacuum deposition method utilising only 10 μg$_{pt}$ cm^{-2} platinum loading, Figure 3. The loading on these electrodes is so low that the CCMs are transparent, Figure 3(a). The performance of these CCMs show that platinum utilisation increases with decreasing loading showing that mass transport still plays a considerable effect in fuel cell systems.

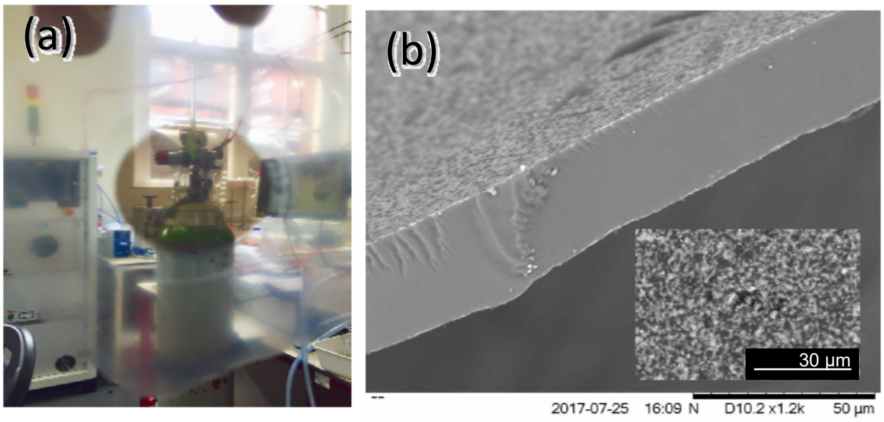

Figure 3. (a) Photograph of transparent CCM produced with 10 μg$_{Pt}$ cm^{-2} on anode and cathode side; (b) SEM of crossection of the CCM in (a) showing uniform catalyst layer with thickness < 1μm

References:
1. C.M. Zalitis, D. Kramer, A.R. Kucernak, *Phys. Chem. Chem. Phys.* **15** (2013), 4329-4340.
2. C.M. Zalitis, A.R. Kucernak, J. Sharman, E. Wright, *J. Mater. Chem.* A **5** (2017), 23328-23338.

Linking electrode behavior at the macro and meso scale to electronic structure

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Electrode materials for Li, Na and Mg ion batteries undergo a series of phase transformations as a result of large changes in concentration during each charge and discharge cycle. The mechanisms of these phase transformations are sensitive to a delicate interplay between cation diffusion, nucleation and interface migration. Powerful phenomenological theories have been developed to describe the electrochemical properties of electrode materials for rechargeable batteries. Phenomenological descriptions capture the essence of equilibrium and non-equilibrium behaviour at meso and macroscopic length scales, relying on a minimal set of variables and materials parameters. Phase field approaches inspired by Cahn-Hilliard and Allen-Cahn type theories are capable of describing many of the diffusional and phase transformation phenomena in electrode materials. Unfortunately, the link between phenomenological descriptions at the meso and macroscopic scale to quantities that can be calculated by solving the Schrodinger equation of the solid remain tenuous in many cases. These links necessarily rely on statistical mechanics approaches due to the central role of temperature and entropy in electrochemical processes.

In this talk, I will illustrate how the application of first-principles statistical mechanics can generate crucial insights about dynamic processes within electrodes and enable the design of new electrochemical energy devices. The approach relies on coarse graining schemes to connect properties at the atomic and electronic scale to phenomenological descriptions of kinetic processes. It enables the first-principles prediction of voltage profiles, ionic mobilities, order-disorder phenomena and structural phase transformations within intercalation and conversion based electrode materials. I will describe a comparative study of the electrochemical properties of Li, Na and Mg based electrodes. Significant differences in electrochemical properties are predicted among Li, Na and Mg intercalation compounds. Layered intercalation compounds undergo many stacking sequence changes upon intercalation of the relatively large Na ion. Such stacking sequence changes are less common upon insertion of smaller cations such as Li and Mg. Important differences also emerge upon insertion of Li, Na or Mg into common spinel hosts. The differences in phase stability among Li, Na and Mg intercalation compounds result in distinct ionic transport mechanisms that have a unique dependence on the ion disordered favoured by different host structures, with important consequences for macroscopic descriptions of diffusional processes in electrode materials.

Modeling of PEM water electrolysis: A review

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The present contribution gives a survey on state of the art modelling of water electrolysers based on proton exchange membranes (PEM). First attempts to describe their operating behaviour by means of mechanistic models have been carried out in the early 1990ies by Millet [1] and Goldberg et al. [2]. Since then a few dozens of further papers dealing with this subject have been published, most of them in the last decade. Those papers have been carefully analysed [3] and are discussed with regard to the considered phenomena in each of the functional layers of the electrolyser.

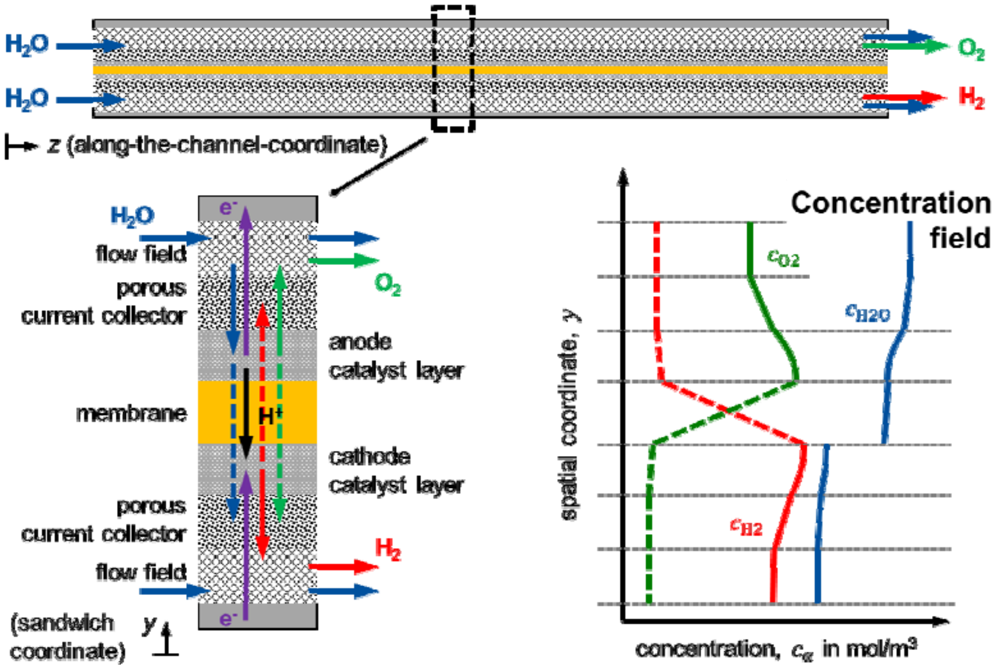

Figure 1: Schematics of a PEM water electrolyser, governing processes and qualitative sketch of the concentration field in the direction of the sandwich-coordinate.

References:
1. P. Millet, Electrochim. Acta 36(2), 263 (1991).
2. A.B. Goldberg, L.I. Kheifets, A.G. Vaganov, S.G. Ogryzkozhukovskaya and A.V. Shabalin, J. Appl. Electrochem. 22(12), 1147 (1992).
3. B. Bensmann and R. Hanke-Rauschenbach, ECS Trans. 75(14), 1065 (2016).

Current Development Trends and Challenges for Redox-Flow Batteries

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Redox-flow batteries use flowing media as energy storage material, which means that power and energy can be scaled up to almost any desired level. With the use of inexpensive energy storage materials and a long service life, a potentially lower storage cost for stationary applications can be achieved. Currently, a large number of combinations of redox pairs and thus very different systems are under development. In turn, only a small number are in commercialization. The main obstacles are the underestimated chemical behaviour of redox pairs and the high costs involved in the development of systems suitable for mass production. For a few years now, two trends have emerged: The classical inorganic systems with their main representatives consisting of vanadium, zinc, bromine and iron and; the aqueous organic flow batteries with different active material combinations, where the system methylviologen/TEMPO and its derivatives are typical representatives.

For all storage types, the commercial success of a system is ultimately determined by the storage costs (LCOE) rather than the investment costs. Therefore, targeted applied research and development requires modelling and simulations in order to identify cost influences and to be able to make targeted optimizations. Stationary storage systems are complicated by the variety of different operating conditions; different grid compositions and; fluctuating generation and loads. For the scaling of storage devices, microgrid simulations in connection with the electrical and thermal properties of the components are crucial in order to achieve the lowest possible LCOE. This in turn, requires models of different storage types that take into account the effects of performance, temperature, state of charge, service life and investment costs. The investment costs are derived from technological-economic models, taking into account the characteristics of the battery components. This in turn requires a battery model, since the investment costs depend largely on the interrelationship between the material properties and performance values of the battery. The techno-economic modelling allows, for example, determination of whether an expensive and efficient material is better suited than an inexpensive one with lower performance values, together with the identification of cost factors and their influence. Battery models usually consist of a coupling of electrochemical properties and fluid properties, however are only valid for cells or stacks and not for systems, since system can incorporate regeneration processes or regeneration cells in addition to process equipment such as heat exchangers and pumps. For the electrochemical models, the electrochemical fundamentals in particular must be taken into account, i.e. the applicability of the respective models and the quality of the obtained data. Especially in vanadium-based systems, the influencing factors on the reactions are so large that, for example, values for reaction kinetics differ by a factor of 107 in the literature. In the past, system models and microgrid simulations have not paid enough attention to thermal properties. These properties, in turn, are also location-dependent and can include significant optimisation potential, particularly for plants in the MW range and with energy efficiencies of between 50 - 90 %.

Perspectives on the Research and Development of Low Temperature Water Electrolyzers

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Hydrogen is today considered the best means by which to store energy coming from renewable and intermittent power sources such as wind and solar. With the growing capacity of localized renewable energy sources surpassing the gigawatt range, a storage system of equal magnitude is required, such as the production of electrolytic hydrogen by water electrolysis. Despite of more than 100 years of experience in alkaline electrolysis systems, and decades using PEM electrolyzers, only a few systems coupled to renewable energy sources are running today, providing the state-of-the-art of this technology. Nevertheless, strong R&D and market interest can be observed for both alkaline and PEM water electrolysis technology, and over the past 10 years, new companies and research projects have emerged, with new leaders being consequently established in this fast growing niche. Advantages of PEM electrolysis over alkaline electrolysis together with novel R&D approaches can potentially reduce the investment costs of PEM electrolyzers. Nevertheless, new materials and the latest characterization methods are promising to support the increase in the current density profiles of alkali based electrolysis. A variety of approaches have been pursued in Jülich to further advance both types. In our recent work, we have shown consistent decrease of the noble metal loadings for PEM electrolyzers, and a recycling approach where close to 98% of all catalysts can be recovered. Also relevant is to consistently access the gas-permeation and durability behavior of PFSA membranes, and to investigate the use of novel electrocatalyst alternatives to tackle the HER, OER and recombination of hydrogen to mitigate crossover. We have also developed cost-effective porous transport layers, wherein the aim was to study the effects of mechanics on cell performance and to prevent damage of components. Gas-water distribution in an electrolysis cell was operando visualized during polarization curve measurement. During stationary operating conditions a discontinuous gas-water exchange mechanism could be observed. All these approaches shall provide crucial information to precisely model and simulate low temperature electrolyzers (under both cell and stack level). We expect that in the following years, frontier advancements on using both electrolysis systems will appear, demonstrating a true capacity to ultimately establish hydrogen as a key player in the energy market, and contribute to a future hydrogen economy.

Insights into Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water

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In recent years, electricity-driven hydrogen production by electrochemical splitting of water has received particular attention because of its potential applicability in decentralized energy storage concepts [1]. Most of the efforts have been focused on the electrochemical reaction occurring at the anode side, the oxygen evolution reaction (OER), since it is source of large overpotentials [2, 3].

Advances in computational studies and in in situ characterizations can now offer novel insights into the OER mechanism, revealing new perspective in the search for advanced materials. However, at present most of the fundamental studies on OER catalysts have been conducted using bulk techniques and materials with low surface area, which is a questionable approach considering that the OER is a near-surface reaction. In this study [4], we couple a cutting-edge synthesis method to produce highly active OER nano-catalysts with time resolved X-ray absorption spectroscopy (XAS) measurements able to capture dynamics of the catalyst electronic and local structure during operando conditions. The use of nano-catalysts not only allows achieving outstanding performance, but also reveals electronic and structural changes at the catalysts surface (given the high surface to bulk ratio of nanoparticles) never observed before. Particularly, we could demonstrate that the key for highly active catalysts is a self-assembled, (oxy)hydroxide top layer. This is completely different from the message of several water electrolysis-related publications, which consider the surface of oxide catalysts as an ideal, atomically flat surface. This new concept completely revolutionizes the currently most accepted view of design principles for highly active perovskite catalysts. It also points towards the paramount necessity of investigating other perovskite properties under operando conditions in order to develop accurate design principles for highly active perovskite catalysts [5].

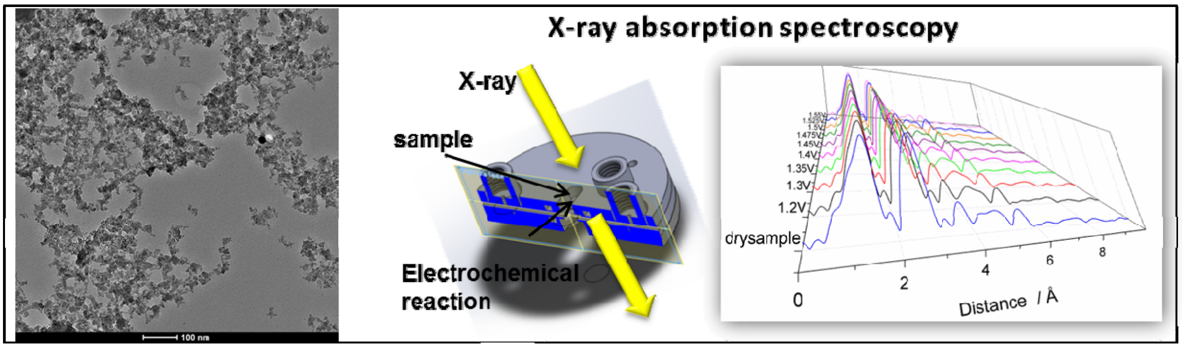

Figure 1: TEM images of a perovskite nano-catalyst produced by flame spray synthesis method (left), sketch for the spectro-electrochemical cell developed to perform operando XAS measurements (centre), example of operando Extended X-Ray Absorption Fine Structure (EXAFS) spectra (right)

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Understanding the Impact of Separators on Lithium Ion Battery Performance

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Microporous polyolefin membranes have been used as separators in lithium ion batteries (LIBs) for several decades, and have been manufactured with a variety of thicknesses, pore structures, and surface chemistries. Here we show how accurate 3D microstructures of LIB can be used to understand how separators impact LIB performance and to generate design guidelines to systematically improve their behavior,

We developed a method to obtain quantitative 3D datasets of LIB separators using focus-ion-beam scanning electron microscopic (FIB-SEM) tomography.[1] We have applied this to wet-stretched polyethylene (PE) and dry-stretched polypropylene (PP) separators, which exhibit distinct morphologies that stem from the different processes used to manufacture them. This allows us for example to quantify the isotopic nature of the PE separator and the anisotropic structure of PP and to run diffusion and mechanical simulations on realistic structures.

Traditionally, when discussing LIB performance, diffusion of lithium ions in the electrolyte-filled pore space is given by the diffusion of lithium ions in the electrolyte scaled by the effective transport coefficient of the microstructure, which is the ratio of porosity and tortuosity along the through-plane (TP) direction between the electrodes. Surprisingly, despite their different morphologies, PE and PP have similar effective transport coefficients. This highlights that traditional microstructural characteristics porosity and tortuosity are not sufficient to predict separator performance. We use topological and network analysis to show why a highly connected isotropic microstructure such as PE is better at homogenising ion concentration gradients that occur in blocked pores and at the separator-electrode interface.[2]

During battery operation, polyolefin separators are compressed by the active particles and electrodes, which alters their microstructure. Based on simulations on the 3D datasets, we show that not only the bulk mechanical properties of the polyolefin but also its microstructure determines a separator's response to compressive loads. Separators with anisotropic microstructures require higher compressive stresses to deform and are better at preserving ion transport paths under compression.[3]

Finally, analysis of the microstructures helps us to pinpoint the origins of the discrepancy in effective transport determination via diffusion simulations and electrical impedance spectroscopy.[4] We show that the transport characteristics obtained by electrical impedance spectroscopy and diffusion simulations are different due to dead-end pores that do not factor into and surface interactions.[5]

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Stochastic microstructure modeling of aggregated particle systems in hierarchically structured electrodes

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A stochastic microstructure model in 3D is developed for the simulation of hierarchically structured electrodes where the active material consists of a system of nanoporous aggregated NMC particles. The aggregated particles are manufactured with different values of production parameters and sintering temperatures, which mainly influence the mean size of primary particles and the porosity. Such aggregated particles are used in electrodes, since they show higher energy densities and lead to a better functionality in terms of electric conductivity [1]. These functional properties strongly depend on two structural features : namely, on the spatial arrangement of aggregated particles in the electrode as well as on the 3D morphology of the nanopores within individual aggregated particles, which, in turn are influenced by the underlying production parameters.

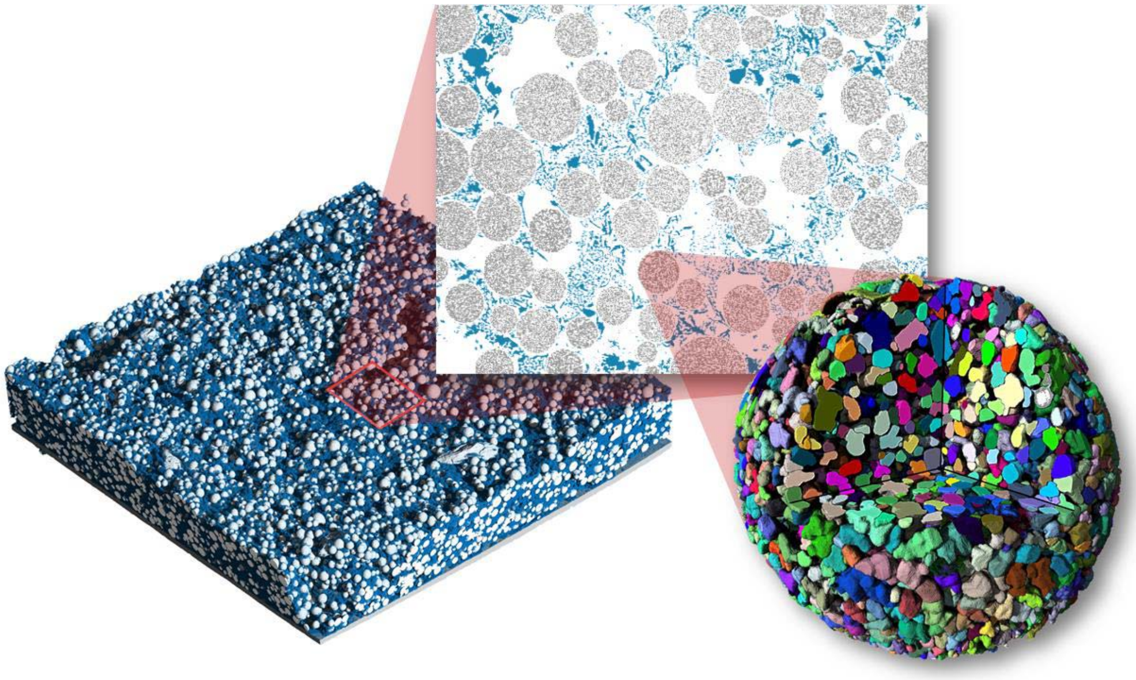

Figure 1: Combination of different measurement techniques for hierarchically structured battery cathodes. Left: 3D synchrotron dataset of aggregated particle system; Center: Planar section of synchrotron data; Right: 3D FIB-SEM dataset of an individual aggregated particle.

Both kinds of structural properties can be analyzed by means of 3D imaging on different length scales. Synchrotron tomography is used for imaging of particle systems and FIB-SEM tomography for imaging of the nanoporous inner structure of individual aggregated particles, see Figure 1. However, 3D imaging is expensive in costs and time and thus it is not possible to obtain a sufficiently large amount of 3D image data, which would be required to analyze the morphology of these particle systems adequately. To deal with this problem, stochastic microstructure modeling can be used to generate virtual, but realistic microstructures in short time in order to investigate the relationship between production parameters and the 3D morphology.

Our approach to stochastic microstructure modeling consists of two steps. First, we model the system of aggregated particles without taking their nanoporosity into account. For this purpose, we represent them by spherical harmonic functions and consider random geometric graphs in order to model their connectivity [2]. In the second step, the nanoporous inner structure of aggregated particles is modeled by an excursion set of a certain class of so-called χ^2-fields [3], which allows us to include a structural gradient observed in tomographic data into the model. After having fitted the model parameters to image data, model validation is performed by comparing structural characteristics on both length scales of simulated and tomographic image data. Moreover, effective electronic conductivities of individual aggregated particles are validated. Here, the effective electronic conductivity is numerically simulated by a goal oriented adaptive cut-cell finite element approach [4]. Thus, our approach allows also for an investigation of the relationship between production parameters and electronic conductivity of individual aggregated particles. The values of effective electronic conductivity of aggregated particles can further be used for a numerical up-scaling of the complete multi-scale system, i.e., as an input for the computation of electronic conductivity of the systems of aggregated particles forming the battery cathode.

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End-of-life prediction of lithium-ion battery cells based on mechanistic ageing models of the graphite electrode

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Limited lifetime is today a major cost driver for lithium-ion battery systems, in particular for stationary energy storage applications where long lifetimes are required. Aging mechanisms are complex and consist of coupled chemical, electrochemical and mechanical processes [1]. Macroscopically, this results in a complex and nonlinear dependence of both calendaric and cyclic lifetime on temperature, state of charge, cycling depth and profile, and current. The present study aims at understanding the relationship between electrode-scale ageing mechanisms and macroscopic calendaric and cyclic lifetime.

We introduce an electrochemical model of a lithium iron phosphate/graphite (LFP/C) cell that includes combined ageing mechanisms: (i) Electrochemical formation of the solid electrolyte interphase (SEI) at the anode, (ii) breaking of the SEI due to mechanical stress resulting from volume changes of the graphite particles, causing accelerated SEI growth, (iii) gas formation and dry-out of the electrodes, (iv) loss of contact of graphite particles with the liquid electrolyte due to electrode dry-out. The model is embedded into a pseudo-3D transport framework including particle scale, electrode-pair scale, and cell scale [2]. A time-upscaling methodology is developed that allows to simulate large time spans (thousands of operating hours) within a few hours of wall-clock time.

The combined modeling and simulation framework is able to predict calendaric and cyclic ageing up to the end of life of the battery cells. The results show a qualitative agreement with ageing behavior known from experimental literature, in particular the dependence of temperature, cycling depth, and average SOC. The introduction of electrode dry-out allows to capture the strong nonlinearity of ageing towards end of life (“sudden death”).

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Balancing Transport with Amphoteric Membranes in All-Vanadium Redox-Flow Batteries at Different Current Densities

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Amphoteric ion exchange membranes (AIEM) are promising candidates for vanadium redox flow batteries (VFBs) combining low area resistance with low vanadium crossover, resulting in improved cycling efficiency compared to the state-of-the-art materials Nafion® (Dupont) and FAP-450 (Fumatech) [1,2]. Furthermore, they are able to balance the electrolyte transport across the membrane yielding high capacity retention and electrolyte utilization [3,4]. However, the net vanadium flux across the membrane is a function of the current density, as the vanadium ions have different migration coefficients related to their ionic charge. In previous work, Darling *et al.* studied the correlation of the net vanadium flux and the current density theoretically and reported an increase in the flux with increasing current densities [5]. We confirmed these theoretical predictions by determining the net vanadium flux both *ex-situ* and *in-situ* for different amphoteric membranes at several current densities. To adjust the ratio of anion and cation exchange capacities in the membrane, bilayered amphoteric membranes were prepared by hot-pressing polybenzimidazole (PBI) films of varying thickness with a Nafion® NR212 membrane. PBI and Nafion® were chosen, since both polymers provide excellent stability and are broadly explored for VFB applications. The PBI-layer is protonated by the acidic electrolyte and acts as an induced coulombic barrier towards cations. The strength of this barrier depends on the charge of the vanadium ions at their outer valence shell. Figure 1 presents diffusivity coefficients of each vanadium ion as a function of the thickness of the PBI-layer (a). When introducing a 3 μm PBI layer on the Nafion® NR212 membrane, the diffusivity coefficients decrease in the order of V(III) (-85%), V(II) (-70%), V(IV) (-55%) and V(V) (-17%) (b), indicating a suppressing influence on the net vanadium transport directed towards the positive side. In fact, strong anion exchange membranes show a pronounced electrolyte flux towards the negative side [3]. An increase of the thickness of the PBI-layer lowers the diffusivity further until the transport of vanadium is fully suppressed.

In a real cell environment, the vanadium flux depends according to the *Nernst-Planck* equation on the diffusive, migrative and electro-osmotic transport and is hence strongly influenced by the electric field gradient, which is related to the current density. This influence is again dependent on the ionic charge of the respective vanadium ion. In contrast to the repulsive interaction of the positively charged membrane, an increase in the current density enhances the flux of vanadium ions towards the positive side. Analogous to the theoretical predictions, a linear increase in the net crossover towards the posolyte was observed with increasing current densities, independent on the type of membrane used (Figure 2). The counteracting effects of the electric field and the fraction of anion exchange groups in the membrane were exploited to balance the net vanadium flux. By varying the thickness of the PBI-layer, membranes can be designed according to a specific current density range, yielding an optimal capacity retention and high efficiencies at the same time.

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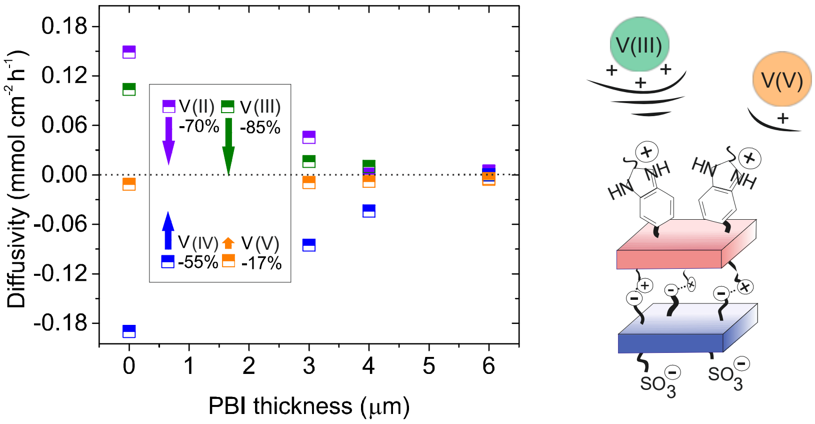

Figure 1: a) Diffusivity of V^{2+}, V^{3+}, VO^{2+}, and VO_2^+ determined from diffusion-cells assembled with Nafion® NR212 membranes hot-pressed against PBI films with different thicknesses. The diffusivity of each ion was measured in separate experiments. b) Schematic illustration of the bilayered Nafion-PBI membrane and its barrier property based on differently pronounced coulombic interactions.

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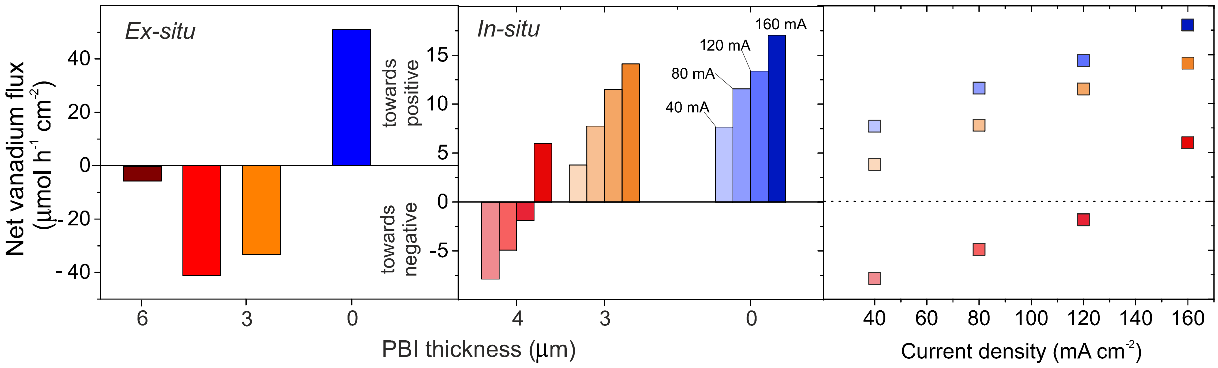

Figure 2: Net vanadium flux across Nafion® NR212 membranes, hot-pressed against PBI-films with different thicknesses. Left: determined from *ex-situ* diffusion coefficients, right: determined by measuring the vanadium concentration of the anolyte and catholyte over 50 charge-discharge cycles at different current densities in the fully charged state.

Acknowledgement:
The authors thank the Swiss Federal Office of Energy (SFOE) for the financial support within the RFBmem project (Grant No. SI/501421-01). TJS thanks CTI and the Swiss Competence Center for Energy Research (SCCER) Heat & Electricity Storage.

Characterization of Carbon Felts for Vanadium Redox Flow Batteries – A Pore Network Modelling Approach

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With a continuous growth in the contribution of renewable energy sources to the electricity grid, grid scale energy storage has become an area of considerable interest. Redox flow batteries allow the decoupling of energy and power capacity, allowing for large scale storage opportunities [1,2]. It has been estimated by the United States Department of Energy that a cost of 120 $/kWh would make the technology viable for grid scale storage deployment [3]. Cost of components and the electrolyte play a key role in reducing the cost of redox flow batteries.

Porous carbon felt materials have been found to be the most suitable as electrode materials for Vanadium Redox Flow Batteries (VRFBs) [4]. These porous materials provide the surface area for the electrolytes on both the positive and negative half cells to react and participate in the energy exchange. SGL Group produces commercially available carbon felt products for this purpose. In this work, three materials from SGL Group are selected to be evaluated for their transport properties with regard to electrolyte flow in VRFBs.

A desktop X-ray computed tomography machine has been used to obtain computed tomograms of the electrode materials. The structure has been segmented to identify the solid regions and the pore spaces [5]. The pore space has been isolated using an algorithm developed by Gostick [6]. An open source pore network modelling tool, OpenPNM [7,8] has been used to investigate the transport properties of the porous felt materials. The properties being investigated include permeability in each of the directions of flow, diffusivities of water, and electrolyte invasion patterns for the different materials, with impacts of activation, ageing, and material differences. Figure 1 shows an example image of the invasion pattern of the electrolyte as it flows through the felt at the start of operation. It was observed that activation of the initially hydrophobic carbon felt materials at 400°C resulted in the surface contact angles decreasing from 130° to strongly hydrophilic (~50°). This resulted in a decrease in the pressure required to saturate the electrode with the electrolyte by over 25 kPa (85% reduction). This would allow the system to operate at lower pressures.

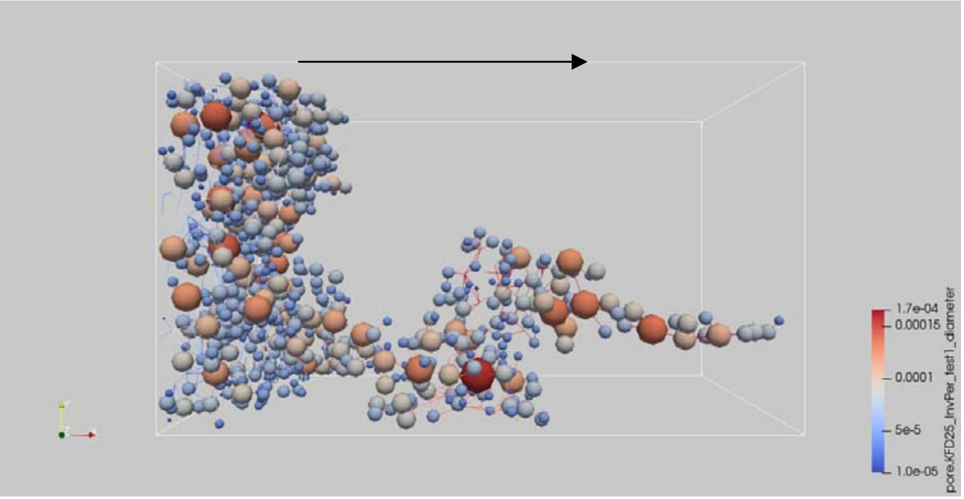

Figure 1: Invasion of liquid into the felt electrode, simulated using OpenPNM. Arrow shows direction of flow.

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A Kinetic Monte Carlo Framework for a Discrete Multiphysics Description of Semi-Solid Redox Flow Batteries

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The invention of semi-solid redox flow batteries (SSRFB) in 2009 provided a new battery architecture for adapting conventional lithium ion batteries to large scale applications [1]. But SSRFBs require significant optimization before they can be introduced to the market. Due to the complexity arising from concurrence of electrochemistry, fluid dynamics, suspension dynamics, and particle dynamics, the system remains poorly understood. The objective of the study is to investigate the fundamentals of a slurry electrode under flowing conditions to provide a better understanding of the multiphysics system. A general systems approach is used to incorporate different phenomena step-wise into a three-dimensional kinetic Monte Carlo framework [2]. The model is able to capture galvanostatic discharge of a multiphase slurry in contact with the current collector and provides a three-dimensional discrete picture of the slurry mesostructure. The slurry consists of active material, which undergoes volume expansion on lithium insertion, and electron-conducting carbon, both of distinct initial sizes and suspended in electrolyte. A parameter sensitivity analysis of the results shows the impact of C-rate, active material volume fraction, carbon volume fraction, and channel depth on capacity. The results of the study are compared to experiments with the objective to optimize a SSRFB by identifying the most relevant physical phenomena. This work also provides a framework to tackle the organized complexity of mesoscales for a wide variety of applications.

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Model Development and Simulation of Flowing Slurry Electrodes for Zinc-Air Batteries

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Slurry or suspension electrodes are gaining a renewed interest for large-scale energy storage technologies due to potentially higher energy densities compared to redox flow batteries [1]. A suspension electrode typically consists of a liquid electrolyte and a solid material, which is chemically active and electrically conducting. For the investigated zinc-air flow batteries employing a suspension electrode, microscopic zinc particles are suspended in an aqueous potassium hydroxide electrolyte [2, 3]. Sedimentation of the metallic zinc is minimized by adding a gelling agent to the electrolyte. The gelling agent and the high particle loading lead to a pseudo-plastic rheological behavior. When the flowable suspension electrode is pumped through the channels of the zinc-air fuel cell setup, the dynamic percolation network within the suspension dictates the active electrode surface area and the maximum discharge power density. Therefore, it is desirable to investigate the influence of the local flow conditions on the particle percolation and consequently the electrochemical performance of the battery cell with adequate simulation methods.

In the developed three-dimensional numerical model for the flowing suspension electrode, the complex, non-Newtonian two-phase flow is approximated by a coupling of an Eulerian continuum description for the electrolyte and a discrete, Lagrangian particle description for the motion and interaction of the microscopic particles. The partial differential equations for momentum, species, charge and energy are discretized by the finite volume method and implemented in the OpenFOAM library [4]. The particle motion including multiple simultaneous particle contacts is described with the discrete element method using the LIGGGHTS library [5]. Coupling between the particle and fluid phase is realized with the CFD-DEM method using the CFDEM library [5], where an empirical description accounts for the momentum exchange between the non-Newtonian fluid and the densely distributed particle assemblies. Due to relatively high particle concentrations, the volume displacement by the particles is considered in the electrolyte continuum model.

A half-cell model for the anode part of the zinc-air flow battery is implemented, which accounts for the flow characteristics via the described CFD-DEM coupling method. Simultaneously, the charge and species transport is considered according to the classic porous electrode theory by Newman [6]. In contrast to electrodes with a static porous matrix, the heterogeneous local porosities change temporally depending on the evolving particle distributions. Additionally, the active electrode surface area in each finite volume is dependent on the percolation network from the considered local point to the current collector surface. To estimate the basic parameters for the charge transfer and species transport, a flat-plate electrode with a flowing electrolyte without particles is simulated and compared to experimental data. Afterwards, a sample configuration of the slurry electrode is simulated with the described model and also compared to corresponding experimental measurements.

Funding by the Federal Ministry for Economic Affairs and Energy (BMWi) of the project “ZnPLUS - Wiederaufladbare Zink-Luft-Batterien zur Energiespeicherung” and the project “ZnMobil - Mechanisch und elektrisch wiederaufladbare Zink-Luft-Batterie für automobile Anwendungen” is gratefully acknowledged.

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Operando X-ray Tomography and Sub-second Radiography for Characterizing Transport in Polymer Electrolyte Membrane Electrolyzer

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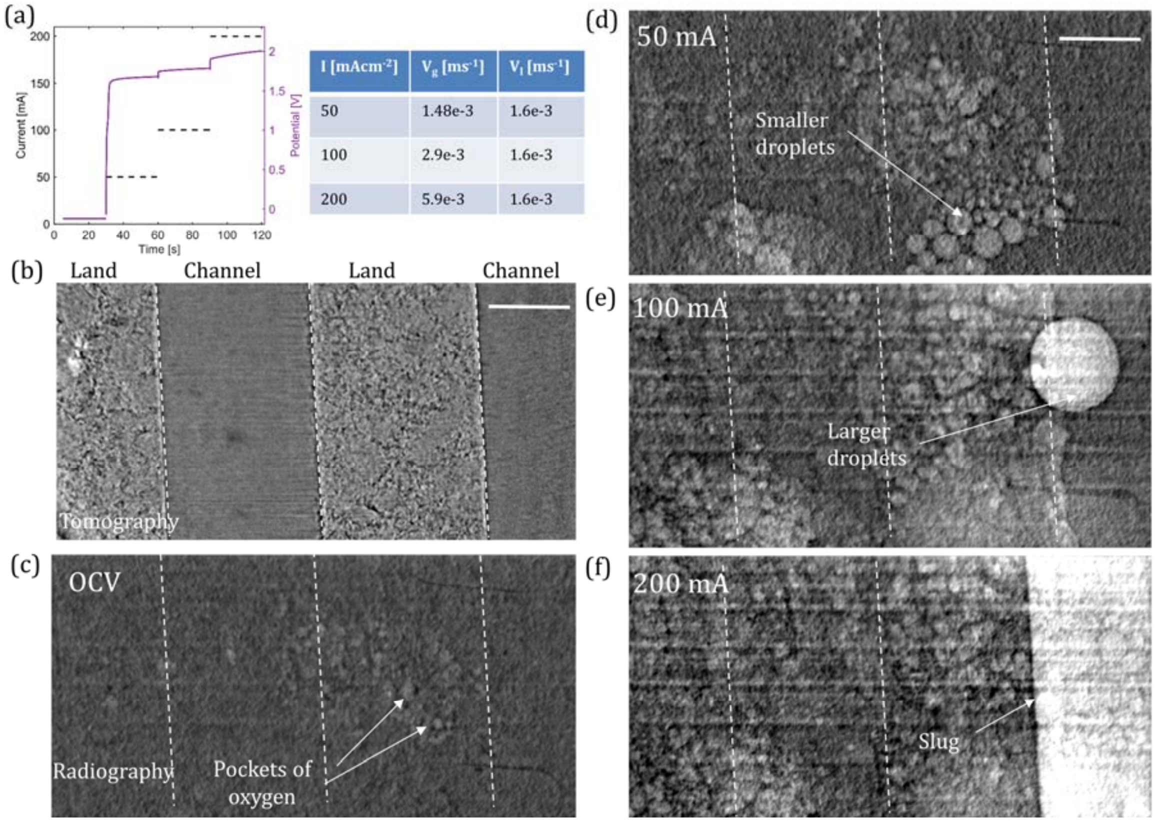
Hydrogen economy is a promising pathway towards decarbonization, where electrolysis is a key process to generate hydrogen gas that acts as an energy carrier. Understanding morphology evolution and transport processes in operating polymer electrolyte membrane (PEM) electrolyzer is a key to reduce its cost and increase efficiency. In this study, a combined *operando* X-ray computed tomography and radiography are used to study transport and degradation in PEM electrolyzer under varied current densities. Tomography enables three-dimensional steady-state imaging, whereas radiography is limited to two-dimensions but captures transient phenomena. The tomography results indicate mechanical degradation of the catalyst layer on the anode side, the process exacerbated by higher current densities. Due to mechanical stresses during oxygen evolution reaction electrocatalyst particles are mechanically ripped off the membrane and are redeposited into the porous transport layer. For catalysts deposited onto novel porous transport layers (PTLs) no significant degradation is observed in a current range up to 1 Acm^{-2}. From the radiography even at lower current densities (50-200 mAcm^{-2}) sub-second exposure time is required to capture transient behavior of oxygen evolution. Depending on current density various channel flow regimes are observed ranging from bubbly to slug flow. With increase in current density oxygen bubble diameter increase and the residence time within the channel decrease, these experimental observations are confirmed with a model.



I [mAcm^{-2}]	V_g [ms^{-1}]	V_l [ms^{-1}]
50	1.48e-3	1.6e-3
100	2.9e-3	1.6e-3
200	5.9e-3	1.6e-3

Figure 1: a) Chronopotentiometric plot for constant current density holds of 50, 100, 200 mAcm^{-2}. The table on the right show calculated gas velocity and liquid velocity. b) Tomography of the location imaged with radiography, c-f) for the current stepping experiment.

Modelling of the supersaturation of dissolved gas in PEM electrolysis cells

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Models for description of mass transport phenomena in PEM (polymer electrolyte membrane) fuel cells are quite common to investigate transport limitations especially at the oxygen side. However, for PEM water electrolysis cells the catalyst layers are barely investigated, despite of their importance.

In the framework of the presented contribution a steady state, one dimensional model (sandwich coordinate – through plane) for PEM water electrolysis was developed. The main focus of the model lays on the investigation of the mass transport phenomena within the catalyst layers. Next to the description of electric and protonic potentials, temperature, gas pressure and liquid saturation, one important state variable is the dissolved gas concentration. The supersaturation of dissolved gases has been proved already experimentally several times e.g. [1]. Within this contribution, the influence of supersaturated dissolved gas concentrations on performance (via Nernst equation) and on gas crossover is shown, as it was already supposed from experimental results [2,3]. The analysis comprises the investigation of the effect of operating parameters, as current density and temperature, as well as geometric parameter as ionomer content, catalyst loading and particle sizes on supersaturation.

The model results are supported by experimental results. Fig. 1 shows that the crossover strongly increases with current density. This increase can be explained by small mass transport limitations within the cathode catalyst layer that lead to supersaturated hydrogen concentrations, thus causes the increases in hydrogen crossover. Additionally, Fig. 1 shows the effect of a different ionomer content within the cathode catalyst layer. Because of smaller mass transport limitations with less ionomer within the catalyst layer the supersaturation is lower and consequently the hydrogen crossover.

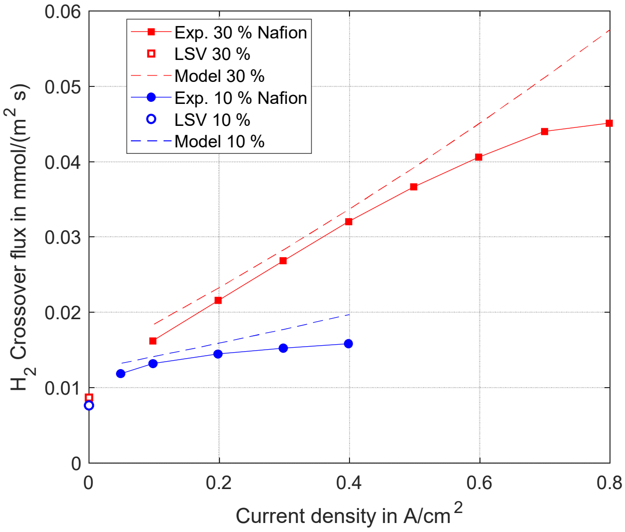

Figure 1: Experimental and model results of the hydrogen supersaturation effect on hydrogen crossover vs. current density for two different ionomer contents (30 and 10 %) within the cathode catalyst layer. Operation conditions: $T = 80$ °C, atmospheric pressure and N117 membrane.

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PEM water electrolysis modelling: Upscaling strategies

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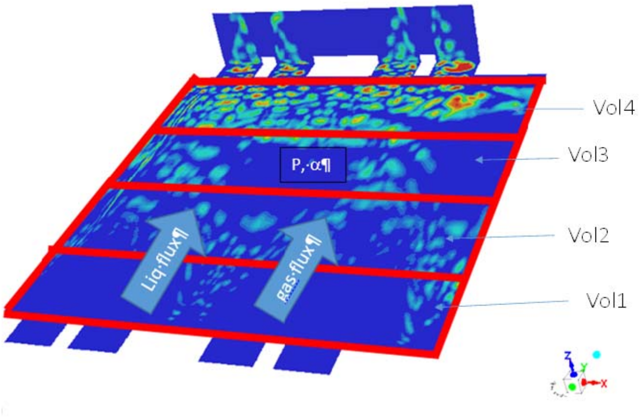
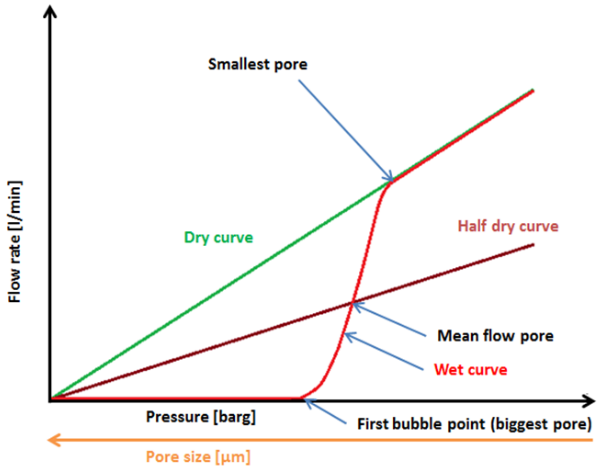
***Keywords**:* PEM water electrolysis, modelling, multiscale

In the frame of the European project MEGASTACK (FCHJU) devoted to the development of a MW PEM electrolysis system, CEA, FRAUNHOFER and SINTEF have participated to the development of several multi-physical and electrochemical empirical or semi-empirical models capable to capture the main mechanisms that occur in the various components of a PEM electrolysis cell under operation. These models have been implemented in the code MePHYSTO_WE developed by CEA for the simulation of the electrolyzer performances. The code is computationally very efficient making sensitivity studies possible. The information obtained from such studies enable rapid exploration of different designs and identification of optimal operating conditions.

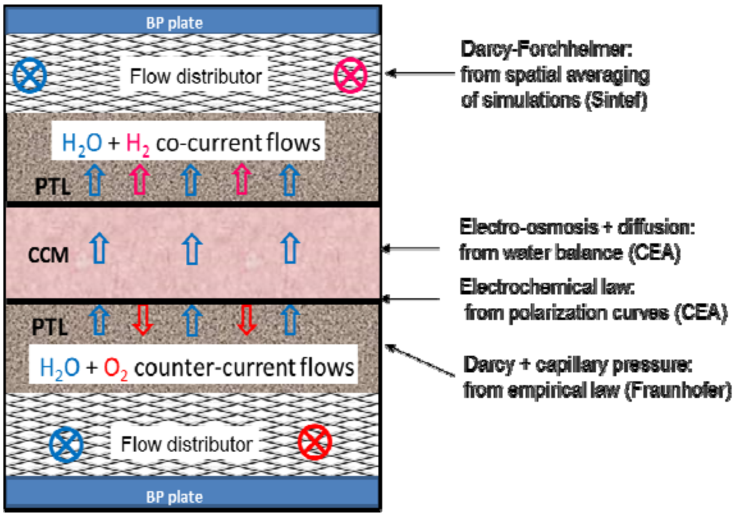
Our presentation describes how the models were obtained for the different components using detailed single and multiphase CFD simulations and several in situ and ex situ experiments. We describe the micro-scale simulation of the flow in the fluid distributor and the upscaling process that provides the macro-scale flow parameters (Darcy absolute and relative permeability's). Next, we detail the experimental and numerical characterisation for the chosen porous transport layers (PTL) (capillary pressure law, absolute and relative permeabilities), and describe the electrochemical measurements used to derive the electrochemical law. Finally, we give examples of what kind of results the MePHYSTO_WE code can provide.



Two-phase flow simulated in the flow-distributor.
The domains for which the detailed CFD results are averaged for use in the MePhysTo_WE code are delimited by red lines.



Typical results obtained by Capillary Flow Porometry: flowrates (liquid, gaseous) as function of pressure drop, e.g. for calculating pore sizes of the porous transport layer.



MePHYSTO_FC code: description of the different process and model components and the physical mechanisms involved in them.

Modeling of SOECs –Physics-based Impedance Analysis of MIEC Electrodes

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A macroscopic model for solid oxide electrolyzer cells (SOECs) has been developed and implemented into the numerical framework NEOPARD-X. It is employed to simulate a commercial electrolyte supported cell in electrolysis mode under various operating conditions (e.g. temperatures, gas compositions,…). The model allows transient, non-isothermal cell-level simulations in 2D or 3D and incorporates comprehensive models for bulk material properties and porous structures. The oxygen evolution reaction is described using global Butler-Volmer kinetics while at the fuel electrode a detailed, thermodynamically consistent elementary kinetic model accounting for surface- and charge transfer reactions is employed.

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

With the help of this physical model, the influence of mixed electronic ionic conducting (MIEC) materials on the cell performance and the impedance spectra is investigated. Further, the catalytic activity of gadolinium-doped ceria (CGO) is investigated. Experimental EIS data are interpreted and critical processes in the cell are identified.

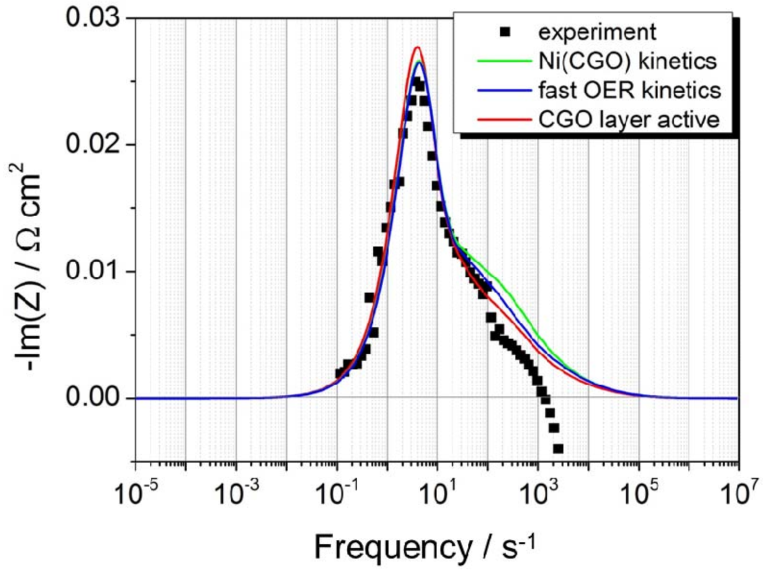

Figure 1: Bode plot of the imaginary part of impedance data at open circuit voltage (OCV), 50%H_2, 50%H_2O, 1123.15K, 10^5 Pa. Black symbols: experimental data, green curve: reaction kinetics on Ni(CGO), blue curve: fast oxygen evolution reaction (OER) kinetics, red curve: with additional catalytic activity of the CGO contacting layers.

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Robust Quality Preserving Numerical Methods for Electroosmotic Flows

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Microscale electroosmotic flows occur in many interesting applications, including pore scale processes in fuel cell membranes and sensing with nanopores. The contribution summarizes recent developments in modeling and numerical discretization approaches for coupled fluid flow and ion transport in a self-consistent electric field. Ingredients of the method are

1. Pressure-robust, pointwise divergence free finite element discretization of the Stokes equations describing the barycentric velocity of the ionic mixture [1,2]
2. Generalization of the Nernst-Planck equations for ion transport to the case of finite ion sizes and solvation effects [3]
3. Thermodynamically consistent, maximum principle observing finite volume method for ion transport including competition for finite available volume [4,5]
4. Coupling approach between fluid flow and mass transport together with a fixed point iteration to solve the combined system [6]

The contribution introduces the models and the discretization approach. It provides recent results of numerical simulations of elecroosmotic flows in nanopores confirming the validity and the advantages of the discretization approach. A number of open problems and challenging directions will be described.

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An open implementation of a two-phase PEMFC model in MATLAB

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In almost three decades of PEM fuel cell modelling, a large number of numerical models has been developed both in science and industry, but almost none have been made publically available. There is a large need for standardization and establishing a common ground in the development of PEMFC simulation codes, to prevent each research group from having to start from scratch. To this day, there are only two known open-source codes capable of simulating the state of the art in PEMFC modeling at the cell scale: OpenFCST [1], a highly capable but heavy FEM package consisting of more than 120.000 lines of C++ code published under the MIT license, and FAST-FC [2], a finite volume tool built on top of OpenFOAM, consisting of about 12.000 lines of code (not counting the required OpenFOAM) published under the GNU GPL v3, which can pose an insurmountable legal barrier for commercial use.

Here, we present the first open standalone implementation of a full-blown, steady-state, non-isothermal two-phase, macro-homogeneous MEA model for low-temperature PEMFCs [3]. It implements the most dominant through-plane transport processes in a 5-layer MEA (Fig. 1): the transport of charge, energy, gas species and water. This results in eight coupled nonlinear second-order partial differential equations, which are numerically solved together. The focus is on code simplicity, compactness, portability, transparency, accessibility and free availability. The model is implemented as a standalone MATLAB function, based on MATLAB's boundary value problem solver, and released to the public under a BSD-like license, permitting unrestricted use for commercial and non-commercial purposes.

In order to establish a new reference for model comparison, validation and benchmarking, we subject our model to a series of stress tests with operating conditions recommended for automotive applications by the Joint Research Centre of the European Commission [4] and report here on the test results.

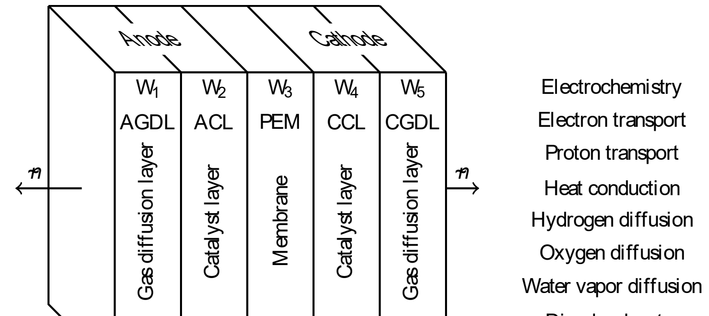

Figure 1: Geometry of the 5-layer MEA model (not to scale) and the simulated transport processes.

Acknowledgements: Financial support from the Swiss National Science Foundation under the National Research Programme "Energy Turnaround (NRP 70)", project no. 153790, grant no. 407040_153790, from the Swiss Commission for Technology and Innovation under contract no. KTI.2014.0115, through the Swiss Competence Center for Energy Research (SCCER Mobility), and from the Swiss Federal Office of Energy (SFOE), is gratefully acknowledged.

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Time-of-flight neutron imaging for the localization of freezing events during PEFC cold starts

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The successful start-up of polymer electrolyte fuel cell stacks (PEFCs) under sub-zero conditions (cold-start) with a minimal input of auxiliary power is an important requirement for the broad market introduction of fuel cell cars. Additionally, the possibility of operating smaller fuel cells with low self-heating capabilities in sub-zero conditions would extend the application range of this technology, e.g. for backup power supply in remote areas. Typically, cold start failures occur when the water produced by the electrochemical reaction freezes and blocks the access of oxygen to the catalyst. However, water produced by the reaction in sub-zero conditions can remain in liquid (super-cooled) state [1]. Building on this fact, novel materials and designs which deliver conditions that favor the super-cooled state could help to improve the start-up and sub-zero operation capabilities of PEFCs.

To this purpose, a method for identifying the aggregate state (liquid or frozen) of water during fuel cell operation is of high interest. We demonstrated the use of energy selective neutron imaging (ES-NI) for the distinction between ice and super-cooled water for the first time in 2013 [2], exploiting the fact that the neutron cross-section differs for super-cooled water and ice at long neutron wavelengths [3], while they are identical at short wavelengths. To distinguish between these two cases, we used a neutron filter, which blocked neutrons with a wavelength shorter than 3.95 Å, and compared the results with a measurement using the full neutron spectrum – a method termed “dual spectrum neutron imaging” (DS-NI). The advantage of this approach over other energy selective methods with higher energy resolution is that a much higher neutron flux is obtained, which allowed us to obtain a good signal-to-noise ratio (SNR) [2]. However, the obtained contrast (1.6%) is very low, making the method particularly sensitive to biases. This method could nevertheless be used to identify local freezing events in a fuel cell with an active area of 50 cm^2 [4].

In order to optimize the contrast, we developed a new setup based on neutron time-of-flight (TOF). TOF neutron imaging is conventionally using short pulses of neutron beam at a pulsed neutron source or a rotating chopper disk with a narrow slit. This allows for discriminating the neutron wavelengths according to their travel time, as the speed of neutrons is wavelength dependent. The new proposed concept uses broad neutron pulses, which strongly increases the flux in comparison to conventional TOF imaging, at the cost of wavelength resolution. With this method, we could significantly improve the contrast (reaching approximately 6%) while keeping a high neutron flux. Here, we will first present test results obtained on a non-operating cell. This cell contained six stacked gas diffusion layers (GDLs) with a total thickness of 1 mm. The GDLs were partially saturated with water. Furthermore, this cell was segmented into 3 adjacent areas with 4.4cm^2 that were separately thermally controlled. A temperature gradient was applied over these three segments to induce local freezing and melting. While the freezing is not visible in a classical transmission based image (Figure 1 (a-c)) – as the water expands locally in the GDL pores – our energy selective approach can clearly identify the liquid and frozen regions (Figure 1 (d-f)). Finally, we will show the application of the method to real fuel cell cold starts.

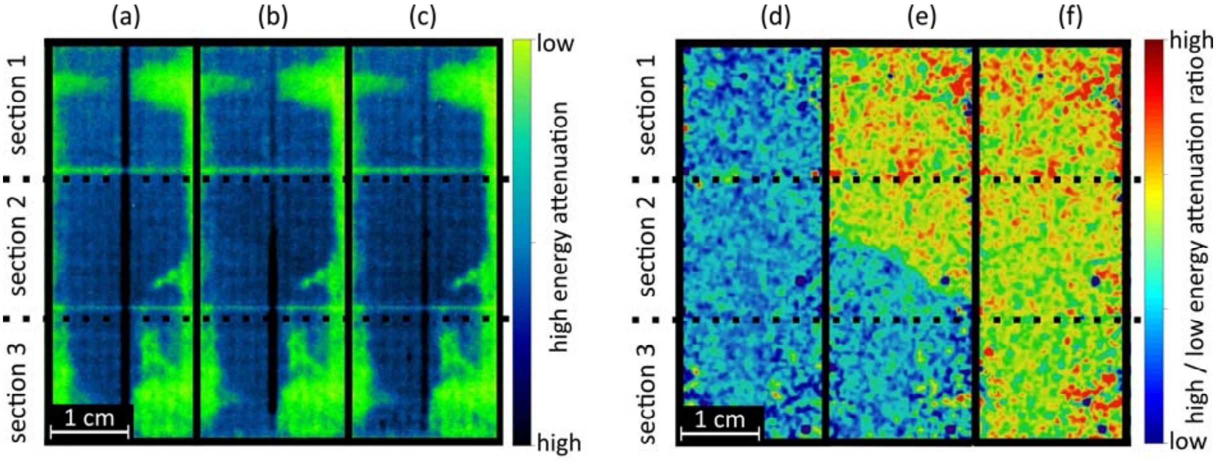

Figure 1: Visualization of the liquid/frozen regions in a non-operating test fuel cell with partially saturated gas diffusion layers. [a-c] High neutron energy attenuation: a higher attenuation corresponds to a larger water thickness. [d-f] Ratio between high and low neutron energy attenuation: A lower ratio is measured for ice compared to super-cooled water.

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Simulation of a high temperature polymer electrolyte fuel cell short stack with OpenFuelCell

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High temperature polymer electrolyte fuel cells (HT-PEFCs), which normally operate between 120°C and 180°C, have many advantages, such as simple water and heat management and high tolerance to carbon monoxide (CO). Both experimental and numerical studies of HT-PEFCs have been conducted in the past in order to analyse the performance of fuel cells.

Experimental measurements typically provide global information. Computational fluid dynamics (CFD) calculations have the potential to provide information in fine detail. Previously, CFD applications were limited by computational power. This has changed with the availability of massively-parallel high performance computing (HPC) facilities. Use of commercial software on HPC facilities are constrained by licensing costs, which makes the adaptation of open-source codes to fuel cell applications most attractive.

A generic open-source computer code, openFuelCell, capable of reproducing every significant physico-chemical hydrodynamic process within a fuel cell, has been developed and refined by the present authors and others [1]. The code was implemented on top of the OpenFOAM® platform, which enables fully-comprehensive calculations to be performed on HPC facilities.

HT-PEFC stacks are composed of repeating units of active cells and liquid cooling units. Several approaches have being used to obtain performance calculations for such stacks. These include: a) treating the the stack as zero-dimensional with no spatial resolution, b) spatially averaging the cells, c) explicitly modelling all the cells and coupling the solutions together to yield the overall behaviour of the stack. Previous work [2] performed simulations on a 5-cell short stack with the approach (b). The authors applied a distributed resistance analogy [3] also known as a porous media approach, to average the geometrical information of each cell and thereby reduce the computation effort. Overall performance and local values of current density and temperature, were calculated and compared with experimental results [4]. However, the fine-scale values cannot be resolved with this method.

The authors of the present work modified and applied the open-source code, openFuelCell to performed detailed simulations for a 5-cell HT-PEFC using approach (c) above. The computational mesh consists of 172×10^6 control volumes. Polarization curves and local current density distributions are compared with previous work [2] with excellent agreement. It can be seen that present code is capable of resolving detailed features, previously unobtainable. Thus, the code may be used for improving fuel cell stack design.

Acknowledgements: This work is partially supported by China Scholarship Council (grant number: 201506230130) .Calculations were performed on HPC hardware of the Jülich and Aachen Research Alliance (JARA), grant JARA0070.

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Characterization and Comprehensive Modeling of Cathode Catalyst Degradation in PEM Fuel Cells

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Catalyst degradation is one of the main inhibitory factors on the way to long-term and stable fuel cell performance. Changes in load and conditions such as temperature or gas humidity during PEMFC operation are known to induce structural changes of the cathode catalyst layer (CCL). Such a deviation from the initial, optimized electrode structure is usually accompanied by loss of electrochemically active surface area (ECSA) and subsequent fuel cell performance deterioration.

In order to meet automotive driving demands, it is crucial to identify the main stressors leading to fuel cell degradation. To date, there exists a multitude of specially designed accelerated stress test protocols which aim to provoke and isolate individual degradation processes. To study electrode aging, cells are usually exposed to repeated potential cycling between a defined lower potential limit (LPL) and upper potential limit (UPL). However, degradation behavior is found to be sensitive to almost every property of the applied potential profile: not only the absolute value of the LPL and UPL [1, 2], but also the dwell time at the respective potential [3], the edge steepness when the potential changes and even the direction of change (anodic sweep, i.e. low to high potential or cathodic sweep, i.e. high to low potential) [4, 5]. As a consequence, slight variations in the applied potential profile can lead to a complete reversion of observed trends [6]. Valid comparison of experimental results thus requires knowledge of the influence of the above-listed factors on physical processes in the CCL. Our work aims at obtaining a comprehensive picture on degradation mechanisms by means of experimental studies and corresponding simulations, with a pronounced focus on the interaction of the various degradation processes.

In this context, we performed an extensive series of in-situ aging experiments over a wide range of operating conditions. So far, over 20 different cells with various catalyst materials and loadings were subjected to standardized protocols for load cycling as well as aging of the catalyst support, for up to 300,000 cycles per cell. Parameter variations between tests included changes in temperature, relative humidity, potential cycle profile (rectangular, triangular) as well as variations in potential dwell time. Characterization by means of polarization curves, cyclic voltammetry, limited current density measurements and electrical impedance spectroscopy was performed in regular intervals.

Further, we implemented a physically motivated, numerical degradation model which accounts for degradation processes that were identified as dominant. These include migration of platinum catalyst particles such as Pt dissolution into the electrolyte and re-deposition onto particles that remain on the carbon support (Ostwald ripening), particle coagulation, and permanent detachment of catalyst particles due to support corrosion. In addition, the model accounts for the formation of Pt oxides (PtO) which lead to a passivation of the respective catalyst sites, as well as chemical dissolution of PtO with subsequent loss of Pt particles.

Following our experimental results and recent findings in literature, we also developed a way to work the so-called place-exchange mechanism [5] into our model. At sufficiently high potentials, Pt oxide is generated. The longer the CCL is exposed to such potentials, the more pronounced an oxide layer will evolve. Between neighboring oxygen atoms, repulsive forces interact such that, at a given oxide layer, it can be energetically preferable for the O and Pt atoms to switch their places. The oxygen atom is then integrated into the Pt compound whereas the Pt atom becomes exposed at the CCL surface. Reducing the potential in this configuration leads to severe reduction of active surface area since all "place-exchanged" Pt atoms are then lost into the electrolyte. Longer dwell times at high potentials are thus associated with encouraged place-exchange and subsequent loss of ECSA [3, 5]. With the place-exchange mechanism established in the model, we could confirm our experimental results that fuel cell performance exhibits a much stronger decrease rate per cycle if the potential dwell time at UPL is large. The next step will be to integrate our degradation model into a full fuel cell performance model, such that in-situ experiments can be compared directly to according performance predictions.

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Origin of the hysteresis between forward and reverse peak in cyclic voltammograms of the alkaline methanol electrooxidation

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While methanol electrooxidation under acid conditions has been widely studied, the mechanism under alkaline conditions is still discussed. In this context the origin of significant hysteresis in cyclic voltammograms was investigated. The combination of experimental data and simulations allows to explain the hysteresis between forward and backward peak for the methanol oxidation in a cyclic voltammogram. We show that similar to the methanol electrooxidation in acidic medium, the hysteresis originates from the reversible formation of platinum oxides at higher potentials.

The mechanism of the alkaline methanol oxidation is still not completely clarified. The information about the exact processes and their kinetics are important to optimize the system in order to approach the promising theoretical performance. Cyclic voltammograms show two anodic peaks, one in the forward and one in the backward scan. During the forward scan methanol starts to adsorb and oxidise when enough catalyst sites are available due to hydrogen desorption. Running from high to low potentials results in a smaller peak that is shifted to negative potential (Fig.1). Goodenough, Prabhuram and Vega showed that under acidic conditions, intermediates from methanol oxidation formed during the forward scan are oxidised in the backward scan whereas Chung, Hou and Tong propose the backward peak to originate from further methanol oxidation. They claim the reversible formation of platinum oxides which reduce the active surface to be responsible for the hysteresis between forward and backward scan.

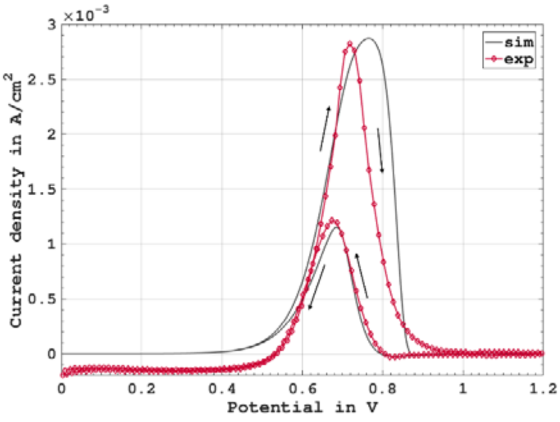

Figure 1: Experimental and simulated cyclic voltammogram of the methanol electrooxidation in aqueous alkaline solution. v = 5 mV/s, room temperature.

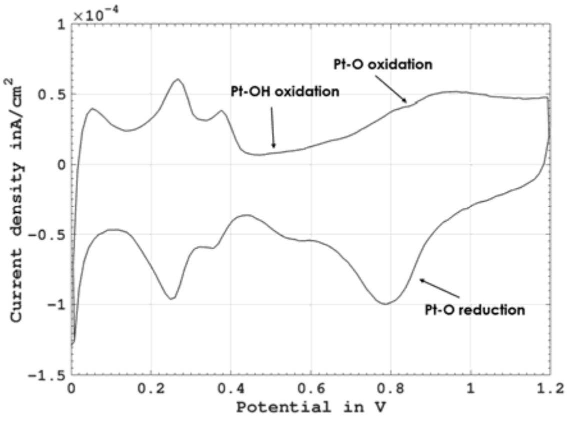

Figure 2: Basic cyclic voltammogram of the alkaline electrolyte (1 M NaOH). v = 50 mV/s, room temperature.

We recorded CVs in a reverse manner, starting from high potentials, and the same hysteresis was observed. This proves that intermediates from the forward scan have no direct influence on the backward course. Additionally, experiments with varied upper potential were performed to investigate the influence on the hysteresis. The higher the upper potential, the stronger the hysteresis. A model including balances for adsorbed methanol species on the catalyst as well as platinum oxide formation was developed. The model can quantitatively reproduce the hysteresis between the forward and backward scan (Fig. 1) and the potential for PtO formation found by parameter fitting is consistent with PtO formation in a basic CV (Fig. 2). The confirmation of platinum oxide formation and its influence on the electrooxidation of methanol facilitate further investigations of the mechanism and the synthesis of adequate catalysts.

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An integrated concentrated solar fuel generator concept utilizing a tubular solid oxide electrolysis cell as the solar absorber

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We present the numerical assessment of the potential of a solar reactor concept which integrates a cavity receiver, a tubular solid oxide electrolyzer (SOEC), and the concentrated photovoltaic (PV) cells into a single reactor for efficient fuel processing under concentrated solar irradiation (see Figure 1). The tubular electrolyzer simultaneously acts as the electrochemical device (for water and carbon dioxide splitting) and the solar absorber (for reactants heating). Concentrated PV cells are mounted on the water-cooled reactor front as the solar electricity source for the SOEC. The partitioning of the incoming concentrated solar irradiation towards the PV and SOEC at the focal plane (reactor front) is achieved by tuning the cavity aperture size and the reactor front size.

A multi-physics axisymmetric model is developed, considering charge transfer in the membrane-electrolyte assembly, electrochemical and thermochemical reactions at the electrodes' reaction sites, species and fluid flow in the fluid channels and electrodes, and heat transfer for the whole reactor. Two electrical coupling strategies between the PV and SOEC are considered: the direct wire connection and the indirect connection via a DC-DC converter. The indirectly connected approach showed a high solar-to-fuel, at the reference conditions. The advantage in efficiency was even larger at high concentrations. For synthesis gas production, the current density threshold for carbon deposition was found to be ~7500 A/m^2, at reference conditions. The reactants inlet velocity was optimized to achieve high efficiency and to alleviate mass transport limitation when operating at high current density. A continuous range of the H_2/CO molar ratio of the synthesis gas was achieved by varying the inlet H_2O/CO_2 ratio, the irradiation concentration, and the operation current density. The two SOEC-cell reactor (connected in series) achieved a higher efficiency (21.7%) compared to the single SOEC-cell reactor, only requiring additional thermal energy input to the reactor.

Our new and integrated solar reactor concept for the solar-driven high-temperature electrolysis of H_2O and CO_2 has the potential to provide a cost competitive approach to solar fuels. The multi-physics model provides a design tool for the assessment of the potential of this reactor technology.

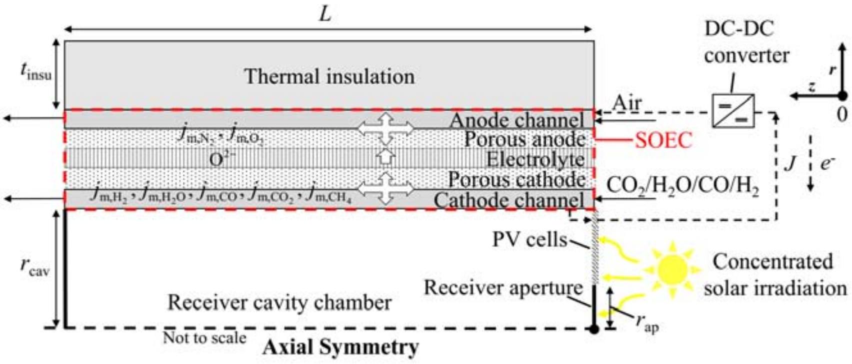

Figure 1: Schematic of the axisymmetric calculation domain for the proposed integrated solar reactor (not to scale). The dashed red box is the SOEC cell domain. The white thick arrows stand for species transport and the dashed black lines stand for current flows. The coordinate 0 point (black dot) is on the aperture (black dot at the aperture domain). The DC-DC converter is present only for indirect connected cases.

High performance full resolution modelling of mass transport and phase change phenomena in anode and cathode sides of PEFCs

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Despite many investigations on water evaporation in cathode gas diffusion layers (GDL) and at moderate temperatures [1,2], little attention has been paid to study evaporation at higher temperatures and at the anode side of the fuel cell where hydrogen is flowing through the gas channels. In this work, parallel multi-GPU direct numerical computations are used to solve fully coupled flow and mas transport equations so as to characterize evaporation at pore level for both anode and cathode sides and at temperatures up to 80°C. Original porous structure and water distribution of a GDL, obtained at 2.5 µm from X-ray tomography, are used while regularized water distributions are also considered to study evaporation at different saturation levels. Key results indicate that **a)** the water evaporation rate in hydrogen flows can be up to 4 times larger than of the corresponding one in air flows at the same gas velocity and temperature as summarized in Fig. 1a, **b)** as shown in Fig. 1b**,** the predicted through-plane evaporation-induced (EI) velocities in the GDL and under hydrogen are mostly upward and an order of magnitude larger than those under air flows. Moreover, at high temperatures (e.g. 80°C), these velocities can become large enough to potentially hinder hydrogen transport to the CL, and **c)** due to the higher evaporation rate of hydrogen compared to air, the former gas experiences an early saturation along the channel, implying that the major downstream part of the GDL may not efficiently participate in the water evaporation as shown in Fig 2.

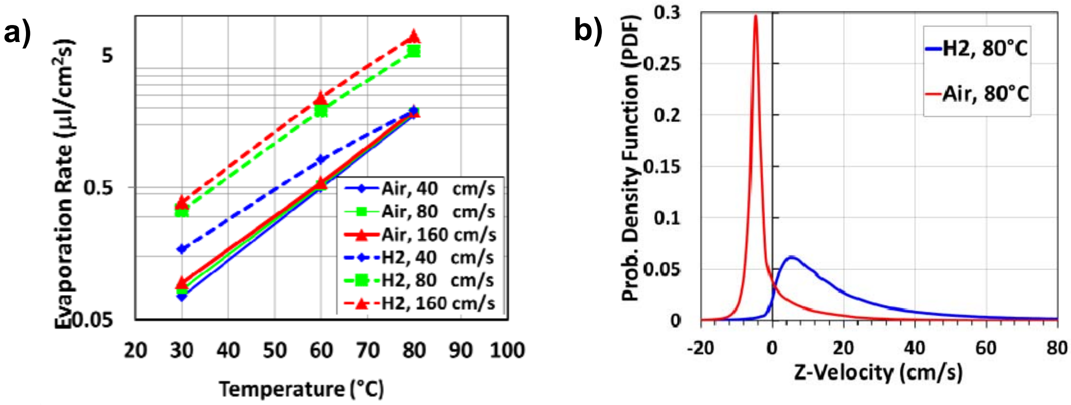

Figure 1: (a) Total evaporation rate at different gas flow rates and different temperatures for air and hydrogen, (b) Probability density function of the vertical through-plane (z) velocities inside the GDL at 80°C.

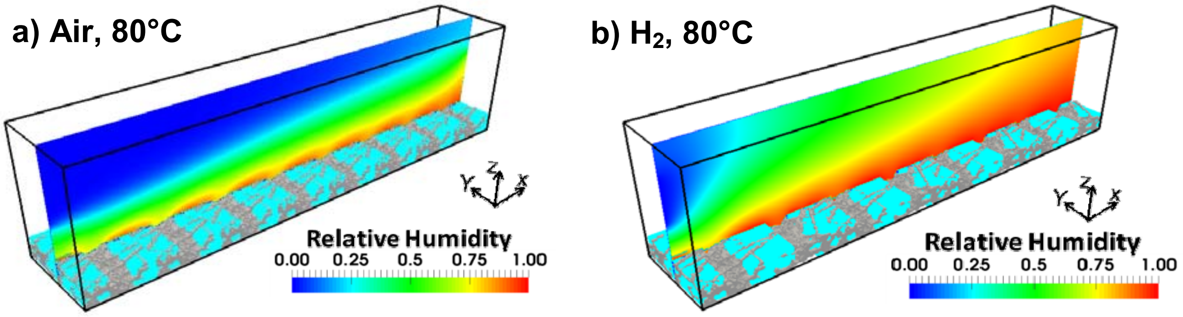

Figure 2: Relative humidity distribution over the GDL saturated with a periodic distribution of rectangular water columns for (a) air, and (b) hydrogen at 80°C and 160 cm/s of gas flow rate.

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Simulation of Water Transport in the Stochastic Micro-structure of Polymer Electrolyte Fuel Cell Using the Lattice Boltzmann Method

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Lattice Boltzmann method is well suited to simulate multi-phase fluid problems in porous media within a mesoscopic scale (micro meter scale). In polymer electrolyte fuel cells (PEFCs), the gas diffusion layer (GDL) is one of main components and it consists of irregular distributed carbon fibers. In the cathode side of PEFC, liquid water is produced and flow through GDL to the gas channel (GC). Simulations were performed according to the conditions of a PEFC operated at 1 A/cm^2. An ensemble of stochastic microstructures was created with a stochastic model for Toray GDL [1]. The water distribution inside the GDL is analyzed. Various liquid water breakthrough points were observed at the GDL-GC interface. The irregular microstructures of the GDL lead to the randomly distributed water breakthrough points and the asymetric droplet shapes. The breakthrough point distances are evaluated by the statistic methods [2]. The local apparent contact angles of droplets are analyzed with polynomial method in detail [3].

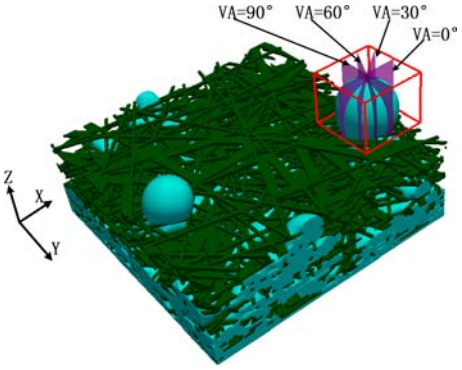

Figure 1: Formed liquid droplets on GDL surface and four view angles (VA) to see apparent contact angles (Green: GDL; blue: water)

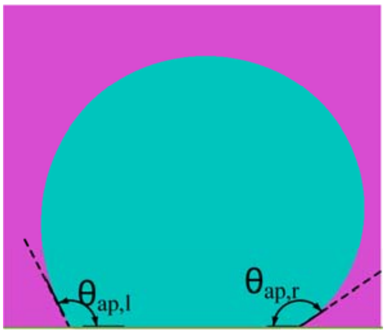

Figure 2: Apparent contact angles on the subsection when VA=0°

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Acknowledgement:
This work was funded by the Chinese Scholarship Council (CSC) [grant numbers 201408080011].
The transport simulations are running on hardware of the Jülich Supercomputing Center [grant numbers JIEK30]

Convection driven droplet detachment from gas diffusion layers

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Droplet formation in the cathode gas flow channel of polymer electrolyte fuel cells (PEFCs) can negatively impact the fuel cells performance due to increased pressure drops or even blockage of reactant gas. Using sub-second X-ray tomographic microscopy (XTM), the liquid water distribution in the gas diffusion layer (GDL) GDL and the flow channel was determined and the behaviour of droplet detachment at the GDL-gas channel interface monitored. The effect of water injection rate on the size and frequency of droplets was monitored using both, fast X-ray 2D radiography (3 ms exposure time) as well as computed tomography (0.75 s scan time, 2.55 s repeating frequency).

For the different water injection rates, the droplet formation was found to be very periodic with the droplet growth showing a repeating pattern. The droplet diameter evolution for two different injection rates is shown in Figure 1 (a). For the case of 1000 nL/min water injection, the droplets were smaller and retained a circular shape almost until detachment, while the droplets formed at an injection rate of 350 nL/min grew larger and evolved into a tear shape after a certain droplet size. For both conditions, the gas flow induced deformation started at a droplet volume of about 9 nL. Above this point, an estimate of the water volume is made using a linear extrapolation of the initial growth rate that is extended to the point in time where droplet detachment was observed. The final droplet volume was estimated to be 17.6 nL at an injection rate of 350 nL/min and 10.3 nL at 1000 nL/min.

Figure 1 (a) and (b) compares the water volume inside the GDL calculated for every 3 μm thick through-plane layer of the discrete voxel based domain. Water volume in the GDL near the inlet was found to be high and decreasing towards the gas channel, corresponding to a high saturation near the inlet and a low saturation near the gas channel. It was found that no changes occurred in the bulk of the GDL when changing the injection rate from 350 to 1000 nL/min. At an injection rate of 350 nL/min, a strong deviation of water volume between scans can be observed in the upper layers of the GDL.

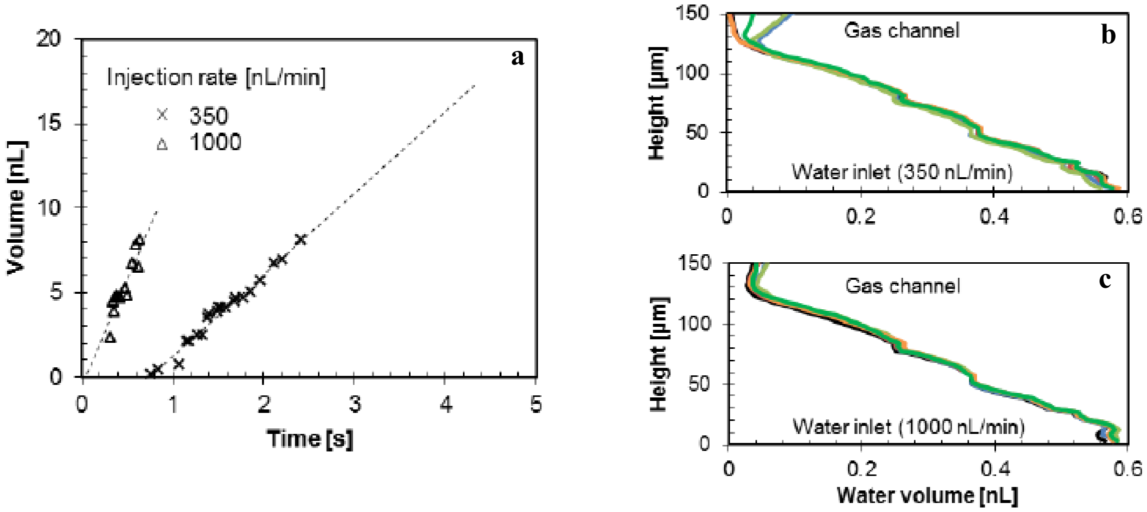

Figure 1: (a) Droplet volume calculated from observed diameters for injection rates of 350 and 1000 nL per minute. Water volume over the height of the GDL domain, for an injection rate of 350 nL/min (b) and 1000 nL/min (c).

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New Porous Nickel-doped Materials for Alkaline Water Electrolysis

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New porous 3D nickel foam electrodes were coated with electrochemical active catalysis materials with a doped nickel hydroxide powder basis [1]. The substituted nickel hydroxide particles pushed the OER's kinetics in alkaline electrolyte. In this research the electrode's efficiency was electrochemically tested through polarization curves and physically characterized with different methods like scanning electron microscopy, video probe and X-ray tomography. For a better understanding of the gas transport, computer simulation of the local transport through the porous layer using VoF-method (volume of fluid using AVL FIRE™ program package) [2] was performed and the two-phase-stream of the gas bubble-electrolyte mixture were investigated. The simulation of the complete cell using Euler-Euler approach [3] furnished precious details about the gas bubble management and hence about the optimal construction design.

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Investigation of liquid water heterogeneities in large area PEM fuel cells using a pseudo-3D multiphysics model

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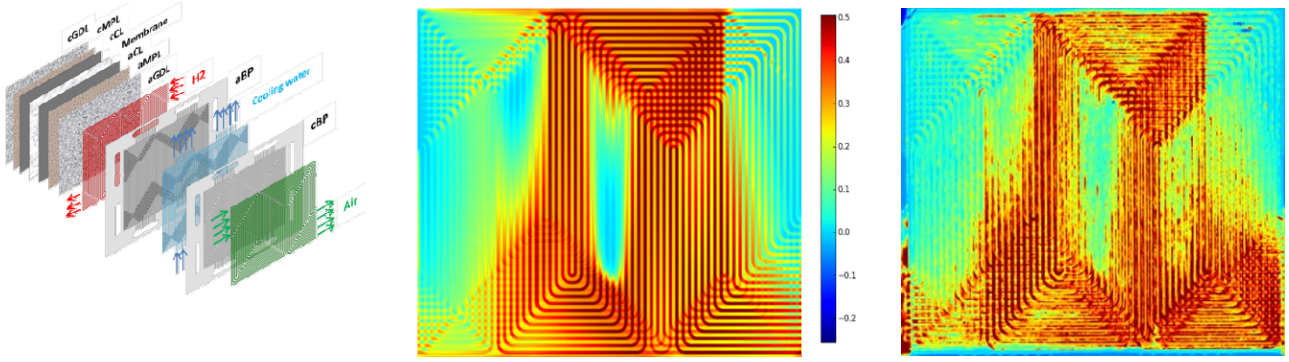
The Proton Exchange Membrane Fuel Cell is a promising candidate for many applications, either stationary or transportation. Of the many barriers, cost and durability represent two of the most significant challenges to achieving clean, reliable, cost-effective fuel cell systems. Effective management of the liquid water and heat produced in PEM fuel cells remains crucial to increase both its performance and durability. Ineffective water and heat management can lead either to liquid-phase water blockage and mass-transport-limited performance or to decreased proton conductivity because of dehumidification of the ionomer. Furthermore, high liquid water content and high temperature are believed to increase several degradation mechanisms.

The study of the combined effects of the heat transfer and water transport is necessary at a local scale but also at the cell level. Indeed, in an industrial fuel cell stack, the thermal and water distribution heterogeneities are greater than in laboratory single cells. The heterogeneities are particularly exacerbated due to the size of the system and are directly related to the design of the cooling circuit.

Physics-based PEMFC stack models of heat and water transfers are useful tools to investigate distribution of local conditions inside a stack. Since both temperature and liquid water distributions are driving forces for degradation mechanisms, a pseudo-3D multiphysics model has been developed to predict at the cell scale the in-plane temperature and species distributions in all the components of the cell, including the cooling circuit [2]. The model considers the cell as a multilayered system (Figure 1.a) and each layer is accurately in-plane discretized to allow the simulation of local temperature and species heterogeneities, including liquid water (Figure 1.b). The transport equations are solved using a pseudo-3D approximation and coupled to an analytical electrochemical model to determine the local current density as function of the local conditions. The main advantage of the model is the prediction of the distributions of current density, species concentrations, water content and temperature in all the components of the cell with a low computation time compared to a full 3D model, while taking into account the real flow-field designs.



(a) **(b)** **(c)**

Figure 1: (a) The reference geometry of the pseudo-3D model consists of 9 solid domains: one membrane, two catalyst layers (aCL and cCL), two micro-porous layers (aMPL and cMPL), two gas diffusion layers (aGDL and cGDL), two monopolar plates (aBP and cBP) and (b) simulated and (c) experimental liquid water thickness (mm) on the active surface area (operation conditions: Temperature=65°C, Relative humidity =50/50, current density=0.25A/cm², anode and cathode gas pressure P_a=P_c=1,5bars, anode and cathode stoichiometry=1,5/2).

The thermal and electrochemical aspects of the model were validated in a previous work by comparison with local temperature and current densities measurements [2, 3]. In this study, we focus on the validation of the model dedicated to two-phase flow modeling and on the investigation of the liquid water distribution over the cell. To that end, the Neutron Imaging, which is an *in-situ* non-invasive technique [3], has been used to determine the liquid water thickness distribution over the cell area for several operating conditions. For neutron imaging experiments, a dedicated stack made of five cells has been built with Aluminum for the end-plates because of its low neutron absorption and of its good mechanical properties.

The distribution of liquid water thickness over the active surface area measured via neutron imaging is presented Figure 1.c for rather humid conditions, demonstrating the ability of the model to accurately and quantitatively predict the localization of the liquid water over the cell area. From a general point of view, both reactive gases and cooling flow-field designs impact the water and heat transport, and therefore the condensation zones. There is more liquid water accumulation in the cold zones of the cathode and near the gas channels outlets in nominal operation conditions. Moreover, the model is also able to predict the liquid water distribution at the rib-channel scale (Figure 2) in the different zones and the different layers of the cell. Liquid water accumulation takes place preferentially at the channels edges, but preferential water accumulation under the rib is also observed at the anode outlet for this design.

Several operating conditions have been simulated to analyze the impact of temperature, humidity and current density on the liquid water heterogeneities. The model is less accurate for higher current densities and temperature conditions for which there is paradoxically less liquid water.

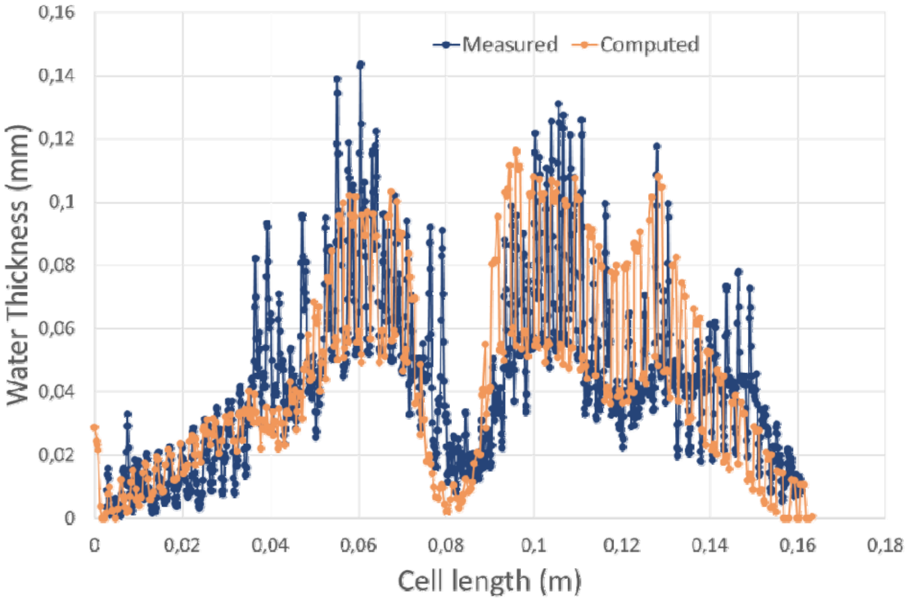


Figure 2: Measured and simulated liquid water thickness profiles corresponding to 50% height of the cell (operation conditions: Temperature=65°C, Relative humidity =50/50, current density=0.25A/cm², anode and cathode gas pressure P_a=P_c=1,5bars, anode and cathode stoichiometry=1,5/2)

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3D Modeling of Chemical Degradation Mechanisms in PEM Fuel Cells

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The PEM fuel cell model of a commercial CFD code [1] is extended by chemical degradation models for the catalyst layers and the membrane. The models are based on the ionomer degradation model by Wong and Kjeang [2] and the carbon corrosion model by Pandy et al. [3]. The ionomer degradation model describes the ionomer mass loss due to hydrogen peroxide formation and subsequent radical attack of the ionomer's side and main chains. The carbon corrosion model calculates the carbon mass loss caused by carbon oxidation and the active area reduction due to platinum oxidation. The degradation models are coupled with a 3D agglomerate description of the catalyst layers, thus taking into account the effect of chemical degradation on the catalyst layer structure: The ionomer and carbon mass losses have a direct impact on the reductions of agglomerate radius and ionomer film thickness affecting the local transport properties and current production.

The overall model is validated against measurements on the 50 cm^2 ZBT PEM fuel cell. For these measurements, the cell has been equipped with a segmented bipolar plate and a segmented measuring board on the anode side. The measuring board can be used to measure the current density distribution as well as the high frequency resistance of every segment.

Figure 1 left shows a comparison between the calculated and measured current density along the cathode flow path for various average current densities. Figure 1 right shows the distribution of the ionic current density in the middle of the membrane. The overall current density gradient is predicted very well. Having a closer look at the 3D current density distribution, one can observe a shift of the current density maximum from the region below the bipolar plate rib to the region below the channel along the cathode flow path. This can be explained as follows: The dry conditions at the cathode inlet lead to a dry membrane at this location causing humidity to be the dominant factor. Farther away from the cathode inlet, oxygen depletion becomes the dominant factor shifting the current density maximum below the channels. The checkerboard pattern at the channel bendings is caused by the electrical resistance of the anodic GDL. In a next step, further simulations will be conducted including the degradation models described above and additional comparisons to measurements will be carried out.

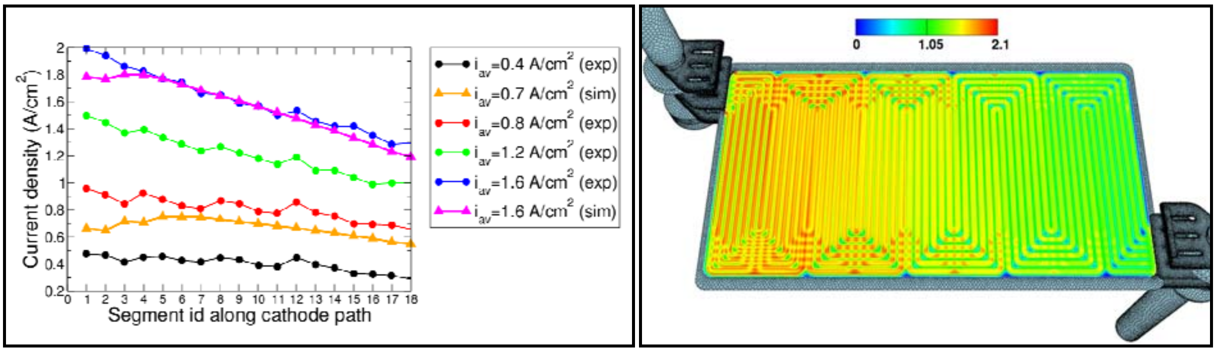

Figure 1: Left: current density along cathode path in experiment and simulation; right: calculated ionic current density (A/cm^2) in membrane

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Electrochemical Detection of Electric Shorts in PEM Fuel Cell Stacks

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Continued Research and Development (R&D) has significantly improved cost, performance, and durability of fuel cell systems. Advancing from lab scale development towards production scale manufacturing requires vital steps to be taken by the fuel cell industry, including (i) design modification of fuel cell systems to make them suitable for mass production schemes; (ii) development of manufacturing and Quality Control (QC) schemes for mass production.

In the course of the commercialization process, pre-production scale manufacturing and QC methods are needed to enable building and testing fuel cell prototypes. As cell pitches are made smaller in order to increase the stack power density defects in the bipolar plates could result in contact points between the anode and cathode bipolar plates. If such a cell is supplied with reactants, contact points will act as electric shorts. High currents through such contact points will result in local hot spots that will cause damage to cell materials. Therefore, QC methodologies to detect these electric shorts are essential for fuel cell manufacturing. One method to detect these shorts is to use a potentiostat across each cell and measure the current. However, such hardware is expensive to build when dealing with fuel cell stacks that have hundreds of cells.

In this work, we present an electrochemical technique that uses the Cell Voltage Monitoring (CVM) hardware that is readily available on standard fuel cell test stations to detect electric shorts in each individual cell of a fuel cell stack. We will first explain the testing methodology and then derive and solve a mathematical model that allows quantifying the contact resistance from CVM measurement. We then validate the model using a single cell that has no electric short, parallel with a known external resistance that simulates a contact. Finally, we validate the methodology on a fuel cell stack with an electric short.

Keywords: PEM fuel cell, quality control, diagnostics, electric short.

Understanding Limiting Processes in Anion-exchange Membrane Fuel Cells

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Abstract

A model describing an anion-exchange membrane fuel cell (AEMFC) has been developed to enable a deeper understanding of the processes limiting the cell performance. The model is physics based and describes a tertiary current distribution on both electrodes. It has been validated to experiments with varying electrode loading and reactant gas pressure. The initial results show that both the anode and the cathode contribute to the overpotential.

Introduction

Polymer electrolyte fuel cells (PEFCs) are a promising technology for renewable transportation systems. The technology is available, but development is needed to make it an economically feasible alternative. A promising alternative to the traditional proton exchange membrane fuel cells (PEMFCs) is the anion-exchange membrane fuel cell (AEMFC) in which hydroxide ions are the conducting species. The alkaline environment facilitates the oxygen reduction reaction, ORR, and enables the use of none-noble metal catalysts, potentially leading to less expensive fuel cells [1].

The alkaline environment leads to different reactions when compared to a traditional PEMFC, since water is produced at the anode instead of at the cathode. Water is also a reactant at the cathode where the hydroxide ions are produced. This results in a more complicated water management as it could potentially lead to dry out at the cathode and flooding at the anode [2]. Further understanding of the cell limitations is necessary to advance the field, therefore this model has been developed to clarify cell processes.

Experimental and Model

For all the experiments, Tokuyama membranes, A201, were used. The electrodes were made in-house using Tanaka 36 % Pt/C catalyst, Tokuyama AS-4 ionomer and solvent to formulate an ink that was drop-casted on the gas diffusion layer (GDL) Sigracet 25BC.

The base case experimental parameters were 0.4 $\mathrm{mg_{Pt}\ cm^{-2}}$, on both electrodes, with pure O_2 and pure H_2, humidified to 95 % relative humidity. The dry reactant gas pressures were varied in the range 10 – 100 % for O_2 and 5 – 100 % for H_2. Dilution was done with argon and the total dry gas flow was kept constant at 7.4 normal $\mathrm{dm^3/h}$. Catalyst loadings between 0.1 $\mathrm{mg_{Pt}\ cm^{-2}}$ and 0.8 $\mathrm{mg_{Pt}\ cm^{-2}}$ were also investigated, with a change in loading leading to a change in catalyst layer thickness.

To understand the water management problems, experiments measuring the water content in the inlet and outlet streams were carried out and used to describe the water transport through the fuel cell.

The model has been developed in COMSOL Multiphysics version 5.3 and the electrodes are modelled as a gas diffusion layer (GDL) and catalyst layer (CL). The gas transport through the layers is solved using the Maxwell-Stefan transport equations with binary diffusion coefficients.

The source term R_i is obtained through Faraday's law combined with the Butler-Volmer equation with a local limiting current density, which accounts for ionomers and liquid water affecting the local mass transport rate of reactants, i.e. oxygen respective hydrogen gas to the catalyst.

$$R_i = \frac{\frac{A\nu i_{loc}}{nF}}{1 + \left\| \frac{i_{loc}}{i_{lim}} \right\|}$$

$$i_{loc} = i_0 \left(a_{ox} \exp\left(\frac{\alpha_a F \eta}{RT} \right) - a_{red} \exp\left(-\frac{\alpha_c F \eta}{RT} \right) \right)$$

A is the specific area of the porous electrode and a the activity of the involved species, defined as the molar fraction of the component or in the case of water as the relative humidity.

Molecular hydrogen was assumed to diffuse through the membrane to a higher degree than molecular oxygen creating a parasitic cross-over current density. This was modelled as proportional to the hydrogen concentration at the anode – membrane interface and all the hydrogen was assumed to react readily at the cathode – membrane interface.

$$i_{cross} = \frac{D_{H_2}(p_{H_2}}{L_{mem}RT}2F$$

The water produced is assumed to be in vapour phase, and the possibility of liquid water formation is neglected in the model.

Results and Discussion

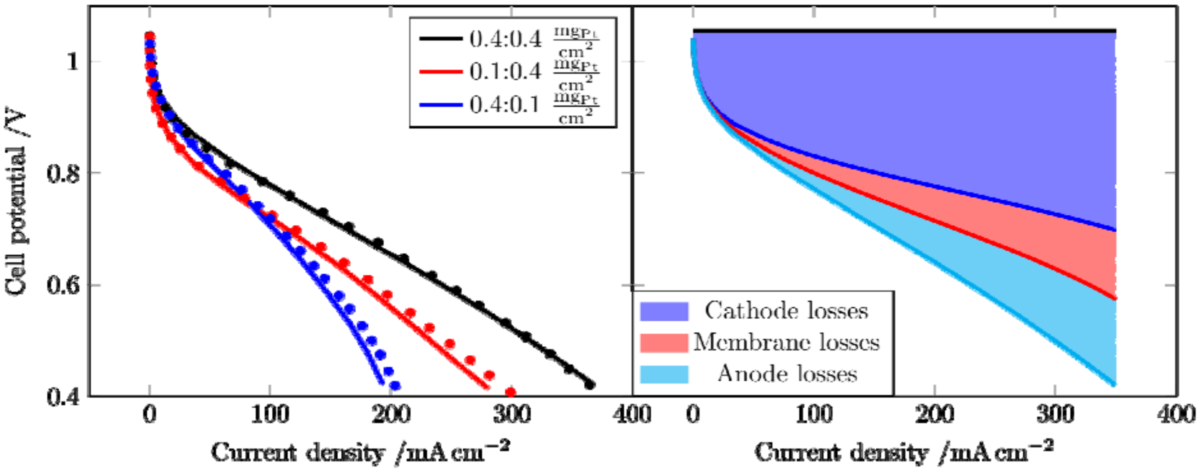

Figure 1: Fit of model to experimental data. Left shows the fit for cathode:anode loadings of 0.4:0.4, 0.1:0.4 and 0.4:0.1 mg of Pt per cm^2. The dots are experimental data while the full lines are simulated results. Right separates the losses for the 0.4:0.4 mg of Pt per cm^2 case, obtained with parameters from the fitted model. The shaded areas correspond to the losses at the different regions and summing them up gives the teal curve, the full polarization curve.

Figure 1 (left) shows a fit of the model to various catalyst loadings. Kinetic parameters for both electrodes, i.e. exchange current densities and transfer coefficients, as well as local limiting current densities and the hydrogen diffusion coefficient have been fitted to the experimental data.

Figure 1 (right) divides the polarization curve into the contributions from anode, cathode and membrane separately. The cathode contributes the most to the overall overpotential, but the contribution from the anode is not negligible, especially at higher current densities.

Looking further into concentration gradients reveal that local dry-out is not a problem, but that effects from the formation of liquid water could affect the cell at current densities above 0.25 A/cm^2. The local limiting current density can account for these effects reasonably well down to 0.4 V, as can be seen in Figure 1 (left).

Conclusions

The polarization of both the anode and the cathode must be considered when studying AEMFCs.

Dry-out is not observed in the model, but flooding could occur in catalyst layers at high current densities.

Acknowledgement

Thanks to the Swedish Energy Agency and StandUp for Energy for funding this research.

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Critical Analysis of Tortuosity Values obtained from Impedance Spectroscopy and X-Ray Tomographic Data

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Performance of porous lithium ion battery electrodes is determined by the transport time for ions through the electrode. While the intrinsic mobility of the ionic species plays a dominant role, also geometric constraints as the porosity and the tortuosity dictate the build-up of concentration gradients and thus the electrochemical behavior of a cell (compare Figure 1). Yet, tortuosity values of porous battery electrodes determined using electrochemical impedance spectroscopy in symmetric cells with a non-intercalating electrolyte[1] are typically higher than those values based on numerical analysis of 3D tomographic reconstructions.[2] We will validate the assumptions behind the electrochemical approach experimentally and theoretically by investigation of the influence of the electronic resistance of the porous electrode on the extracted ionic resistances using a general transmission line model. Second, using a macroscopic setup with known tortuosity, we prove that the ionic resistance quantified by the transmission line model indeed yields the true tortuosity of a porous medium. Based on our findings, we analyze the tortuosities of porous electrodes using both X-ray tomography and electrochemical impedance spectroscopy on electrodes from the same coating and conclude that the distribution of the polymeric binder phase, which is not imaged in most tomographic experiments, is a key reason for the underestimated tortuosity values calculated from 3D reconstructions of electrode microstructures.

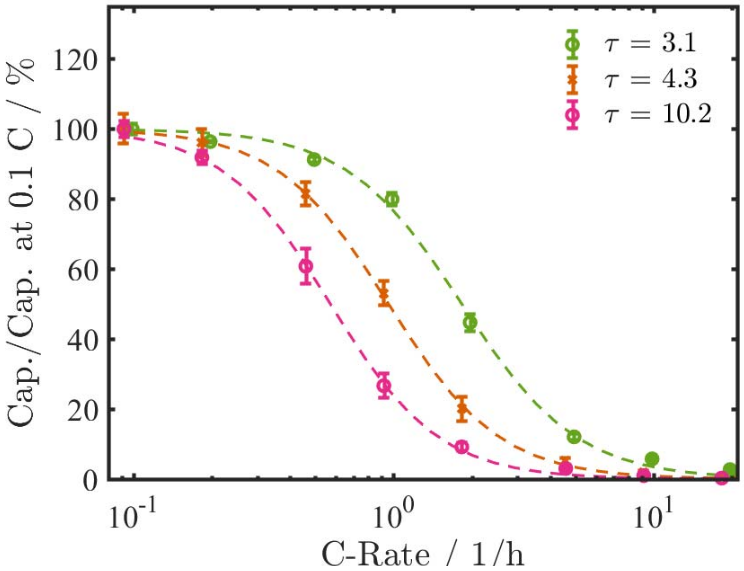

Figure 1: Normalized percental mean intercalation capacities of three nominally identical porous graphite anodes (same porosity, thickness, loading etc.) each, with different tortuosities for constant current charging rates from 0.09 1/h to 20 1/h until 5 mV cut-off vs. metallic lithium reference electrode is reached. Errorbars indicate the standard error of the mean values from 3 cells.

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3D Imaging and Multi-Scale Modeling for Positive Electrode Materials of Lithium-Ion Batteries

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Electrode and materials microstructures in lithium ion batteries are critical due to their influence over the capacity and power capability [1, 2]. Therefore, investigations on these microstructures using diverse methods from porosimetry studies to direct microscopy observations with correlation to electrochemical performances is a field of high interest. Indeed, determining the influent microstructure parameters will allow the enhancement of battery storage performances and power capability.

Within this framework, models of microstructures and direct transport computer simulations have been presented recently where structure changes of the different components within the electrode were found to influence the batteries' parameters [3,4]. Some studies have even suggested ways to optimize the effective electrical conductivity of the electrode and this by virtually modifying the shape of the carbon binding domain [5].

Aiming to better understand the influence of active material microstructure on battery parameters, we have led a study that combines, microscopy imaging, direct electrochemical simulations and electrochemical characterizations. More precisely, three NMC active materials (Nickel, Manganese, Cobalt: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) composed of the same chemical components, but differing by their particle microstructure have been selected to prepare electrodes with similar composition and loadings. Microscopy imaging of these electrodes allow us to have access to their microstructures. We have performed segmentation operations to differentiate between the three different phases (the active material, the carbon-binder and the pores) present within the electrode. After what, the microstructures are used to perform effective properties' calculations as well as to develop direct electrochemical simulations to probe the influence of the active material particles' structures on the battery performances. The electrodes are also tested in coin cells to determine experimentally their electrochemical properties.

The electrochemical model we present in this talk is similar to the thermodynamic consistent transport model of Li-ion developed by Latz et al. [6]. Precisely, a finite element study on lithium concentrations and ionic and electric potentials within the battery microstructure will be proposed and discussed. Thus, the evolution of the electric and ionic potentials as well as charge and mass transport are probed in order to correlate the impact of the materials microstructures to the experimentally observed electrochemical performances.

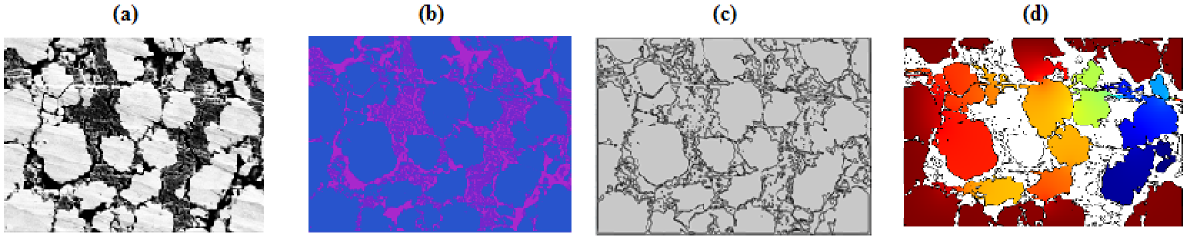

Figure 1: (a) A Scanning Electron Microscopy image of a $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ based electrode. (b): Segmented version of the image in (a) into 3 domains represented by 3 different colours. (c): Geometry of the imaged electrode generated from (b). (d): Example of Lithium atoms diffusion simulated within the active material particles using COMSOL Mutliphysics software and the geometry of (c).

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Influence of the electrode microstructure on the effective electronic and ionic conductivity of Lithium Ion Batteries using discrete element methods

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The performance of lithium-ion batteries (LIB) is strongly influenced by the composition and fabrication of the electrode structures. On the one hand, the used material and its microstructure plays an important role. On the other hand, the mechanical densification processes, such as calendering or sintering, impact on the quality of the battery. Here, the effective conductivities of both the solid phase and the electrolyte phase are being considered as the performance parameters and is being modelled using discrete element methods.

A variety of tools have been proposed in the past to model electrode structures, see [1]. First, an initial structure can be generated according a given distribution of AM and CB using the Random-Close-Packing algorithm (RCP) [2], where a randomly distributed, densely packed and overlap-free assembly of spheres can be created. Secondly, the given assembly can be densified by either simulating compression using the Discrete-Element-Method (DEM) [3] or mimicking sintering processes with a Numerical-Sintering algorithm (NS). Lastly, percolated clusters of the conducting phase can be identified using [4] and translated into an equivalent electrical circuit, where the Resistor-Network method (RN) can be used to calculate an effective conductivity - or performance for that matter - of the given electrode structure.

There are several ways one can enhance the conductivity of a cathode with. For one, due to the low electrical conductivity of the active material (AM) inside a LIB electrode, carbon black (CB) powder is being added to overcome this drawback. Further, the electrode is being densified mechanically to establish more conducting pathways and therefore enhancing conductivity. However, this method leads to a decrease in the electrolyte volume or the pore space, respectively, which results in a lower ionic conductivity.

In the presented work, discrete element methods are being presented to model both the electronic and ionic conductivity. Due to the efficiency of those methods concerning the calculation time and computational resources, parametric studies are made possible to find an optimized microstructure with any given material, such that electronic and ionic conductivity would reach the best value.

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Heterogeneity of Lithium Ion Battery Electrodes and its Influence on Electrochemical Performance

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Graphite is a key material in the lithium ion battery industry. Due to its low cost, mechanical robustness, and suitable electrochemical properties, graphite is used in 95% of rechargeable lithium ion batteries. Also next generation negative electrode (anode) materials such as silicon are being commercialized in the form of graphite-based composites. At the same time, graphite anodes often play a role in battery degradation and failure, e.g. with lithium plating on the graphite at the separator/electrode interface. Available materials range from low cost, flake-like graphite to more expensive, milled spherical graphites, providing cell manufacturers the opportunity to consider performance and cost trade-offs.

To reduce complexity, the microstructure of a lithium ion battery (LIB) has been traditionally discussed and incorporated into simulations using a homogenized picture, where one value of porosity or tortuosity describes effective parameters for the entire electrode.[1,2] However, as a glance at a scanning electron microscope image of commercial LIB electrodes reveals, particle size and shape distributions result in non-uniformities in microstructure that appear at different length scales. Non-uniformity in the microstructure can cause heterogeneity of the local current density during operation, which has implications for battery performance, safety, and durability.[3,4] Heterogeneous local current densities lead to a spatially varying state of charge (SOC), not only reducing the accessible capacity[5] at high cycling rates, but also risking overcharge or dis-charge of parts of the electrode. For anodes made of graphite,[6] overcharging is especially critical because it leads to metallic lithium plating with accompanying degradation and safety issues.[7–10]

The availability of tomographic techniques with (sub-) micrometer resolution enables the study of heterogeneity at the micrometer length scale in three dimensions.[11] In combination with three dimensional electrochemical simulations, correlations between electrode microstructure and battery performance can be better understood.[12]

At the example of four different graphitc electrodes found in commercially available LIBs, we demonstrate the occurrence of microstructural inhomogeneity and its influence on the electrochemical performance. X-ray tomographic microscopy is used to obtain three-dimensional representations of the microstructure. Inhomogeneity created by variations in particle shape, size, and electrode manufacturing is quantified and electrochemical simulations, validated with the results of galvanostatic cycling experiments, are used to understand the influence of this inhomogeneity on battery performance.

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Electro-chemo-mechanical simulation of 3D-microstructures for lithium-ion batteries

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Deformation processes in electrode structures affect the long-time performance and aging of lithium-ion batteries. The imbalanced intercalation of the lithium ions into the lattice causes large concentration gradients. The stresses resulting from these gradients can damage and destroy the battery cell. The computational simulation of the stresses during charging and discharging support the virtual development and optimization of batteries.

A micromodel coupling lithium-ion diffusion and electric potentials [1] to a linear elasto-plastic model is applied. The resulting problem is discretized on a regular voxel grid with a finite-volume method and solved by an adaptive iterative scheme. The algorithm does not require the assembly of a Jacobian and applies the immersed interface method for the electro-chemical problem [2]. An established elastic solver optimized for non-linear heterogeneous structures [3] is generalized to describe mechanical strains resulting from lithium-ion intercalation. Numerical examples on several structures are given, including academic structures, and microstructures given by computer tomography compared with microstructures drawn from stochastic models [4]. Figure 1 shows a comparison of the lithium-ion concentration and stress invariants in two 3D-microstructures of anode material charged with C-rate 1 at 40% state of charge.

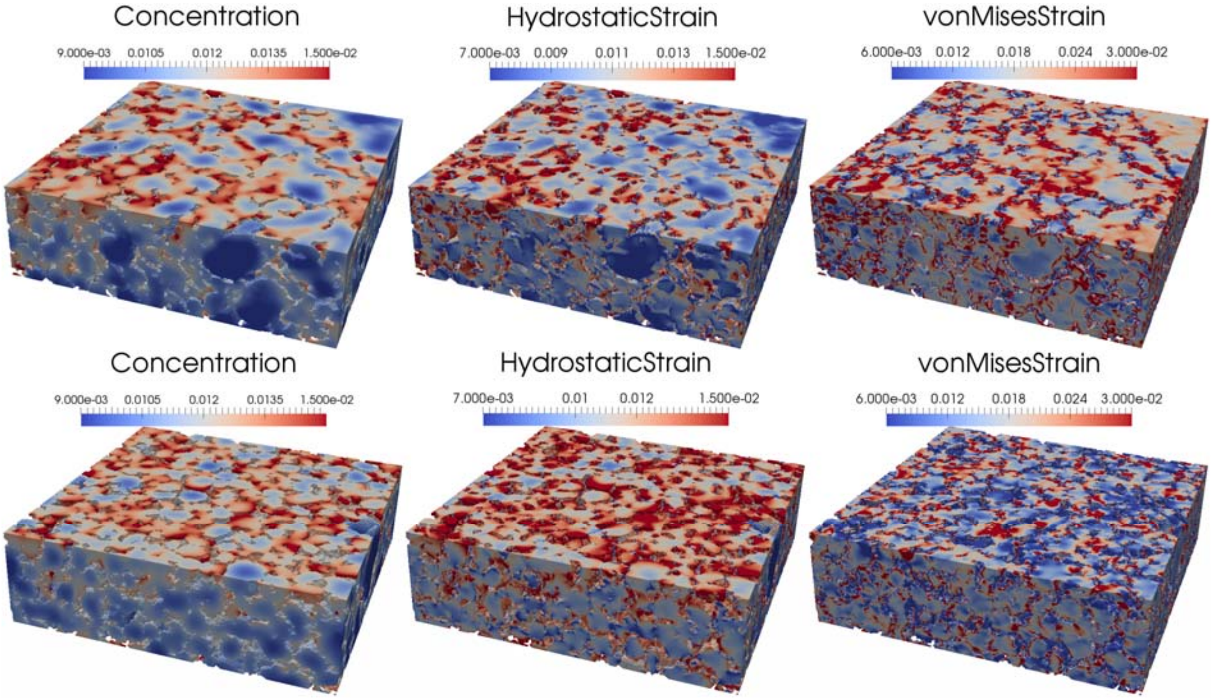

Figure 1: Comparison of lithium-ion concentration, hydrostatic strain and von-Mises strain (from left to right) for both tomographic (top) and simulated 3D microstructures (bottom).

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Experimental Validation of Simulated Ionic Resistances in Laser-Structured Electrodes

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Geometrical constraints are a large drawback for Li-Ion batteries in moving toward high-loading electrodes as longer diffusion pathways severely affect the rate capability of the cell. Laser-induced pathways for faster Ion-transport through the electrode have been shown to mitigate this effect and improve the rate-capabilities of Li-ion batteries.[1,2] This process irreversibly removes electrochemically active material, which, especially for more expensive cathode active materials like NMCs, can increase the production cost. To determine optimal geometric properties which allow for maximum performance with minimal material loss we will use COMSOL to model blocking-condition Electrochemical Impedance Spectroscopy (bcEIS) in laser-structured electrodes and study the influence on the ionic resistance for various geometries. With the ionic resistance of unstructured electrodes measured using bcEIS and simple geometric measurements of the electrode, we are able to determine all model parameters experimentally. In a validation step, we will measure the geometric properties of the laser-structured electrodes using Scanning Electron Microscopy, determine their tortuosities and compare them to modelled values. We will show the improvements due to structuring for different geometries as well as varying electrode thicknesses and porosities on the ionic resistance and additionally show the influence of these values in electrochemical rate tests, as seen in Figure 1.

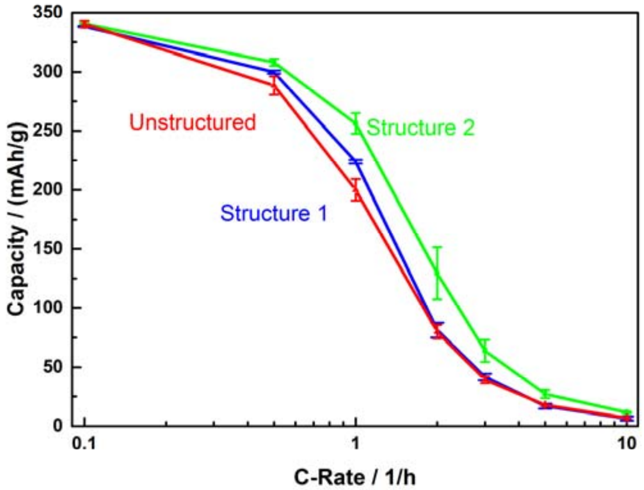

Figure 1: Li-intercalation rate test on graphite anodes; Samples with two different structures are compared to an unstructured electrode. The material removed during the laser structuring process compared to the unstructured electrode was ~8.8 and ~6.2% for Structure 1 and 2 respectively, showing the improvement due to the optimized geometry in Structure 2; Swagelock T-Cell setup, 0.5C CCCV delithiation, CC lithiation between 1.5 and 0.01V vs. Li-metal reference electrode.

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Microstructure-Resolved Impedance Simulations for the Characterization of Li-Ion Battery Electrodes

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Li-Ion batteries are commonly used in portable electronic devices and state-of-the-art electric vehicles due to their outstanding energy and power density. At high current densities, e.g. during fast charging, the transport of Li-ions in the electrolyte is decisive for the performance of the battery cell and optimized electrode designs are required to reduce mass transport limitations. In this respect the impedance of the porous electrode is a characteristic performance indicator and is commonly evaluated integrally with the help of equivalent circuit models. However, often the performance of the electrode is affected by local structural inhomogeneities due to compression in the calendering process or an unfavorable binder and/or carbon black distribution. For instance, it was found that harsh drying conditions cause binder migration to the electrode surface and consequently reduce the rate capability [1]. In this contribution we present simulated impedance spectra of Li-ion battery positive electrodes based on 3D microstructure-resolved simulations [2] which allows us to study in detail the effect of local structural inhomogeneities on the electrode impedance and, thus, performance.

NMC electrodes with different thickness and density were prepared and characterized electrochemically by galvanostatic cycling and electrochemical impedance spectroscopy. Impedance spectra were recorded on symmetrical cells [3] which are especially advantageous for the characterization of electrode transport properties. Reconstructions of the electrodes were created with the help of synchrotron tomography and a 3D stochastic structure generator. The resulting microstructures are then input to microstructure-resolved electrochemical simulations. Impedance spectra of the symmetrical cells and half-cells with Li counter electrode were simulated with a potential step and current relaxation technique [4]. With the help of our simulations we are able to extract the contribution of the carbon black and binder network to the overall pore transport resistance by comparing our simulations to the experimental data. Additionally, we use different models for the spatial distribution of binder and carbon black to mimic different drying conditions and investigate the effect on the electrode impedance and cell performance.

Acknowledgement
This work has been funded by the 'Bundesministerium für Bildung und Forschung' within the project HighEnergy under the reference numbers 03XP0073C, 03XP0073D, and 03XP0073E.

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Influence of non-spherical active material particles on the macroscopic cell performance of three-dimensional battery simulations on the microscale

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Lithium-ion batteries are a wide spread technology used as energy storage systems for portable, mobile and stationary applications. The key challenges for the further development of lithium-ion batteries are the increase of energy density and high-rate capability for high-performance applications. Although the outer dimensions of such battery systems range from centimetres to meters, the electrodes themselves are made up of a microscopic heterogeneous particulate system. Hence, the lithium transport processes, as well as the electrochemical intercalation reactions, are taking place within the particulate microstructure of the electrodes. Therefore, the electrode's microstructure, i.e. the shape and the arrangement of the active material particles, affects the macroscopic cell performance directly. In order to be able to optimize the battery production of lithium-ion batteries it is inevitable to gain a deep understanding of the mentioned transport processes. As these are difficult to measure experimentally, a spatially resolved three-dimensional model of a lithium-ion battery half-cell, focusing on the positive electrode, was developed.

The model consists of two non-overlapping subdomains. On the one hand, there is a solid electrode, which is made up of electrically connected active material particles of different particle sizes and shapes. On the other hand, there is a liquid electrolyte subdomain filling the pore volume in between the electrode particles. It is assumed that the cathode consists of $LiMn_2O_4$ as active material and the separator is modelled by effective transport properties. In order to make the numerical results, which are obtained from the microscale simulations, representative for macroscopic cells, the computational domain is designed such that it can be periodically extended in x- and y-direction.

Often simulations based on idealized electrode microstructures, which are made up of e.g. smooth spherical [1], [2] or cubic [3] particles, are conducted. In this contribution our focus will be on the extension of the computer-generated periodic electrode microstructures to non-spherical shapes of the active material and its influence on the simulated macroscopic cell performance.

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Modelling Lithium/Electrolyte Interfaces for Li-Metal Batteries

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Energy storage systems are necessary to reduce our dependence on fossil fuels. Specifically, lithium batteries currently have an important impact on the development of electric mobility in the form of electric vehicles, hybrid electric vehicles, and plug-in hybrid electric vehicles [1]. The traditional anode material in these devices is graphite. Lithium metal, however, has the lowest reduction potential in the electrochemical reactivity series and a high theoretical specific capacity. Therefore, replacing the common graphite anode with a metallic Li foil in rechargeable lithium batteries can significantly improve their energy density. This means that current problems regarding Li metal/electrolyte stability, such as safety risk and low coulombic efficiency [2], need to be solved. Research efforts are necessary to find more stable electrolytes in contact with this reactive electrode material, and which also can mitigate the Li dendrite formation during battery cycling.

In this research project, we apply computational materials modelling, as a complementary technique to experimental studies, to explore the interface between the different electrolytes and electrolyte additives and the Li metal surface at the atomistic levels [3-5]. Density functional theory (DFT) and molecular dynamics (MD) simulations are used to study several potential electrolytes, including organic liquid and solid polymer electrolytes for the Li metal batteries, in order to investigate their electronic structures, stability, degradation and dynamical/transport properties when in contact with the Li metal. X-ray photoelectron spectroscopy (XPS) data is simulated, and directly compared with experimental counterparts.

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Electrochemical Modeling and its influence on Na-MCl$_2$ cell design

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Na-MCl2 cells are increased temperature secondary cells that are based on thick positive electrodes in the order of magnitude of 1 cm. The high electrode thickness leads to strong, cycling history dependent spatial inhomogeneities of charge transfer current during cycling as observed in post-mortem studies [1] and in situ X-ray diffraction [2]. The electrodes consist of solid salt and metals, impregnated by a liquid electrolyte. Modelling and simulation especially of the positive electrode helps in understanding the characteristics of the technology. Special interest is on variables, which are not easily observable in operating cells. The distribution of chemicals and current during operation is investigated, especially the influence of the cell geometry on these variables.

Model formulation

The model is formulated as a multiphysics system, dealing with the electronic current, the ionic current and the species concentration of the major species involved in the reactions. The reactions are assumed to take place in the dissolved phase and subsequent chemical dissolution or precipitation takes place. This avoids case studies and allows an easy implementation of concentration effects especially on the reversible potential, which are experimentally observable. A thermal model can be coupled to the electrochemical model to simulate non-isothermal effects if desired.

Due to the low solubility of $NiCl_2$ in the $NaAlCl_4$ liquid electrolyte, passivation of the nickel surface plays an important role. The Ni^{2+} ions created in the charge transfer reaction are required to pass through the $NiCl_2$ layer to leave the Ni surface. This can lead to a significant resistance contribution for charged cells. Such a resistance increase is measured in Na-$NiCl_2$ cells. An analytic function is derived to account for the effect of passivation.

Influence of geometry

Geometries with reduced symmetry like the common monolithic cell introduce spatial anisotropy that is very interesting to be investigated. Current concentration in the solid electrolyte that occurs as a consequence of the geometry can have a detrimental effect on cell life. Simulation can help to quantify the effect of these inhomogeneities and assist the cell design process.

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Multi-scale and multi-physics simulation of all solid-state batteries

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Lithium-ion batteries represent one of the core technologies in every type of electrified car. In the near future, energy density of battery cells can be further improved by different measures, e.g. by using new high-capacity active materials. Recent evaluations of various materials with the perspective of automotive industry can be found in [1] and [2].

A disruptive technology revolution would be the so called all solid-state battery, were the liquid electrolyte is replaced by a solid electrolyte. In [3], ion-transport mechanisms and fundamental properties of different solid-state electrolytes are reviewed. In addition, pure lithium metal could be used in solid-state batteries as the anode material. A dramatic increase in energy density would be the consequence, much higher than what could be achieved based on the evolution of conventional technology. However, many physical effects and actual problems of all solid-state batteries are still far from being completely understood. One example is the complex interaction of electrochemistry and mechanics. Therefore, further intensive research that combines theoretical, numerical and experimental methods, is required in order to develop all solid-state rechargeable batteries that meet the future requirements of automotive industry.

In this presentation we will provide a brief overview of challenges and open issues concerning all solid-state batteries and how simulation approaches at different scales can contribute to resolving them. Therefore, we will present recent simulation results of different research activities, thereby addressing the whole range of length scales in a multi-physics context from atomistic level, where basic material specific questions can be answered, up to cell level. One main focus of this approach is to be able to evaluate the performance of new materials in an early development status.

As one specific example for simulations on electrode and cell level, recent results on the modeling of mechanical effects in all solid-state cells will be summarized. Due to the use of a solid electrolyte instead of a liquid one, mechanical aspects are much more critical for a successful realization of these kind of innovative cell concepts. This work establishes a three-dimensional model, which accounts for the volume change of cathode particles, as well as the volume change of the lithium metal anode. Here, a multi-physics approach is used that includes both electrochemistry and structural mechanics. This represents an important step towards a consistent, fully-coupled mechanical-electrochemical-thermal cell model applicable for all solid-state batteries.

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Modelling Space Charging in Multi-carrier Solid Electrolytes

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Design of all solid-state batteries requires theoretical knowledge about how solid electrolytes behave under applied voltages. Both theoretical [1] and experimental [2] studies have investigated the structure of space-charge layers in solid electrolytes near lithium metal and shown that space charging impacts their performance. A clear picture of space-charge layers can, in particular, advance the understanding of failure modes that originate at the Li/solid electrolyte interface, such as dendrite nucleation [3-5], supporting the design of all solid-state batteries that achieve higher power density. Braun *et al.* [6] modelled the space-charge layers of solid electrolytes between biased blocking electrodes and included the effects of deformation stress on space-charge-layer structure. The dynamic response of space-charge layers remains unclear, a gap which has motivated us to produce a model that accounts for space charging and faradaic currents in parallel.

This presentation will introduce a dynamic electrochemical-mechanical model of multi-carrier solid electrolytes (i.e. doped solid superionic lithium conductors) based on a generalized version of Newman's concentrated-solution theory [7]. The local electroneutrality constraint is relaxed by including Poisson's equation, which also allows Lorentz forces arising from space charge to be considered in a momentum balance. Onsager–Stefan–Maxwell transport equations describe multicomponent diffusion, relating thermodynamic driving forces (i.e., gradients of voltage, carrier concentrations, and stress) to carrier flows in a thermodynamically consistent way. A momentum balance accounts for the coupling of different transport processes that include these driving forces. Coupling of diffusion and momentum is founded to impact the structure of space-charge layers and the battery performance substantially. We will illustrate the general applicability of this framework to the study of fully coupled electrical, mechanical, and electrochemical phenomena in multi-carrier solid electrolytes in both static and dynamic scenarios.

The presentation will close with applications of this new framework to doped $Li_7La_3Zn_2O_{12}$ (LLZO) garnet. The critical current and impedance will be discussed, and the theory will be compared to several experimental results.

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Parametrisation of the Single Particle Model for Lithium-ion Cells

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Besides their widespread use in consumer electronics, lithium-ion batteries are becoming a technology of choice in automotive as well as grid and off-grid energy storage applications. Such large-scale battery systems require advanced and more accurate diagnostics and prognostics tools to maximize the battery performance over its lifetime. Increasingly, researchers are investigating the use of electrochemical lithium-ion battery models to enhance the state estimation and prediction capabilities of battery management systems (BMSs), for example by allowing fast charging while minimizing degradation [1-3].

In recent work [4-5], we have shown that electrochemical models, including the Newman pseudo two-dimensional (P2D) model [6], can indeed be used for lithium-ion battery state estimation. However, an important challenge remains as whether the parameters of such electrochemical models, including geometrical and physical properties, can be estimated for commercial cells from available measurements of voltage, current and temperature. Previous studies attempting the parameter estimation of electrochemical lithium-ion battery models, such as [7-8], have revealed the challenging nature of this identification problem and shown that not all model parameters can be estimated uniquely and with satisfactory confidence.

We present here and in a recent pre-print [9] a structural and practical identifiability analysis of an electrochemical model for lithium-ion batteries, the single particle model (SPM) [10]. The SPM is a simplification of the P2D model, valid at low currents, which neglects electrolyte dynamics and assumes uniform reaction rate across each electrode. The structural identifiability approach allows determination of which parameters can be identified in principle from measured cell data. The approach first involves grouping the parameters and partially non-dimensionalizing the SPM to reveal that there are only a small number of unique grouped parameters, excluding open-circuit potential, required to fully parameterize the SPM. Then, by asking whether the transfer function of the linearized model is unique, we show that these parameters can be identified from experimental data provided that the electrode open-circuit potential functions have a known and non-zero gradient, the electrode parameters are ordered and the parameters describing kinetics in both electrodes are combined into a single charge-transfer resistance.

We then investigate the practical identifiability of the SPM by performing parameter estimation against experimental frequency-domain electrochemical impedance spectroscopy (EIS) data at various depths-of-discharge (DoD). This practical analysis confirms the crucial role played by the electrode OCP dependency on DoD for the parameter estimation of dynamic parameters. If the gradient of an electrode open-circuit potential is zero, the parameters associated with this electrode cannot be identified; this is shown on Figure 1a where the minimum of the cost function is extended along the anode parameter (*i.e.* the anode parameter is unidentifiable) since the anode OCP is almost flat at this DoD. At 10% DoD however, Figure 1b, both the anode and cathode OCPs have a significant gradient resulting in a smaller minimum region, *i.e.* more accurate parameter estimate. We show that EIS data at several DoDs may be combined to obtain confident parameter estimates for both electrodes, Figure 1c. Finally, as a separate validation, the parametrised model is also shown to provide good predictive capabilities in the time domain, exhibiting a maximum voltage error of 20 mV between model and experiment over a 10 minute dynamic discharge.

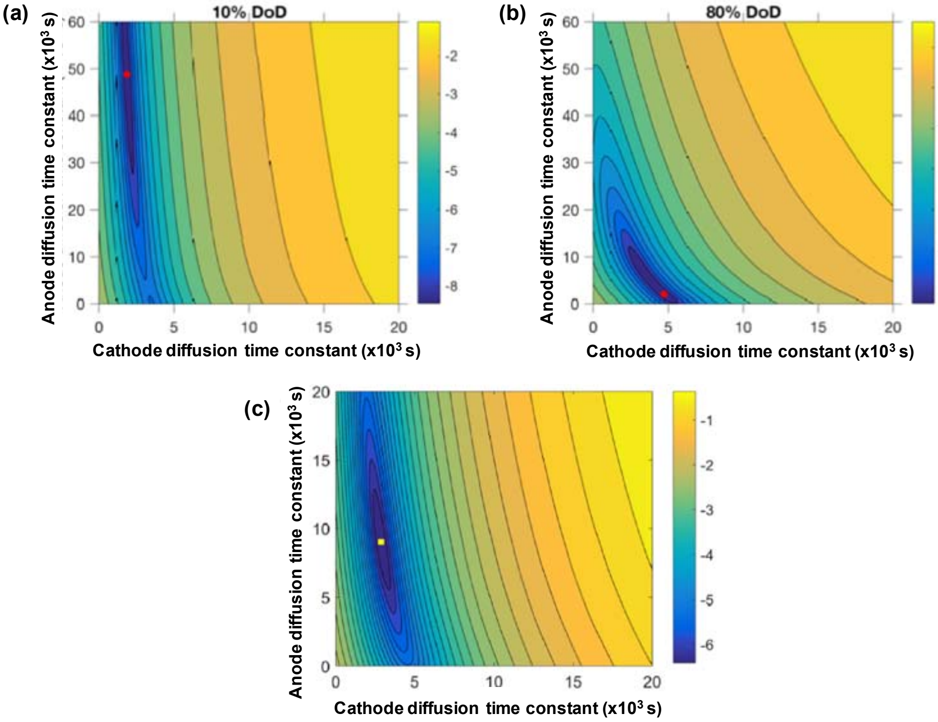

Figure 1: Contour plots of the cost function for the parameter estimation of the single-particle model as a function of estimated anode and cathode diffusion parameters (diffusion time constants) based on (a) EIS data at 10 % DoD, (b) EIS data at 80 % DoD, and (c) combined EIS data at 10 % and 80 % DoD.

Acknowledgements
Financial support is gratefully acknowledged from EPSRC UK (EP/K002252/1) and from Samsung Electronics Co. Ltd. through a collaborative research project between the Samsung Advanced Institute of Technology and the University of Oxford.

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An efficient two-dimensional cell model for lithium-ion cells based on pseudo-spectral collocation method

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In the electric vehicle (EV) sector, large-format cells have significant advantages compared to small-format cells due to their reduced share of inactive components and design simplifications of the pack and battery management system (BMS) [1]. On the contrary, a large-format cell may suffer from negative effects arising from local changes of physical and chemical material properties which are induced by non-uniformities in the potential and temperature distribution across the electrodes. Modeling approaches that take multi-scale and multi-domain (MSMD) electrochemical, electrical and/or thermal effects into account have proven to be a suitable tool to investigate non-uniform cell behaviour. However, due to the increased complexity, much effort has been made to reduce the computational cost while maintaining the ability to describe mass and charge transfer reactions of MSMD models. MSMD models are usually structured in a modular model framework consisting of multiple submodels solved in separate computational domains at particle, electrode, and cell level (Figure 1).

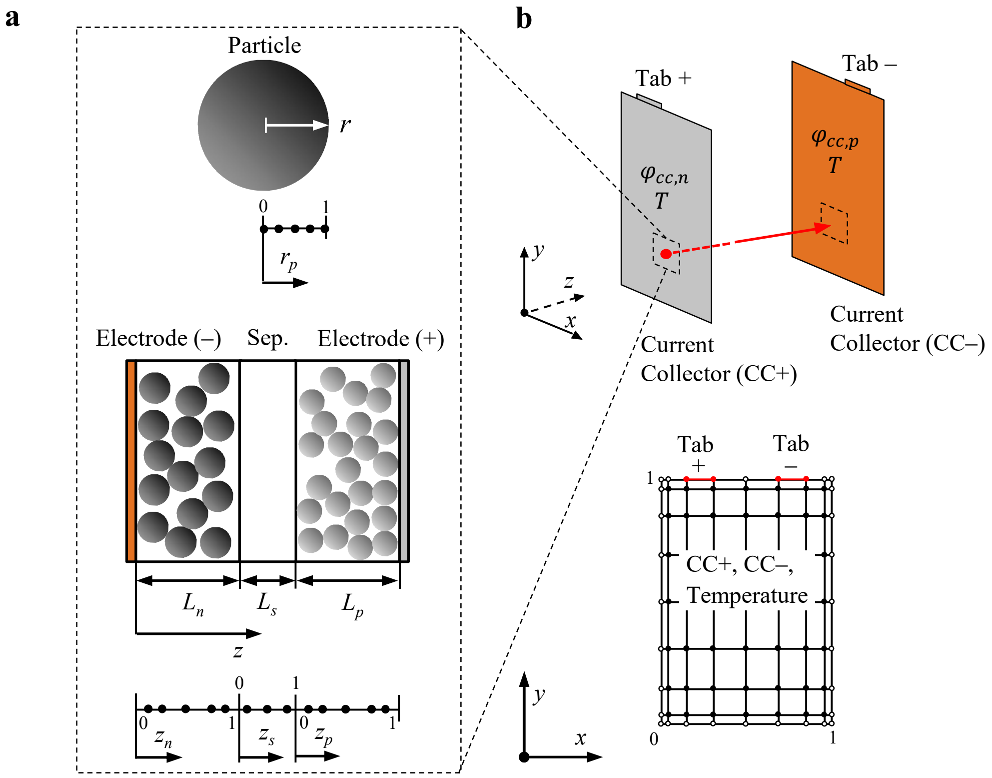

Figure 1. Schematic of a) the porous electrode with spherical particles and b) the current collector geometry. A corresponding computational grid (collocation points) is presented below each submodel for clarification.

To the best knowledge of the authors, MSMD models based on pseudo-spectral methods that include a two-dimensional (2D) representation of the current collector geometry cannot be found in literature. Orthogonal collocation method is adapted for a 2D electrochemical model including the height of the current collector as an additional dimension (p3D) [2]. In a recent work, a 2D thermal model for a cylindrical cell design based on Galerkin collocation method has been published [3]. Both works show superior computational efficiency compared to standard numerical methods such as finite difference method.

At electrode level, most MSMD models are based on adoptions of the p2D (pseudo two-dimensional) porous electrode model developed by the Newman group [4,5] or simplifications such as single particle models (SPM). The spatial discretization of typical p2D models lead to a high number of coupled differential algebraic equations (DAEs) with around 600 equations depending on the complexity and required accuracy of the problem. Considering even a simplified 2D single layer cell representation with the additional dimensions “x” and “y” (Fig. 1), a coupled MSMD model, consisting of several p2D models and spatially resolved potential and temperature distribution, increases the computational burden significantly. Therefore, reformulation techniques are a promising method to improve simulation efficiency due to the low number of DAEs and fast convergence behavior [6].

In this work, we present a computational efficient MSMD modeling framework for large-format lithium-ion cells using model reformulation based on pseudo-spectral collocation and Lobatto3A method. As shown in Fig.1, model reformulation is applied for a coupled p2D electrochemical and 2D electro-thermal model for a chosen planar cell geometry. The proposed model shows an up to 10 - 30 times faster computational time while maintaining its accuracy compared to the finite element solution. Furthermore, the ability of the model to predict cell behavior at high current rates arising from diffusion limitation in the electrodes is demonstrated. To investigate the model accuracy, simulation quantities such as potential distribution, heat generation and temperature distribution for various constant current discharge profiles are examined. The simulation model is validated for a nickel-manganese-cobalt (NMC111) chemistry at discharge current rates of up to 10C.

All model equations are solved by means of the commercial finite element software COMSOL Multiphysics 5.2a. The computational effort to solve the different models is determined by using a MATLAB - COMSOL interface. Due to the greatly reduced computational time, our work aims to foster the development of spatially resolved MSMD models that can be applied in fields such as online estimation or cell-design optimization where high accuracy and fast computation are required.

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Is parameter estimation with a pseudo-2-dimensional battery model more than curve fitting?

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Since its development in the early 1990s [1], the Doyle-Newman model has been applied to a significant number of different Lithium-ion batteries. Whenever a model was validated with electrochemical measurements, certain model parameters were adjusted to fit the simulation to the experiment. In addition, simulation-based parameter estimation was used to gain knowledge about physical quantities and the internal cell processes, i.e. characteristics which are not or difficult to measure directly [2].

More recently, the approach of simulation-based parameter estimation provoked questions about uniqueness, identifiability and physical meaning of the derived model parameters [3,4], or to put the question in a nutshell: Is parameter estimation with a P2D model more than curve fitting?
In this work, it is shown that a classical C-rate test does not provide sufficient information to determine the characteristic fitting parameters of a Doyle-Newman model, namely solid phase diffusion coefficients, exchange current densities and conductivity of the electrode's microstructure containing active material, conducting additives and binder.

Furthermore, different strategies are discussed to quantify and to overcome limitations of parameter estimation. First, a nested point estimate method [5] is introduced to quantify global second order sensitivities of model parameters. Second, the benefits of additional experiments like half-cell measurements, electrochemical impedance spectroscopy, and experimental parameter variation are demonstrated. Third, a microstructure model extension is introduced which increases the accordance of the sensitivity of the model and the experiment. Also, it can be used to reduce the size of the parameter space by providing further physical insight. And fourth, aspects of uniqueness and credibility of the derived model parameters are discussed critically.

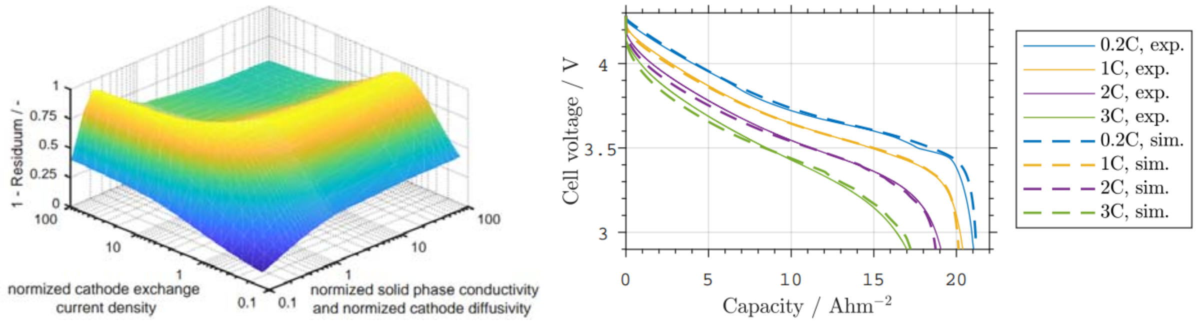

Figure 1: Fit accuracy for a 2D parameter variation; parameter sets in the yellow area provide an excellent fit (left). Model validation of the P2D model vs. experimental C-rate test (right).

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Battery degradation modelling for optimal control of grid-connected lithium-ion batteries

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The lifetime of a lithium-ion battery is a key element in the business case for grid-connected batteries. Battery degradation is the result of many different processes, some being more dominant than others, depending on the operating conditions.

Various battery degradation models exist, of differing complexity, accuracy and data-requirements. The simplest model is a linear degradation model assuming a maximum energy throughput over the battery's lifetime. A second class are the empirical degradation models, interpolating large data sets. Different empirical models include different operating conditions, depending on the dominant degradation mechanisms appearing in the data set. Thirdly, electrochemical degradation models try to capture the physics of the degradation processes. Various electrochemical degradation models exist, e.g. for the growth of the SEI layer [1], for particle fracking [2], lithium-plating [3], etc. Even for the same physical degradation mechanism, many different models are used. For example, for the growth of the SEI layer, some only consider the reaction itself ('a rate-limited process') [1], while others only model the diffusion through the SEI layer ('diffusion limited process') [4], and yet others include both [5].

Figure 1 shows the results of various electrochemical degradation models for various cycling regimes. The figure shows the contribution to lost capacity due to the growth of the SEI layer in dark blue, due to surface cracking in light blue, due to loss of active material in green, and due to corrosion of the current collectors in yellow. As can be seen, the different mechanisms have a very different impact on capacity fade depending on operating conditions.

If a degradation experiment is set up with only a limited number of cycling regimes, it risks missing the effect of certain degradation mechanisms on the overall battery life. For example if high temperature tests are undertaken, the degradation can be explained with SEI growth only. An 'accurate' degradation model might then only include the SEI growth. But using this model for a stationary application will yield wrong results because when the battery is at room temperature, significant loss of active material might occur which is totally ignored by the assumed model.

Therefore, the choice of the model has profound implications for the accuracy and validity of the model. However, this is often ignored in economic optimisations or optimal-control applications. They often select the degradation model based on its complexity or data-requirements without properly addressing the accuracy or validity of the model. This work will give a systematic overview of the different degradation models available, and compare them based on validity, accuracy and complexity. Implications for degradation-aware optimal control of batteries will be discussed.

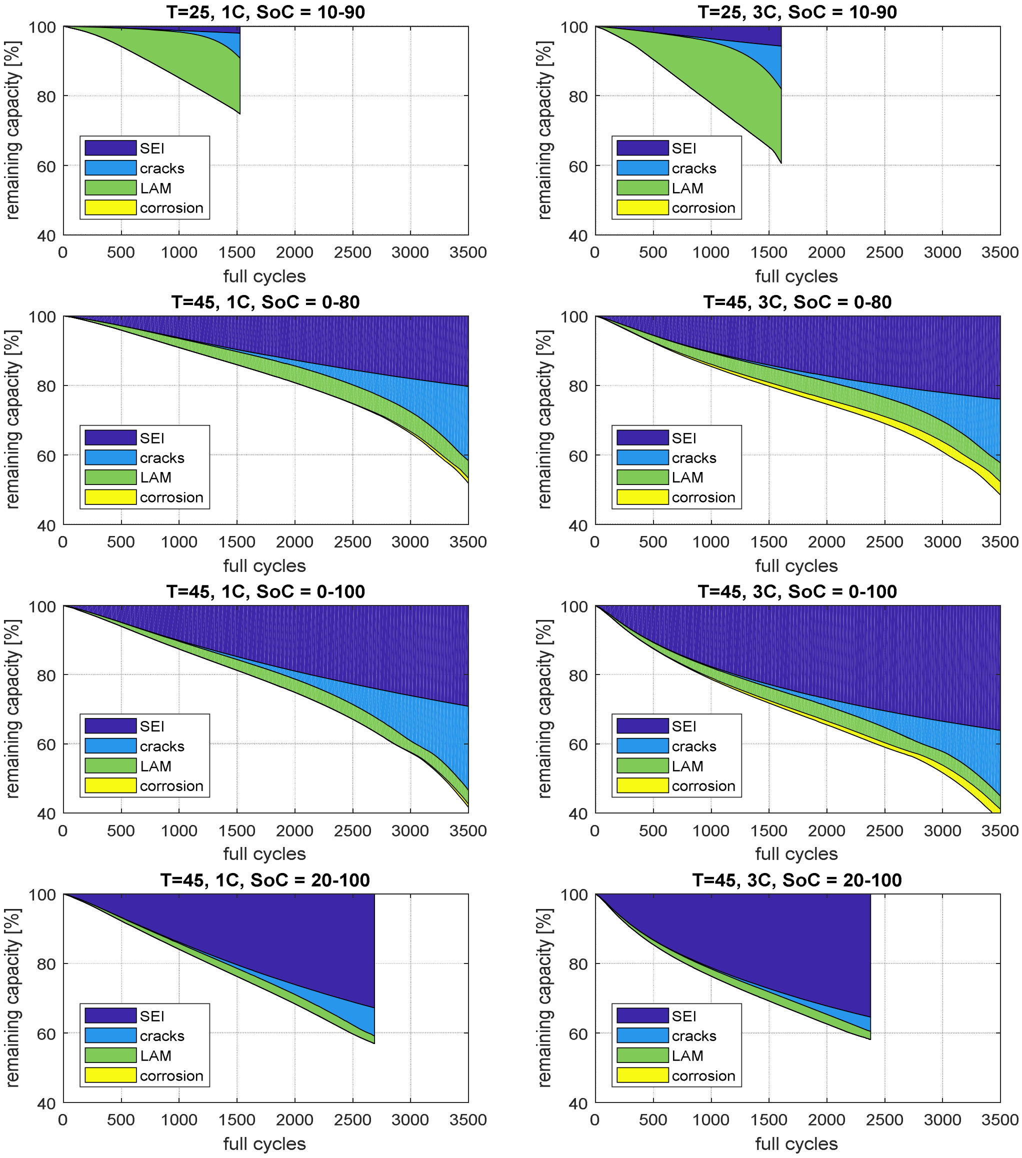

Figure 1 : the simulated contribution of various battery degradation mechanisms for different battery cycles. The mechanisms simulated are the growth of the SEI layer, the surface cracking due to due to mechanical fatigue, the loss of active material due to mechanical fatigue, the increase of battery resistance due to corrosion of the current collectors. The battery cycles were simulated at different temperatures and in different state of charge windows.

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Fast mode switching effects on battery degradation

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Beginning with studies on incorporating energy storage with large batteries into residential energy systems outfitted with renewable generation sources, it became readily apparent that the battery usage in such scenarios had little in common with classical cycling regimes traditionally employed for cell characterization [1]. The transient, irregular power production and storage coupled with electrical demand profiles of the same nature result in usage patterns where frequent switching between charge and discharge modes occur, along with control systems which favour maintaining the battery in a high state of charge. Subsequent experiments aimed at determining the extent of capacity fade as a function of state of charge (SOC) for very shallow and localized cycling revealed not only a significant state of charge dependence for degradation, but also that the extent of degradation was significantly less under very shallow (± 2.5% SOC range) cycling when compared to full cycles, normalized by the total amount of current experienced.

The present study aims to provide mechanistic level insights to account for the observed behaviour of a smaller degree of cell degradation when rapid switching between charge and discharge modes occurs. To this end, an efficient P2D Doyle model [2] was refined and used to investigate the prevailing conditions inside the battery for cycles at constant current and duration, but of various amplitudes centred at 50% SOC. These tests were done on LiNMC 2200 mAh 18650 cells to provide capacity fade data for the cases studies by the simulations.

The main findings of the study were that the time-dependent build-up of lithium in concentration in the anode correlated closely with the observed capacity fade level (Fig. 1) of each different cycling amplitude. For fast switching cases, the proportion of the cycle period without an excess of lithium ion present or transported into the anode was more substantial and was found to be in direct proportion with the observed extent of capacity fade (Fig. 2). In terms of the fundamental kinetics of cell degradation, the simulations clearly showed that the transport and presence of lithium in the anode, whose concentration is a driver of the rate of SEI growth, is restricted under fast mode switching operation and correspondingly produced less cell degradation.

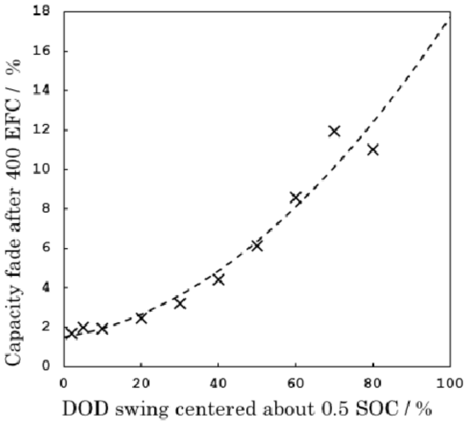

Figure 1: Measured capacity fade for LiNMC 18650 cells for various cycling amplitudes centred at 50% SOC.

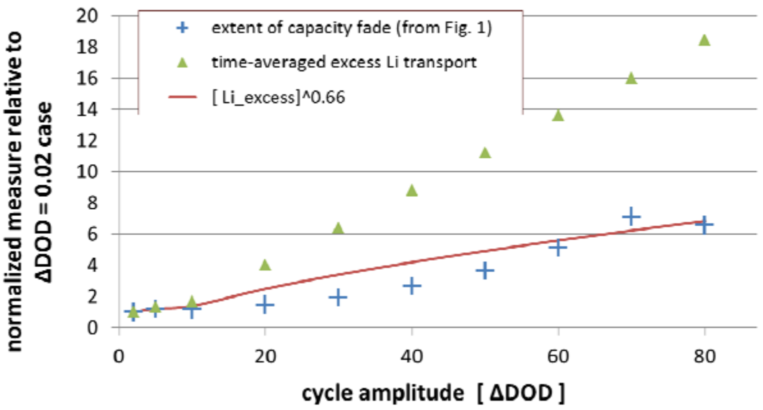

Figure 2: Comparison of excess Li transported to anode with capacity fade as function of cycle amplitude.

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Phase-field Modeling on Li-ion Batteries

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Li-ion batteries are currently the most important energy storage devices and are the most attractive solution for the instability of renewable energy. In pursuit of larger capacity, potential battery systems with new electrode materials are introduced. However, many of these electrodes experience irreversible mechanical degradation already after few charge/discharge cycles due to high stresses. These stresses arise from changes in lattice dimensions and crystal structures, which are associated with overall volume changes and phase separation. Phase separation often occurs during (de-)lithiation in the electrode particles made of materials such as crystalline silicon (Si), tin (Sn), antimony (Sb) and their oxides for anodes, as well as cathode material, i.e. LixFePO4 and LixMn2O4. In return, the chemically induced mechanical situation, such as elevated stress and fracture, can have an impact on the battery behavior on different levels, including active particle behavior, particle-particle interaction, particle-composite interaction, and eventually the cell performance.

To understand electro-chemo-mechanical behavior of phase-separating materials, phase field simulations which couples Cahn–Hilliard-type diffusion model and large deformation mechanics are carried out for the active particles and electrode composites. Thereby the electrochemical reaction is modelled through a mechanically informed Butler–Volmer equation to account for the influence of the phase change and mechanical stresses on the reaction fronts. Moreover, phase-field fracture model is also employed to account for the crack prorogation during de-lithiation and thermal treatment of electrode materials. Furthermore, on the basis of the particle model, a modified single-particle battery cell model is employed to describe the cell performance under different discharging C-rates. For the numerical simulation, novel finite element methods are employed for a direct treatment of the fourth-order Cahn–Hilliard equation and a flexible representation of the particle geometry.

Based on the outlined models, finite element simulations were carried out, and a serials of results were obtained on electrode particles [1-3], interconnected particle networks [4], composite electrodes [2] and battery cells. Figure 1 shows illustrative simulation examples. Results reveal the electrochemical reactions on particle surfaces, phase interfaces and crack surfaces, as shown in Figure 1a. It demonstrates that during delithiation, initial crack notches propagates due to core-shell phase separation and crack branches when phase interface overtakes the crack tip. Reaction rate is increased since newly cracked surfaces are exposed to electrolyte. In composite electrodes, concentration distribution and deformation inside electrode particles and matrix have strong interactions with each other during charge and discharge processes(Figure 1b). Particle geometry also plays a crucial role in electrochemical behavior of electrodes. In phase-separating materials, interconnectivity across particles can largely influence concentration distribution across particle networks, resulting in current “hot spots” (Figure 1c) as shown by X-ray microscopy (STXM) images on V_2O_5 nanowires. Representative examples based on STXM images are simulated to discuss the factors that will influence phase separation during non-equilibrium lithiation and delithiation, as well as relaxation towards equilibrium. The simulation reveals that particles with a slight advance during (de-)lithiation at the beginning will strengthen their advance at the expense of neighboring particles, in a fashion of winner-takes-all. Simulation results show very good agreement with experimental observations of STXM.

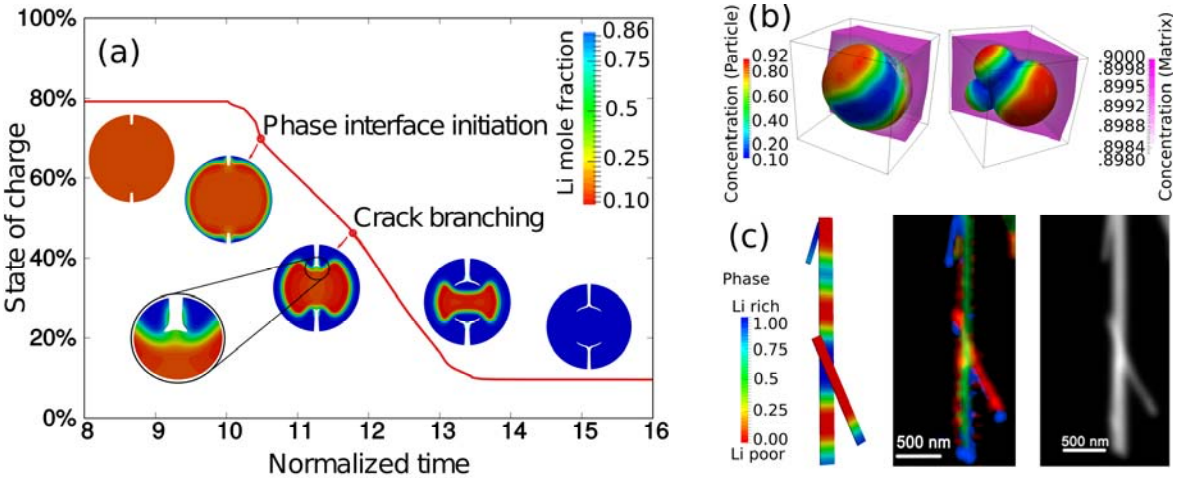

Figure 1: Simulation results of (a) crack propagation in a electrode particle during delithiation, (b) lithiation in composite electrodes and (c) lithiation across interconnected particle network.

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Local Inhomogeneities and their Impact on Lithium Plating in Lithium-Ion Batteries

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The deposition of metallic lithium on the surface of graphite electrodes, also known as lithium plating, is one of the major degradation mechanisms in lithium-ion batteries. The common approach for electrochemical simulation of lithium plating is the use of a volume averaged microstructure combined with a phenomelogical approach describing the plated lithium [1,2]. The impact of metallic lithium is hybridized with the growth of a solid-electrolyte-interphase into an additional resistance term included in the overpotential of the lithium intercalation reaction. Even though volume average models allow for some investigation of spatial inhomogeneities on electrode level and a mismatch of electrodes [3], inhomogeneities on pore scale cannot be resolved. We will present a new electrochemical model, which includes plated lithium as an explicit surface phase. This allows for a smooth transition from dominantly intercalation to pure lithium deposition. This approach is able to describe the well-known stripping plateau occurring during discharge of a plated lithium-ion battery. Additionally, an impact of the plating onset on the cell voltage could be identified.

The model describes the growth of a lithium film on the surface of anode graphite particles. Three reactions are relevant: the intercalation reaction between electrolyte and graphite, the metallic lithium deposition and a charge-neutral insertion of the plated lithium in the supporting graphite. Without the presence of plated lithium, lithium ions can intercalate from the electrolyte into the graphite. During plating the lithium ions get deposited from the electrolyte on the surface of the anode and form a neutral lithium atom. Prolonged deposition results in an growing lithium phase on the surface. The presence of a large lithium phase can prevent the intercalation from the electrolyte into the graphite. The metallic lithium on the surface is not thermodynamically stable. It can either react with the electrolyte to form the solid-electrolyte-interphase or intercalate charge neutral into the supporting graphite. The developed model is implemented in the electrochemical simulation framework BEST [4], which is based on a thermodynamically consistent transport theory [5].

The electrodes of lithium-ion batteries often do not exhibit a degradation, which is homogeneously distributed [6]. The new plating model is therefore applied to an anode microstructure, where several electrochemical parameters are spatially varied. It will be shown, that an inhomogeneous solid-electrolyte-interphase (SEI) can favour or hinder local lithium deposition.

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A Nonlocal Species Concentration Theory: Application to Phase-separating Lithium ion Battery Cathode Particles

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A nonlocal species concentration theory is introduced from a nonlocal free energy density to describe diffusion and phase changes in a material showing phase segregation, and it can be interpreted as a generalization of the Cahn-Hilliard theory. In principle, nonlocal effects beyond an infinitesimal neighborhood are taken into account. This theory incorporates two second-order partial differential equations involving second-order spatial derivatives of species concentration and an additional variable called nonlocal species concentration, and is computationally less demanding than the fourth-order Cahn-Hilliard equation. In this theory, the nonlocal free energy density is split into the penalty energy density and the variance energy density. The thickness of the interface between two phases in phase segregated states of a material is controlled by a normalized penalty energy coefficient and a characteristic interface length scale. We implemented the theory in COMSOL Multiphysics® for a spherically symmetric boundary value problem of lithium insertion into a $Li_xMn_2O_4$ cathode material particle of a lithium ion battery. The two above mentioned material parameters controlling the interface are determined for $Li_xMn_2O_4$ and the evolution of the interface between segregated phases of this material is studied. Comparison to the Cahn-Hilliard theory shows that nonlocal species concentration theory is more accurate when simulating problems where the dimensions of the microstructure such as phase boundaries are of the same order of magnitude as the problem size. This is typically the case in nanosized particles of phase separating electrode materials in lithium ion batteries. For example, the nonlocality of nonlocal species concentration theory turns out to make the interface of the local concentration field thinner than in Cahn-Hilliard theory.

Non-linear Lithium-Solid Polymer Electrolyte Interface Kinetics Investigated by Millisecond Current Pulses

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Understanding the interface kinetics between Lithium and solid polymer electrolytes (SPE) is crucial for the development of Lithium metal batteries. Electrochemical impedance spectroscopy (EIS) [1-3] is typically limited to small signals close to equilibrium. In principle, a non-zero offset current can be applied. In doing so, a concentration gradient is introduced in the electrolyte phase. Thereby, current density and salt concentration at the working electrode are varied at the same time, which is why a detailed model and exact knowledge of the concentration-dependent transport properties of the solid electrolyte is required to interpret the data. Millisecond current pulse experiments overcome these limitations. This technique has been used by Scarr [4], Moshtev *et al.* [5], Geronov *et al.* [6], and Churikov *et al.* [7] to gain insights into the properties of interfacial films between a Lithium electrode and several liquid electrolytes. We present results of a short pulse amperometry technique for a SPE with Lithium electrodes. Millisecond current pulses up to several mA/cm^2 are applied to a symmetrical cell and the voltage response is recorded with sub-microsecond time resolution. From these data it is possible to extract the interface overpotential and the voltage relaxation curve. The measurement of the current–overpotential relation allows the direct experimental revision of the kinetics for the Lithium-polymer electrolyte interface, which was assumed to follow a Butler–Volmer behavior by Doyle *et al.* [8], as well as Ferrese and Newman [9] in line with micropolarization measurements by Sequeira and Hooper [10]. However, the latter were limited to the linear Butler–Volmer regime. Our results for an extended range of the polarization curve (Figure 1) show significant deviations from Butler–Volmer kinetics.

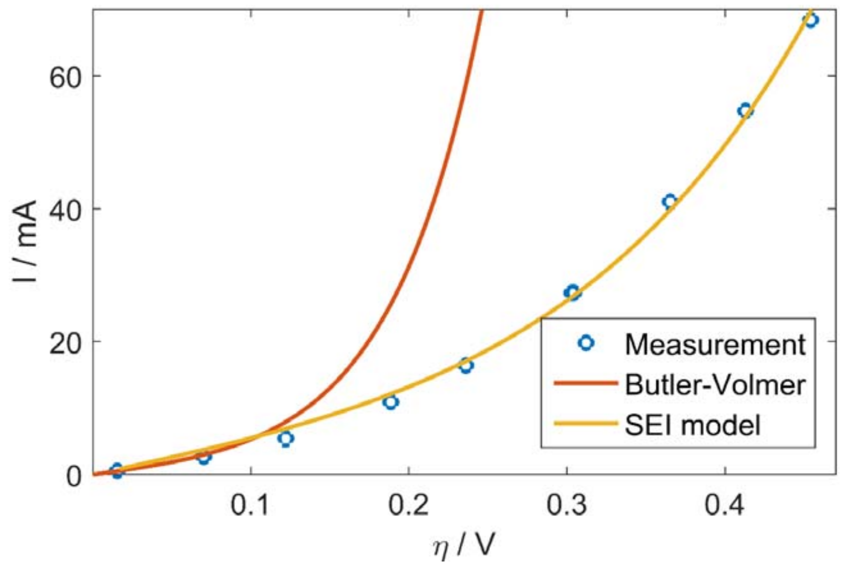

Figure 1: Interface polarization measured values compared to Butler–Volmer kinetics and the SEI model.

However, the data can be fitted successfully by a hyperbolic sine law similar to the SEI model by Peled [11]. Merely, the physical interpretation of the fit parameters leaves room for discussion. The analysis of the voltage relaxation curve shows considerable deviations from an exponential decay. The data suggest the presence of two distinct time constants for the relaxation. Furthermore, measurements with a reference electrode setup were performed in order to investigate the symmetry of the Lithium dissolution and deposition kinetics. Current pulse data were collected by the same procedure mentioned above but alternating the current direction for the same current several times. By this, the overpotentials of the same interface but opposite current direction can be compared. The results show almost symmetrical kinetics. These findings will be discussed in more detail and compared to the predictions of Butler–Volmer kinetics, the SEI model [11] and the point defect model [12,13].

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Electrochemical modeling of intercalation electrode $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$: Determination of transport and kinetic properties

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The vast commercial application of $LiNi_xMn_yCo_zO_2$ (x+y+z = 1) as the positive electrode in lithium-ion batteries has led to extensive study of its properties. Fundamental understanding of the physicochemical processes in the active materials in lithium-ion cells contributes to better battery design such as increased energy and power density. In this study, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) is investigated, since it is a commercially available material, and also for its structural and electrochemical similarities to other NMC variants with higher Ni contents. To develop lithium-ion batteries that can perform under various temperature conditions, the influence of temperature on the internal process has to be understood. Therefore, the transport of lithium in NMC111 at different potentials and temperature effects are investigated systematically at 10, 25 and 40 °C.

Electrochemical model parameterization is carried out as a means to study and quantify the processes governing lithium transport in the NMC111 electrode. The 1D+1D (pseudo-2D) model is based on concentrated solution porous electrode theory describing migration, diffusion and intercalation kinetics. Combined with experimental results from galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS), model fitting is carried out using a least square fitting tool in COMSOL Multiphysics.

The work focuses on evaluating the solid phase diffusion coefficients of lithium and the electrochemical rate constants in NMC111 as a function of state-of-charge under effect of different temperatures. Both lithium transport through solids and charge transfer kinetics at the electrolyte/electrode interface contribute to performance limitations. Therefore, both issues are investigated extensively. In agreement with theory and literature, the solid phase lithium diffusion coefficient increases with temperature [1]. As a particular problem, the lithium-ion diffusion coefficients in NMC111 reported in literature show wide variance with more than two orders of magnitude using different modeling and measurement techniques [2,3,4]. With this quantitative analysis of NMC111 behavior and performance spanning temperature and state-of-charge, we hope to contribute to improved predictive models for the performance and degradation in NMC111-containing lithium-ion batteries.

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The Controversial Surface Reactivity of $Li_4Ti_5O_{12}$ in the Aprotic Electrolyte Disclosed with XPEEM

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Whether $Li_4Ti_5O_{12}$ (LTO) electrodes can induce reduction of the commonly used aprotic electrolyte and develop a stable surface layer at 1.55 V vs. Li^+/Li remains a subject of controversy. Understanding the reactivity of both electrode and electrolyte is considered to be a key step to ensuring a stable electrolyte/electrode interface and thus a long-life span of Li-ion batteries. Here, we make use of x-ray photoemission electron microscopy (XPEEM) to gain information on individual particles composing a commercial-like LTO electrode (Figure1.A) to determine the nature/origin of the LTO interface instability. In XPEEM, maps of the x-ray absorption spectra (XAS) of the sample are acquired with nm spatial resolution to yield surface-sensitive local electronic and chemical characteristics. The local XAS spectra acquired at the C K-edge on carbon (Figure 1.B) and LTO particles (Figure 1.C) show that reduction of the electrolyte occur only on the latter particles and exclusively during lithiation. Simultaneously, we detect a second reaction at the same potential, leading to a partial dissolution of the organic/inorganic species covering the LTO particles. This behavior correlates strongly with the Li^+ insertion/de-insertion and the thermodynamic stability of the electrolyte. With the support of DFT calculations, we conclude therefore that the origin and the mechanism of the electrolyte reduction relates to the adsorbed solvent on the LTO outer plans, driven by the insertion of solvated Li^+ [1]. The adsorption of solvents leads to a shift of their LUMO to energies below the operating potential of LTO and favoring a reductive electron transfer process (Figure 1.D). This study highlights the potential of XPEEM to investigating the complex electrode/electrolyte interface reactions for improving our understanding and the development of solutions to engineering the surface of Li-ion battery electrodes.

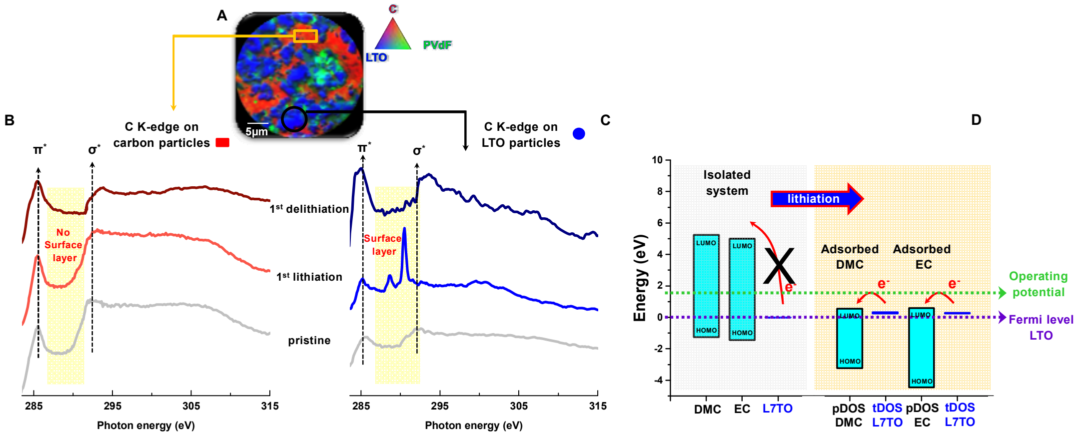

Figure 1: (**A**) XPEEM elemental map showing the distribution of carbon (red), active material (blue) and PVdF binder (green) on LTO pristine electrode. Local XAS at the C K-edge carried out on individual particles of carbon (**B**) and LTO (**C**) in pristine, lithiated and delithiated electrodes. (**D**) HOMO/LUMO levels of DMC, EC and L7TO (lithiated anode) calculated before (on isolated systems) and after lithiation (adsorption of DMC and EC on L7TO surface).

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Abstracts for Poster Presentations

2-D + 1-D PEM fuel cell simulation and validation

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In technical applications of PEM fuel cells usually the cathode supply is set to a low stoichiometry (1.5 - 1.8) to achieve a high system efficiency. This inevitably results in large gradients of the cathode media in the flow field channels from the cathode inlet to the outlet. The oxygen content is reduced by approximately 50 % and the humidity increases rapidly up to full saturation or even higher, depending on the operating conditions. Due to the intrinsic properties of state of the art membranes with a thickness of 15 μm and lower, a significant diffusion driven water transport cycle within the membrane and thus the fuel cell is caused. In the counter flow mode (air <=> H_2) water diffuses through the membrane from the humid cathode outlet to the dry anode inlet, then it is transported with the anode flow to the anode outlet, and there it diffuses back through the membrane to the dry cathode inlet, again being transported to the cathode outlet. This leads to an advantageous internal water management effect resulting in a self-humidification of the cell. An advanced PEM fuel cell CFD simulation is able to calculate these transport phenomena and the subsequent self-humidification effects. It is noteworthy, that PEM fuel cell models, which are typically included in PEMFC system simulations, do not include these transport phenomena.

Here, a 2-D + 1-D model is presented, that firstly is able to meet the requirements of short computational times, necessary for system simulation, but secondly is also able to calculate the internal water transport processes, mentioned before. The model is designed with n segments along both flow fields allowing a distinction between the conditions at the inlets and outlets of the media channels. Additionally, the model is 2-D, since the macroscopic flow field structures, like the double serpentine channels of the flow fields and their geometries, can be included using a correlation table for the anode and cathode segments. Hereby it is possible to calculate in detail the water transport phenomena within the cell. By consequently optimizing the model for short computational times it is possible, despite the 2-D channel resolution, to include the model in system simulations.

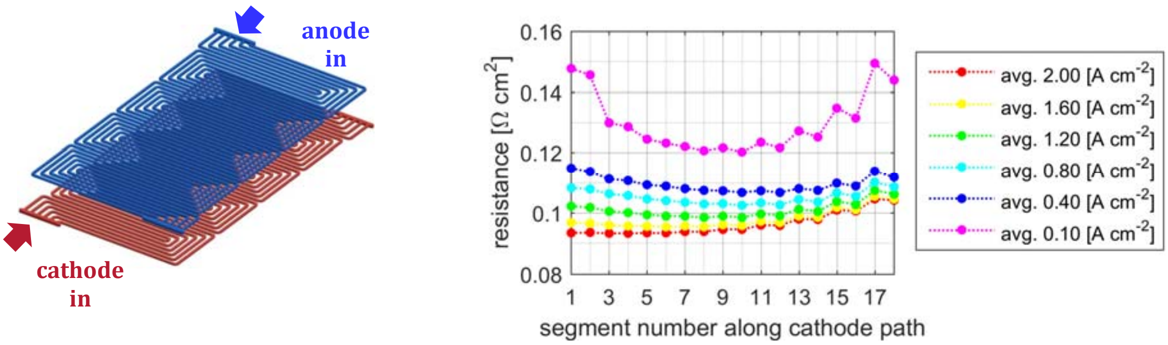

Figure 1: Flow field channels of the simulated PEM fuel cell and the calculated local area related resistances for different current densities

The basic structures as well as the essential processes of the model are presented. Furthermore, a validation will be shown with a data set containing 2-D spatially resolved current density and membrane resistance data, describing both, calculated as well as measured values.

PEM Fuel Cell Electrochemical Noise Measurement, Analysis and Modeling

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Electrochemical noise (ECN) is a well known electrochemical method such as electrochemical impedance (EIS) or cyclic voltamperometry for example. In 1960-1970th V.A. Tyagai developed the basics of this method and he was the first who carried out a lot of high quality systematic experiments and put mathematical background in to calculations to show that ECN can be a promising electrochemical method [1]. Form 1970th till present days B.M. Grafov works on theoretical background of this method [2]. The most popular ECN method became in corrosion field due to large easy to measure amplitudes of potential and current noise during metal corrosion. Several groups of scientists used this method for electrochemical power sources ECN measurement [3]. The most of them concludes that ECM method can be successfully used for electrochemical power sources degradation monitoring. In our early works we shown that ECN method can be used for PEM fuel cell aging monitoring [4].

Now we are working on a model of polymer electrolyte hydrogen-air fuel cell operating under different loads to describe ECN behaviour. The fuel cell is loaded to a constant value precision resistors and noise fluctuations are measured and recorded on it. Several load values are used to verify the model at different conditions in series of experiments.

We use spectral power densities (SPD) calculation method as a primary stage of calculations. 3 different slopes on SPD spectrums are observed. In our model two sources of current noise are used to describe them. First of them is associated with cathode reaction and it is parallel with oxygen reaction faradic resistance and double layer capacitance. In our model we use the values of faradic resistance and double layer capacitance obtained from electrochemical impedance. Those values are shown to be very good to approximate high frequency slope and most part of mid frequency plateau. These fuel cell impedance components act as an low-pass filter for the current noise source. The value of a load resistor is also included in to calculations. The nature of other low frequency noise source is not absolutely clear yet but it comes from the process of water drops formation on a cathode. We got good agreement of our model calculations with experiment data for different loads in wide range of DC currents. The results are shown in Figure 1.

With the help of simulation by proposed model it became possible to calculate the values of current noise amplitudes of introduced noise sources. We plan to use our model to calculate noise sources amplitudes during fuel cell aging to find out if they can be the remaining lifetime indicators of a fuel cell or the other-type electrochemical power sources.

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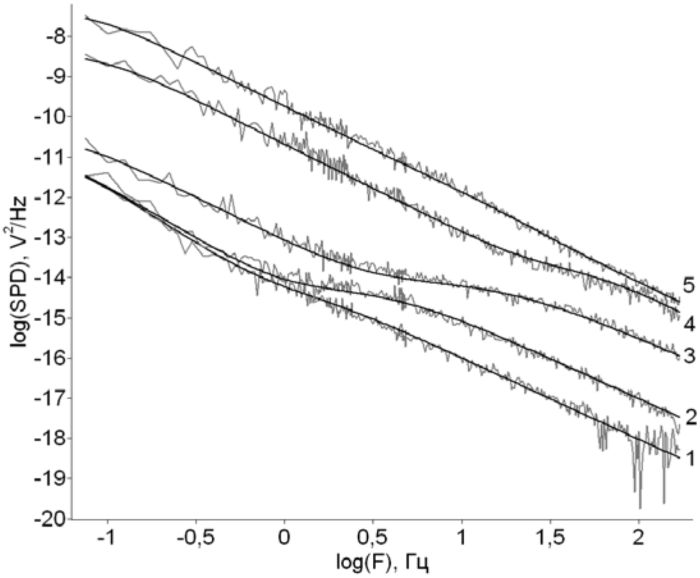

Figure 1: Experimental SPD spectrums and those simulations by proposed model for different load currents of fuel cell: 1 – 0.08A, 2 – 0.023A, 3 – 0.19A, 4 – 0.5A, 5 – 1.06A. Solid lines – model simulations, noisy curves – experimental.

A common framework for the simulation of next-generation metal-sulfur batteries

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Modern Lithium-ion batteries based on intercalation chemistry hold more than twice as much energy by weight and are ten times cheaper as the first commercial versions sold by Sony. But today they are near its limits. Metal anodes for 'beyond Li-Ion' batteries, such as Lithium-sulfur or Lithium-air, promise higher energy density and lower cost.

In recent years magnesium-sulfur batteries are discussed as an attractive next-generation energy storage system. Magnesium can be directly used as anode material due to its dendrite-free deposition and thus increases the safety as well as energy density of such a cell. Two electrons are stored per Mg atom which compensates the rather low discharge potential of magnesium-sulfur cells of 1.7 V and provides a high capacity of 3832 mAh/cm3 and 2230 mAh/g with an energy density of over 3200 Wh/l [1]. Such an energy density is beyond that of lithium-sulfur batteries and is, therefore, very promising for automotive and stationary applications. Furthermore, magnesium and sulfur are both naturally abundant, low in price and non-toxic.

However, magnesium-sulfur batteries are in a very early stage of research and development. The system suffers from similar problems like the early Li-S batteries which are a low coulombic efficiency and cycle life, mainly associated with the well-known polysulfide shuttle. Moreover, the reactions at both the positive and negative electrode are not yet fully understood but similar sulfur reduction mechanisms are generally assumed [2].

In order to harvest the conceptual similarities between lithium and magnesium sulfur batteries we formulate a common framework for metal sulfur batteries. In a multiscale approach we describe both the processes in sulfur host materials (e.g. meso/mricoporous carbons) and on cell level (1+1D). The transport of dissolved species is modeled by the Nernst-Planck equation and sulfur red/ox kinetics are described by a reduced mechanism which is able to reproduce the key experimental results for Me-S batteries [3]. Therefore, the model is able to capture the kinetics of sulfur redistribution in the cell during cycling driven by the polysulfide shuttle. By taking into account side reactions at the negative electrode we are able to describe the experimentally observed decrease in coulombic efficiency and capacity.

In our presentation we focus on the investigation of common properties of Li-S and Mg-S batteries, and more importantly key differences between the two. The simulation results will be compared to in-house experimental data measured on sulfur/carbon composite electrodes, such as charge and discharge curves as well as electrochemical impedance spectra. For these experiments the Mg-S and Li-S cells under investigation are identical with respect to dimensions, cathode material and electrolyte solvent. In close collaboration with the experimental groups at DLR and HIU we aim at guiding new developments of the Mg-S system.

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Transport Simulation in Gas Diffusion Layers of High-Temperature Polymer Electrolyte Fuel Cells and Analysis of Surface Characteristics

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In polymer electrolyte fuel cells (PEFC) the gas diffusion layer (GDL) is a key component on the way to efficient mass transport. Gases have to be transported from the feeding channels to the membranes electrode assembly (MEA). Efficient fuel cell operation requires that the electrodes are sufficiently supplied by fluid fuels from the channels. Also, reaction products must be transported away from the electrodes. The GDL also has to provide electric contact to the bipolar plates but its major task is the mass transport of these fluids. The GDL is typically composed of materials based on carbon fibers, e.g., paper, woven and non-woven textiles.

The structure of non-woven and paper-type GDLs in real fuel cells was analyzed by x-ray synchrotron under different local compressions [1]. In previous studies, gas transport was simulated in compressed and uncompressed microstructures in through-plane and in-plane directions of the GDL, both in real structures and in stochastic equivalent geometries [2, 3]. For communication with other regions – e. g., air channels – the situation at the GDL/channel interface might be important. The velocity distribution at the GDL/channel interface of one realization of a stochastic GDL structure is shown in Figure 1. The homogeneity of the gas flow at this interface is analysed and its correlation with volume based properties is evaluated.

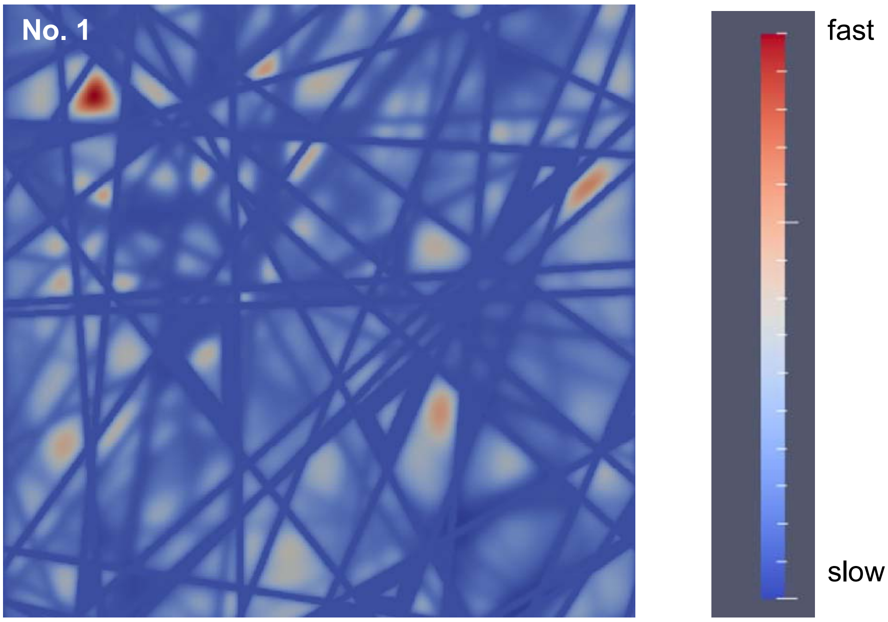

Figure 1: Through-plane gas flow in two realizations of paper-type GDL

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Digital Battery Development with GeoDict

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The resource demand for the worldwide battery production is forecasted [1] to soon exceed the available resources. Thus, more efficient use of battery materials is needed, as well as finding and testing new battery materials. A common challenge in battery development is balancing fast charging, high energy density, battery security, and cost efficiency.

Current battery development is a cumbersome process consisting of many cycles of building and testing new prototypes. Our software GeoDict® [2] represents a revolution in battery development by using simulation to greatly reduce the number of development cycles until the next generation batteries can be shipped. In this talk, we present the workflow for digital battery development.

First, 3d scans of the sample's microstructure (battery or electrodes) are easily imported into GeoDict and segmented to form a digital model. The necessary bulk material properties are assigned to the battery model and its charge curve and its capacity are calculated using the Fraunhofer's BESTmicroFFT [3-6] solver, recently integrated into GeoDict. The computation results are compared to the desired target properties, such as high energy density or fast charging. In addition, GeoDict calculates microscopic properties like electrical and thermal conductivity, diffusivity, and permeability that strongly depend on the microstructure.

Aiming to improve the target properties, a virtual twin is modelled with GeoDict that exhibits the same pore and grain statistics, and the same material properties as the input material sample. The material geometric properties of the virtual twin are analysed at the microstructure level (e.g. tortuosity, individual pores and grains identification, pore and grain statistics). Then, its microscopic properties are computed, such as electrical and thermal conductivity, diffusivity, and permeability. A virtual twin created with GeoDict makes possible to digitally modify material components quickly and repeatedly. The final goal is to alter geometric properties like tortuosity, and material properties like electric conductivity until the target properties are reached and the next generation battery is found.

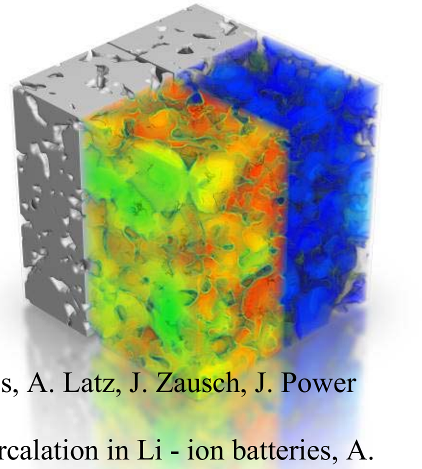

Figure 1: Combined picture of battery microstructure (gray) and Lithium concentration (colored) created by GeoDict.

Keywords: Li-Ion Battery, Grain Identification, Simulation.

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Modelling and Simulation of Porous Electrodes with Multi-Scale Homogenisation techniques

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I will give an overview on the modelling procedure of porous insertion electrodes with homogenisation techniques. Basis for this approach is a sophisticated modelling framework for electrochemical systems on the basis of non-equilibrium thermodynamics [1-4]. Some key aspects of this model framework are (i) thermodynamically consistent boundary conditions taking into account charge transfer reactions and capacitive effects at the electrode-electrolyte interface [5-7], (ii) the dependence of the conductivity and the transference number on the (local) ion concentration, (iii) predictivity and validation of the thermodynamic factor, (iv) accounting for incomplete electrolyte dissociation [8], and (v) self-consistent incorporation of the open circuit potential for various electrode materials. The homogenisation of this model framework for a porous medium allows then the determination of the porosity, tortuosity, and interfacial area based on a real micro-structure model, as well as the derivation of homogenised equations for this porous electrochemical system. Numerical simulations of charge/discharge cycles show the validity of this approach, and potential extensions regarding ageing effects are finally discussed.

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CFD-DEM Simulation of the Carbon Black Distribution during the Mixing Process

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The technology of lithium ion batteries provides the opportunity of storing energy and providing it on demand. In order to establish lithium ion batteries as a stable, reliable and efficient energy storage their capacity and performance are to be further improved. This requires gaining a deeper insight into the function and behaviour of the individual components and their interactions among each other. Nanostructured carbon, also known as Carbon Black (CB), mainly can be found in the cathode serving as a conductive additive. Various experimental studies show a big influence of the CB distribution on the microstructural charge transport behaviour of electrodes and therefore on the overall cell performance [1–3]. Further publications describe the correlation between the CB distribution and the chosen dispersing parameters [4–6]. Due to the size of the CB particles (~10 nm) analysing the CB distribution and consequently optimising the mixing process requires a new approach. These can be achieved by simulating the CB aggregate distribution during the mixing process.

Therefore, a multi-scale CFD-DEM simulation was set up to describe the CB microstructure during the slurry production. Firstly, the CB aggregates were described and modelled by using the Tunable Dimension Method. Furthermore, the algorithm was extended by using a Fibonacci Lattice [7] in order to create aggregates out of a predefined particle size distribution. The time required creating an aggregate with a specified fractal dimension and the deviation of the obtained aggregate from the specification depending on its size were analysed. Finally, the influence of a simple shear field on the aggregate structure was studied. This allows predicting the change of the CB structure during the mixing process and therefore describe the influence of the mixing process on the overall cell performance.

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Local faults identification on a PEM fuel cell by external magnetic field measurement

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Many technological locks prevent the deployment of Proton Exchange Membrane Fuel Cell (PEMFC), cost and durability represent two of the most significant challenges to achieve clean, reliable, and cost-effective PEMFC systems. Particularly for stationary applications, reliability and durability are critical to PEMFC successful deployment. Solving these shortcomings will be a great opportunity for a decisive breakthrough towards mass-diffusion of the current PEMFC technology. The long-term electrical performance losses are bridged to either the degradation of the MEA constitutive materials or thanks to specific operating conditions (flooding, drying, etc.).

Up to date, PEMFC diagnosis by electrical measurement has widely proven its efficiency. Electrochemical techniques, such as polarization curve, current interruption, and electrochemical impedance spectroscopy (EIS), have been popularly employed for fuel cells diagnosis. Measurements of cell voltages are the simplest to perform and to (often) interpret voltage drops, indicating failures necessitating the immediate shutdown of the stack. EIS is also a well-established diagnostic and modelling method that has been widely used in electrochemistry due to its flexibility (which enables covering a wide range of aspects of fuel cells) and accuracy [1]. Routine experimental methods based on different techniques devoted to the evaluation of cell state (Cell voltage, polarization curve, EIS, etc.) are certainly powerful, but remain insufficient when dealing with the heterogeneous aspects of the aging phenomena at stake in the cell and even more within a stack [2]. Therefore, techniques allowing local measurement of PEMFC parameters at the cell and stack level, are of major interest to sense localized aging phenomena and understand degradation mechanisms.

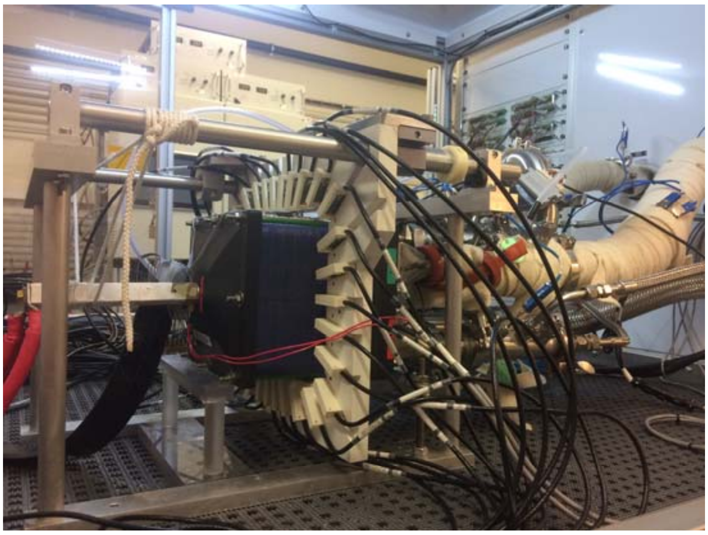

Figure 1 Photo of the PEMFC stack GENEPAC and the measurement system

Non-invasive methods based on measurements of the magnetic field induced by current distribution within the stack have been proposed for PEMFC stack diagnosis [3]. The external magnetic field measurement is a new and original technique, which consists in placing the magnetic sensors around the stack, to measure the magnetic field generated by the current flowing through. Previous work [4] has revealed an inverse method to determine the internal state of a PEMFC stack from a non-intrusive magnetic measurements. The results of this work have demonstrated that a set of non-intrusive magnetic sensors (without change in the stack operation) can be integrated onto the PEMFC systems to identify local default; this fault detection results from the identification of internal current density distributions (using inverse problem). The originality of our approach is that it requires a very small number of magnetic field measurements. The measurement system is very easy to perform on an operating PEMFC without cluttering the environment. The number of measurements is reduced down to 30 while maintaining an acceptable resolution within a very short delay against ca. 15 minutes with the previous methods [3]. The major advantage is that the internal state of the stack does not vary during the measurement time. The low number of sensors is made possible thanks to assumptions on the current distribution and to an adequate choice of positioning and orientation according to the stack dimensions. The Figure 1 presents the PEMFC stack on the test bench including the external magnetic field measurement system. The 30 magnetic sensors are fixed on a single plane around the GENEPAC stack and enable an instantaneous measurement. This single plane of sensors is moved along the stack length to perform measurement on the three locations.

The experiments described in this section are performed to identify the changes in current distribution through the stack when anomalies are induced either by changing operation conditions or by a local fault within a PEMFC. In the first case, inhomogeneous distribution of the current can be observed by varying the air stoichiometry and air hygrometry around the nominal conditions. In the second case, the active surface of five cells was covered with a resin which inhibits this area.

The Figure 2 shows the reconstructed current density distribution in the case of a localized fault on the upper left corner of the stack. This local fault (3D fault) has been successfully identified and the associated current density distribution was calculated by the inverse magnetic model.

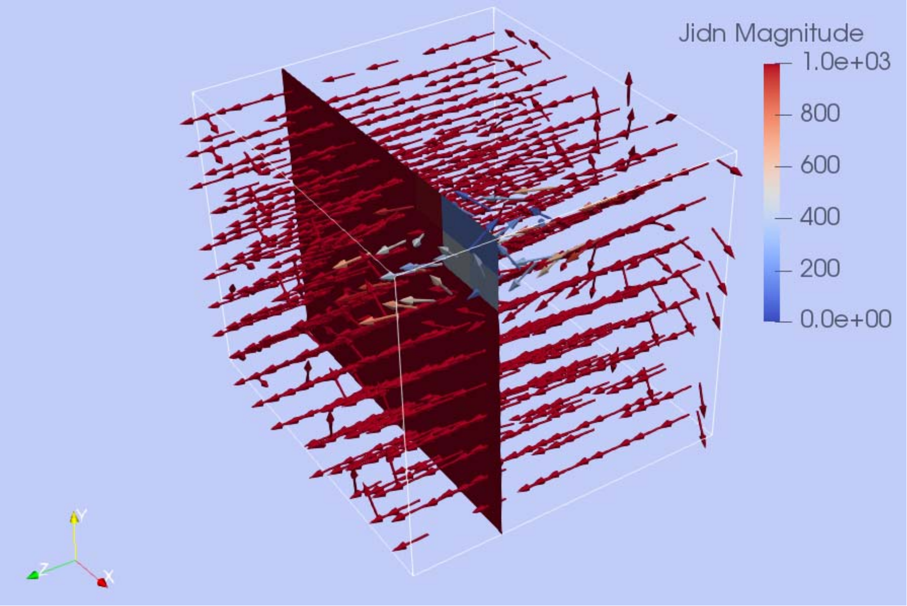

Figure 2: Identified current from the external magnetic field generated by the localized fault

In this study, an innovative magnetic tomography approach was proposed in order to reconstruct faults in PEMFC stacks. A sensor array was developed and designed to be sensitive only to current heterogeneities. The sensitivity of our system has been demonstrated for air stoichiometry or air hygrometry changes as well as for localized anomalies.

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Method to Determine In-Plane Tortuosity

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The quest for reaching higher power density at higher discharge rates has led the research into three dimensional architectures (laser structured, interdigitated etc.) for the battery electrodes[1]. One of the reasons for their improved performance is their ability to access lithium ions from more than one direction as compared to traditional planar electrodes. In such cases, tortuosity anisotropy becomes an important aspect to understand the improved performance and simulate the battery system[2]. The use of transmission line model to determine through-plane tortuosity is well established in the literature[3] whereas the literature on in-plane tortuosity is scarce.

In this presentation, we derive a method to extend the transmission line model to measure the in-plane tortuosity. The additional information of in-plane tortuosity of an electrode will be critical for modeling novel electrode architectures. The combined use of through-plane and in-plane tortuosity will act as an indispensable tool to design better electrodes and validate battery models. Figure 1 shows comparison of through-plane (τ_{T-P}) and in-plane (τ_{I-P}) tortuosity of two different electrodes consisting of MCMB (spherical) and flake-like graphite materials.

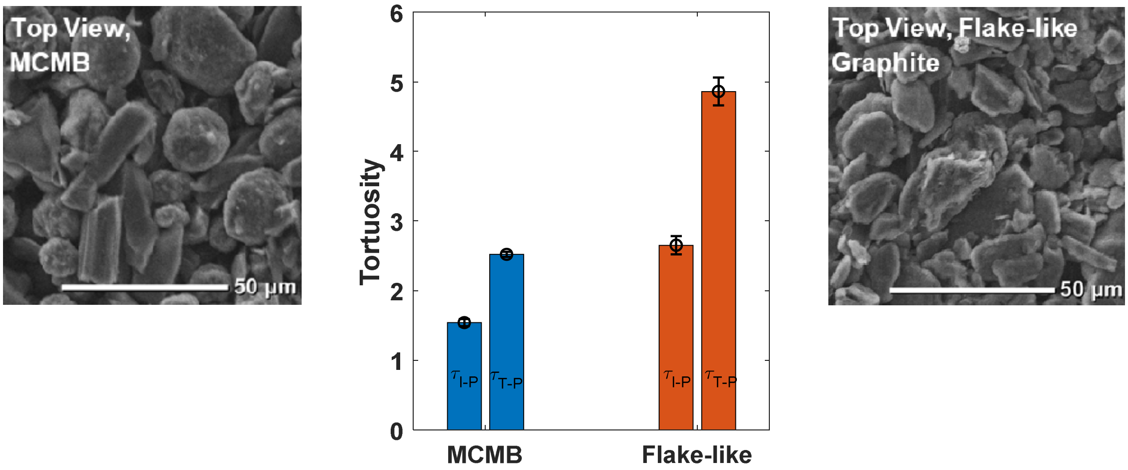

Figure 1: τ_{I-P} and τ_{T-P} of MCMB based electrodes (MCMB 97%, PVDF 3%, porosity ~48%) and Flake-like graphite based electrode (Graphite 94%, PVDF 6%, porosity ~55%). The error bars represent the standard deviation from 2 measurements. SEM images of MCMB and flake-like graphite based electrodes are shown in left and right respectively.

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State Estimation of Lithium-Ion Cells using a Physicochemical Model based Extended Kalman Filter

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Physicochemical processes in lithium-ion batteries are nowadays widely described by porous electrode models such as the Newman-type[1] pseudo-two-dimensional (p2D) model. Compared to empirical models such as the equivalent-circuit-model (ECM), higher parameterization effort, less accuracy and larger computational demand impede the broad application of physicochemical-based state estimation algorithms in battery management systems (BMS). To tackle this issue, a numerical reduction of the p2D-model is presented by replacing the solid-state diffusion equation with three different approximations. As used in the original Newman-type[1] p2D-model, the Duhamel-Superposition-Integral (DSI) is implemented in the presented model of a MCMB/$LiCoO_2$-cell. In comparison to this benchmark, a Polynomial-approach[2] (PP) and an Eigenfunction-method[3] (EM) are analyzed under constant and dynamic load scenarios. The PP- and the EM-modified p2D-models are further used to gain two different state-space representations of the set of partial differential equations in order to be able to apply an Extended Kalman Filter (EKF). Simulation results generally revealed a notable speed-up of the computation time under both constant and dynamic load scenarios whilst the accuracy was reduced especially during dynamic loads for the PP-approach. The EM-approach showed a similar accuracy compared to the benchmark at a higher computational effort. Combined with an EKF, both the PP- and EM-reformulated models showed a rapid convergence in correctly estimating the cells states from the overall applied current and resulting cell voltage which allows for enhancing fast charging protocols whilst avoiding Li-plating or for a reliable power prediction.

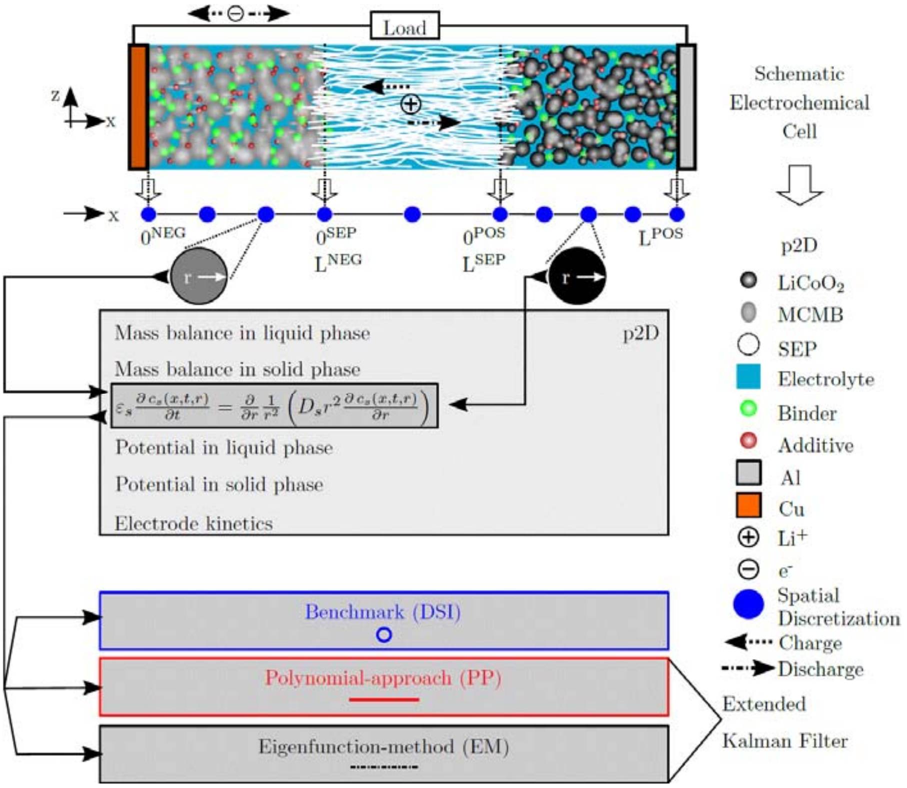

Figure 1. Schematic representation of the MCMB/$LiCoO_2$ lithium-ion cell and the corresponding Newman-type[1] p2D electrochemical model including the main equation system and the three different approximation methods for the solid-diffusion equation.

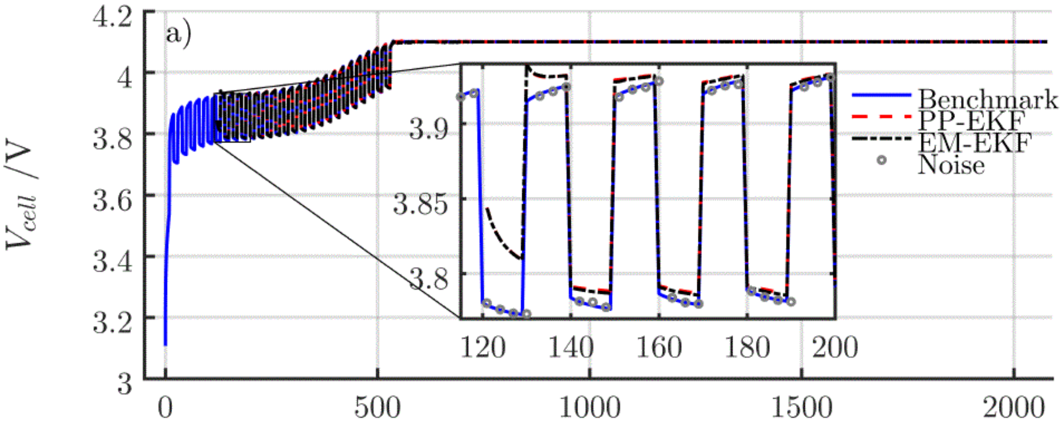

Figure 2. Simulation results of the PP- and EM-p2D model combined with an EKF during a dynamic charging scenario.

All simulation models were implemented in Matlab2016b and calculated on a desktop computer with an Intel(R) Core(TM) i5-6500 CPU @ 3.20 GHz processor and 16 GB of RAM.

The simulation results showed a 3.5 times faster solving procedure of the p2D-model and the least number of iterations for the PP-approach compared to the DSI-benchmark under constant load scenarios. The EM-approach required the largest number of iterations and the highest computational effort during constant and dynamic load profiles, but showed a six times higher precision in simulating the cell voltage compared to the PP-approach. In short, the EM-approach proved its suitability for dynamic load profiles to gain accurate simulated states of the cell whilst the PP-approach is recommended for constant loads and very fast computation times.

The simulation results for the reformulated p2D-models using the EKF showed a remarkable delay in time for estimating local states (e.g. concentrations, local potentials) compared to the recovery of global states (e.g. cell voltage) based on the underlying current and cell voltage. This delay needs to be taken into account in terms of control strategies for fast charging profiles in order to avoid undesired side reactions such as Li-plating. With the aid of the local estimated states, the minimum potential in the anode can be evaluated and used in application[4] to maximize the charging current. Again, the EKF using the EM-approach is more accurate in terms of dynamic load profiles compared to the reformulated model with the PP-approach which makes it suitable for this application. Furthermore, no significant differences in computation time could be observed during the three charging scenarios which supports the application of the EM-approach in this case.

Acknowledgement:
This work has received funding from the European Union's Horizon 2020 research and innovation programme under the grant 'Electric Vehicle Enhanced Range, Lifetime And Safety Through INGenious battery management". (EVERLASTING-713771)

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Operando in-plane neutron imaging study of water/gas distribution in PEM water electrolyser under various operating conditions

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The increasing share of intermittent renewable energy sources and the pursuit of alternative fuels for mobility set high demands on energy storage solutions, where hydrogen can play an important role due to its low storage cost. One of the promising technologies to convert electrical energy into a chemical fuel is Polymer Electrolyte Water Electrolysis (PEWE), which has been a topic of extensive study in recent years. A particular area which is still not well understood is the water/gas distribution within the porous media and catalyst layer, which can have direct impact on overall performance and reliability of the system. As studied by Suermann et. al. [1], the structure of PEWE porous transport layers (PTL) can have an impact on the performance. To understand this, a better knowledge of the transport mechanisms within PTLs is of high interest. Published papers seem to be contradicting each other, which proves that this topic is not trivial and is still far from conclusion. Lee et. al. [2] did an extensive study on bubble formation and gas pathway establishment in PTL using a model setup based on local controlled gas injections, claiming that depending on gas flow the two phase transport regime is either capillary fingering (at low flow rates) or viscous fingering (at high flow rates). This claim is based on the observation that increasing flow rate leads to decrease in local gas saturation. Hoeh et. al. [3] reported in-operando X-ray radiography showing that increasing gas production leads to an increase of gas pathways (identified by additional locations of bubble formation). Contrary to Lee et al., they assumed that this translates to a higher gas saturation in the PTL for high current densities. However, neither of these studies does report the measurement of gas saturation within the PTLs under real operating conditions. Here, we present our latest results using neutron imaging to measure the gas saturation distribution across the PTL in an operating small scale electrolyser. Neutrons have the unique property of being able to penetrate through a variety of materials – including the titanium used for PTLs – while providing a high contrast for liquid water, making them a particularly useful tool for the study of water/gas distribution in PTLs. Thanks to our previous developments for fuel cell imaging using an anisotropic approach [4], we are able to image the water/gas distribution across the PEWE structure with high resolution. In our previously published paper [5], we observed that a gradient of water/gas distribution across the anode PTL is established with currents as low as 0.1 A/cm^2, and remains virtually unchanged at high current densities. We recently focused on the details of gas evolution at very low current densities. Our observation (Figure 1) shows that the gradient of water/gas distribution is readily established at a current density as low as 2 mA/cm^2, with only small changes occurring in the region near the electrode when increasing the current density. This behaviour indicates a negligible impact of the viscous forces over a wide range (3 orders of magnitude) of gas evolution rates, and is rather consistent with the hypothesis of a pure capillary fingering regime.

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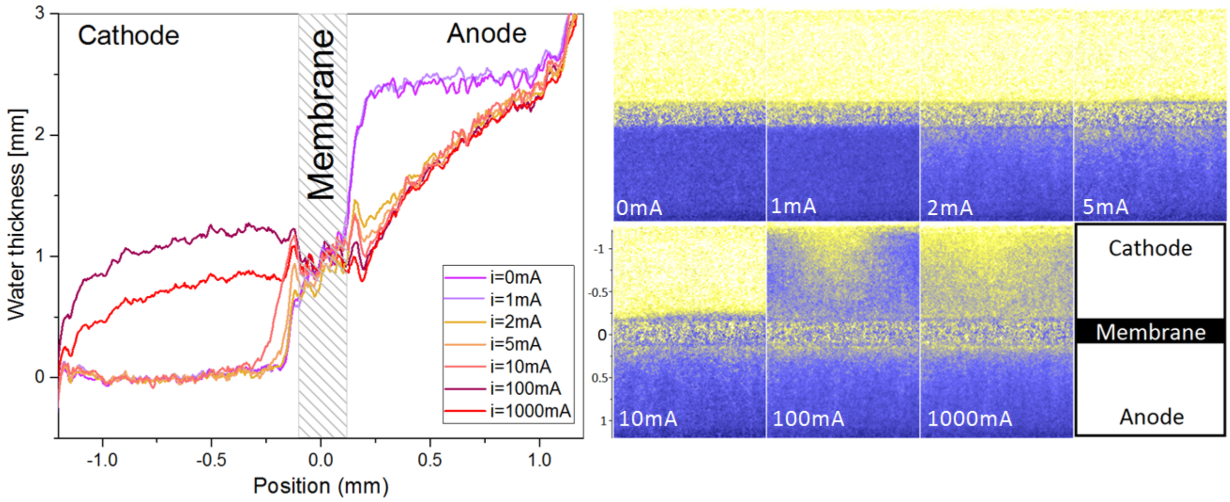

Figure 1: Gas water and gas distribution within porous media of PEM water electrolyser, a) water thickness profiles across the membrane, b) Images corresponding to given profile curves.

Prediction of cyclic ageing and storage ageing in a lithium ion battery using an electrochemical model

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Prediction of ageing for lithium-ion cell is essential. However this is a complicated area with few modelling techniques available. The influence of cycling and storage on capacity fading side reaction is investigated for the first time using an electrochemical model. Thus this paper is a unique attempt towards developing a model which can predict combined cycling and storage. Also this work establishes guideline for calculating the SEI properties based on storage ageing experimentation. Very few works correlated the experimentally observed degradation characteristics with properties of SEI layer or chemical characteristics of a battery. The conventional cyclic ageing correlation cannot be used for storage ageing due to the weak relation of degradation with SoC. In this case, the cycling correlation predicts almost the same degradation at lower SoC and at higher SoC, which is counter intuitive to experimental observations. This limits the applicability of an electrochemical model for HEV storage-cycling drive cycle since the ageing characteristics predicted during the storage time will be erroneous.

In this work, the Pseudo Two Dimensional Model (P2D) equations are modified to include a continuous solvent reduction reaction responsible for capacity fade which is well established and widely applied in previous literatures [1, 2, 3, 4]. The capability of this model to predict the SEI layer growth and internal resistance increase under different operating conditions is carefully used to analyse the storage and cycling reaction contributions. The critical parameter controlling the rate of SEI layer growth is the side reaction coefficient. Another important parameter is the temperature of the battery which is found to accelerate cell ageing. However, in this work, the analysis is limited to iso-thermal condition since the dependency of temperature on cell operating parameters is complex.

For the cycling test, the cells are cycled between voltage limits at 1.2C discharge and 0.3C charging. Capacity characterisation tests are performed after every 100 cycles. For the storage test, the cells are stored at 25°C and the capacity test has been performed after 73, 139, 202 and 297 days to calculate the remaining capacity left in the cell. The over potential of the side reaction reduces to zero for a storage condition where no external current is applied. Therefore, the intercalation current density reduces to zero. However, the ageing solvent reduction side reaction current density is non-zero for storage. The capacity fading solvent reaction parameters are limited to the interfacial surface area and the side reaction exchange current density. The side reaction coefficient in the electrochemical model is adjusted to match the experimental prediction and conclusions are made based on the variation. The storage condition is also used to fine tune the SEI properties to match the experimental investigations.

Table 1 shows that the modified-side reaction-electrochemical storage ageing model is successful in predicting the degradation characteristics eliminating the influence of other parameters like temperature and DoD. Herein, the storage degradation characteristics of NCA chemistry cell can be captured by two types of correlation, exponential and parabolic, out of which the model with parabolic fit gives higher accuracy which is evident from the validation data presented in Table 1. The parabolic correlation directly takes into account of additional side reactions at 20% SoC into the model therefore, as discussed earlier, introducing more data points into the correlation improves the prediction accuracy to cover the unknown reactions.

Figure 1 shows the model performance on a combined cycling-storage weekday drive cycle. The model is successful in showing the SEI layer growth pattern for different usage conditions like storage, cycling and charging. The rate of SEI growth changes with these conditions; storage and cycling show moderate SEI growth whereas charging shows highest. Therefore, from this analysis, the user can intelligently mitigate against the conditions, which have adverse effect on the life of the battery.

Table 1: Error comparison of different ageing models compared to experimental data for different storage SoC.

	RMSE (Ah) 20 % SoC	RMSE (Ah) 50 % SoC	RMSE (Ah) 90 % SoC
Independent Reaction	0.018 (±0.4 %)	0.0085 (± 0.1%)	0.0495 (± 0.8 %)
Exponential fit	0.072 (± 1.8 %)	0.022 (± 0.5 %)	0.058 (± 1.3 %)
Parabolic fit	0.033 (± 0.8 %)	0.013 (± 0.3 %)	0.056 (± 1.2 %)

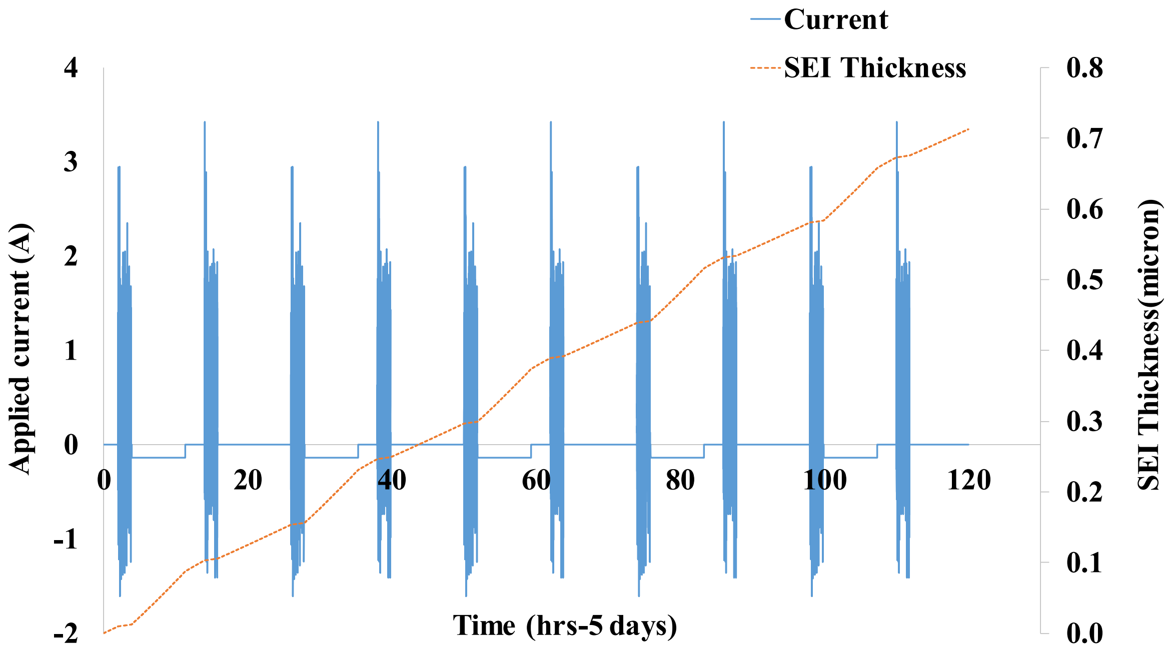

Figure1: Model performance and SEI layer growth pattern with combined cycling- storage drive cycle over a week.

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Studies of Water Distribution in the Gas Diffusion Layer of Polymer Electrolyte Fuel Cells using X-ray Tomographic Microscopy

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Polymer electrolyte fuel cell (PEFC) has been recognized as an efficient energy converter which turns the chemical energy stored in hydrogen fuel to electrical energy. The water generated during operation can saturate the pores of gas diffusion layer (GDL) and hence impede the gas feed to the catalyst/GDL interface. To achieve higher performance and enhance commercialization, water management by GDL is vital to ensure sufficient reactant gases delivery and product water removal. Water distribution in the GDL has been investigated by X-ray tomographic microscopy (XTM) for high temporal and spatial resolution operando imaging. The influence of reduced XTM scan time on image quality has been studied with an in-situ XTM at the TOMCAT beamline of the Swiss Light Source (SLS) at Paul Scherrer Institute (PSI). In this work, 3D XTM studies of water distribution in GDL under PEFC operando condition are presented (see Figure 1). Size distribution and feature detectability [1] of local water accumulations and the GDL pore structure will be analysed in order to enable subsecond X-ray tomographic microscopy as a tool understanding the impact of transient water transport processes in GDL on PEFC performance.

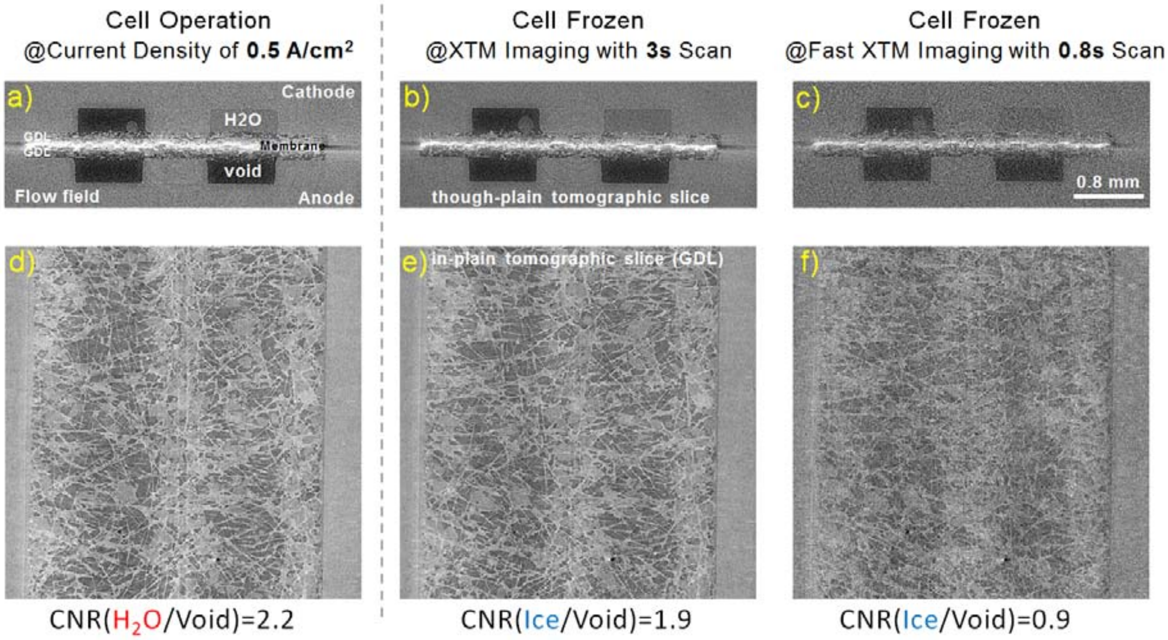

Figure 1: Tomographic 'through-plane' slice of a double channel PEFC with operation and imaging condition a) cell operation at current density of 0.5 A/cm2 with a 3 s scan; b) cell frozen at -17 °C with a 3 s scan; c) cell frozen at -17 °C with a fast 0.8 s scan; d), e) and f) are Tomographic 'in-plane' slices of figure a), b) and c), respectively. Contrast-to-Noise (CNR) ratio between void and water/ice is given indicator for image quality.

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(contribution by O. Birkholz and M. Kamlah moved to Oral Presentations section , page 74)

High-temperature behavior of a lithium-ion LFP/graphite cell: Simulative and experimental investigation of DSC, ARC and external short circuit

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Due to their high power and energy density, lithium-ion batteries (LIB) play a key role in present and future energy storages. However, this technology was always accompanied by single incidents of thermal runaway drawing attention to its safety [1], [2]. Understanding the underlying processes of thermal runaway and the behavior of LIB at elevated temperature is therefore of special interest.

The presented model of a cylindrical lithium iron phosphate (LFP)/graphite lithium-ion cell is based on a multi-physics multi-scale (1D+1D+1D) approach [3] (see Figure 1). It is evaluated by simulating differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), and external short circuit test (ESC). We demonstrate the high flexibility of the underlying model by simulating the cell under these very different conditions encountered in the three different experiments. Hereby, a two-step thermo-electrochemical formation mechanism of the solid electrolyte interface (SEI) is an important new model assumption. The model is able to qualitatively reproduce experimental data to up to around 200 °C and extreme high discharge rates of up to 100 C (see Figure 2). Parameters and assumptions of the model could be evaluated via comparison to experimental results of DSC, ARC and ESC, as these experiments show complementary sensitivities towards specific model parameters like particle size of active material, heat capacity of the cell or kinetics of side and main reactions. This study indicates how high-temperature experiments might be used to identify or confirm parameters of a multi-physics model of a LIB.

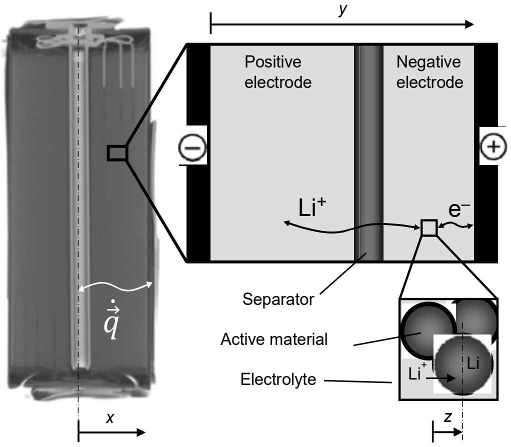

Figure 1. Scheme of the model

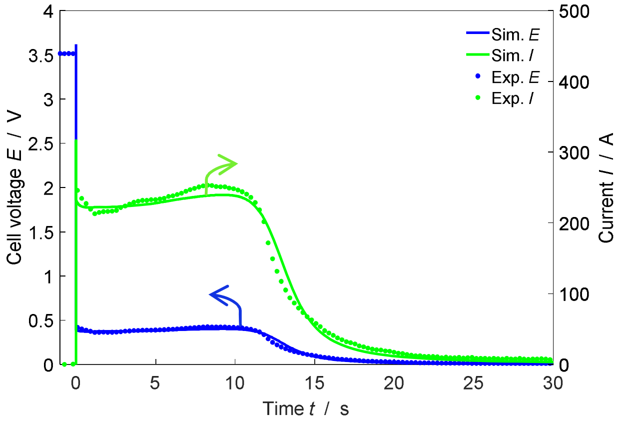

Figure 2. External short circuit of LFP/graphite cell

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Modifying Microporous Layers for Polymer Electrolyte Fuel Cells

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One of the requirements to ensure a high and stable performance of a polymer electrolyte fuel cell (PEFC) is the management of proper transport through the gas diffusion media (GDM). Water is needed in the membrane for it to be ion-conductive, but water accumulation can block the reactant access to the catalyst layer (CL), known as flooding. The most common strategies to improve water management consist in coating the gas diffusion layer (GDL) with a fluorinated polymer and adding microporous layer (MPL). The coating increases the hydrophobicity of GDL which helps to avoid flooding. The MPL improves the GDM-CL interface, since it limits the mechanical damage produced to the CL while assembling and reduces the contact resistance. It also has a significant influence in water management.

The specificities of water transport in the MPL's and their characteristic requirements are yet to be fully understood. Contradicting results are frequent and comparing experiments can be difficult due to the lack of standards. Nevertheless several research groups have studied the MPL: the water transport through it, the influence of the MPL's chemical and physical characteristics in PEFC performance, and different modifications have been attempted [1].

In accordance with the studies suggesting that cracks or large pores favours water management, Lu et al. performed laser perforation on the MPL and observed an improvement in operation performance [2]. Other approaches consist in changing the hydrophilicity of the MPL. Kitahara et al. have tested the incorporation of a hydrophilic layer next to the CL, also showing performance improvement [3]. In our group, we have developed a technique to fabricate GDL's with patterned wettability. This favours the separation of water transport and gas transport pathways, helping to reduce mass transport losses [4]. We have also been able to successfully extend this modification to the MPL, chemically modifying its wettability (Figure 1).

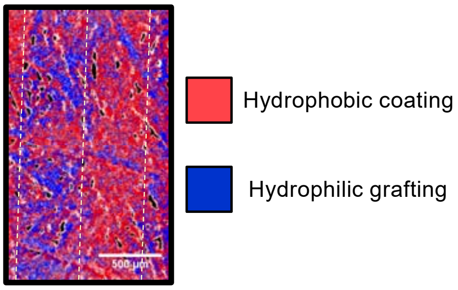

Figure 1: SEM-EDX map image of a patterned wettability modified MPL

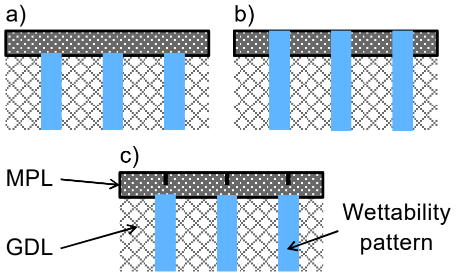

Figure 2: Schematics of the patterned wettability GDLs with modified MPLs. a) Hydrophobic b) Patterned wettability c) Patterned porosity

During the presentation the incorporation of different MPL modifications (see Figure 2) to the GDL with patterned wettability will be discussed, including the synthesis feasibility and possibilities of up-scaling, and the impact of the MPL modification on water distribution and performance.

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Multiphase transport through porous PEM electrolyser components and its influence on electrochemical performance

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A numerical modelling

Performance of proton exchange membrane water electrolysis (PEMWE) cells depends, among other influences, on the counter current transport of water and oxygen within the porous transport layer (PTL) [1]. Disturbed water supply to the anode or insufficient oxygen removal can cause undesired mass transport overpotentials. In this study, the transport processes within the PTL are described with a continuum, two-phase two-component model which originates from the modelling of subsurface processes [2]. It was already successfully applied for modelling different flow fields within PEM fuel cell gas diffusion layers [3] which suggest that an adoption to the description of mass transport phenomena in PEMWE is possible. Besides the model's evident dependency on the thermodynamic state and on boundary conditions, capillarity, intrinsic permeability and relative permeability are found to be more influential model parameters than e.g. porosity and diffusivity. According to the model, convective transport is enhanced by high intrinsic permeability and steep capillary pressure-saturation relations. The latter causes high gradients in gas pressure which results in lower gas saturations and presumably favourable reaction kinetics. Relating model parameters to the PTL properties, we derive suggestions for the PTL's structure and wettability in order to reduce mass transport overpotentials. For instance, since higher porosity not only increases permeability but also ohmic resistance, tortuosity and pore size distributions need to be taken into account when optimizing PTL structures. The modelled results are validated by experimental results obtained from polarization curves.

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A homogenized multiphysics model for predicting SOC stack performance

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A solid oxide electrochemical cell (SOC) stack is a highly complex system due to the number of components, materials and physics involved. Therefore, stack design is essential for the long-term performance of this technology. Stack failure mechanisms which can damage or destroy the stack, e.g., thermal gradients in the stack leading to compressive stresses and contact loss between the cells and interconnects, too high pressure drops across the stack blowing out the stack components or overheating of the stack due to poor heat management, are determined by the operation mode (gas flows, fuel composition, current density, operating temperature, cell voltage, etc.). Multiphysics models are able to estimate profiles of critical variables (temperature, pressure, stress, etc.) and consequently can be used to concoct safe-operation parameter windows.

State-of-the-art (SoA) numerical models of SOC stacks generally include millions of control volumes / degrees of freedom (CFD / FEM) to be able to describe all the stack components, e.g., manifolds, flow channels, multiple cell layers etc. Even with SoA computer clusters, such models are computationally expensive, i.e., long computational times and energetically demanding to use for the purpose. Usually, only a repetitive unit of a stack (e.g. one cell with interconnect and frame) is chosen for modeling as a compromise. Yet, such assumption limits the model from studying specific stack challenges e.g., conditions at the end-plates, where the thermal profiles are different.

A three dimensional (3D) multiphysics stack model is presented here. The model is computationally efficient as it covers fast full stack simulations as well as long-term operation studies, without the need for computer clusters. The model is built upon the so-called *homogenization* concept, where the geometric features are embedded in an effective medium, i.e. detailed geometry (channels, interconnects, cells, etc.) is indirectly and not explicitly represented. By this method, all gas species coexist in one computational volume/element, and all the components are being represented by effective expressions reducing heavily the number of computational volumes/elements required. The model considers fluid flow, heat transfer, species transport, electrochemical reactions and ionic/electronic transport as well as thermal stresses.

The model background, i.e. the implementation of the *homogenization* concept regarding the different physics included, is presented here. Furthermore, this concept is verified and thermal profiles, current-density curves, and other profiles describing operation conditions are shown.

Understanding and Improving Ion Transport in Lithium Ion Battery Separators: Experiments & Simulations

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Li-ion battery (LIB) separators are porous membranes that electronically isolate the battery's electrodes yet allow ionic transport between them. As a result, the optimal separator design is a tradeoff between high cycling performance and battery safety [1]. Separator performance is commonly described by the ratio of the conductivity of the pure electrolyte, σ_0, divided by the conductivity of the separator filled with electrolyte, σ_{eff}, the so-called MacMullin number, N_M [2]. Thus, the MacMullin number also relates the diffusion coefficient of ions in the electrolyte, D_0, to the effective diffusion ions in the electrolyte filled separator, D_{eff}, and therefore can be described as ratio of the separator's tortuosity, τ, and porosity, ε [3],

$$N_M = \sigma_0/\sigma_{eff} = D_0/D_{eff} = \tau/\varepsilon \quad (1).$$

Equation (1) suggests three different approaches for determining the MacMullin number of separator membranes: (i) the ionic conductivities σ_0 and σ_{eff} can be measured using electrochemical impedance spectroscopy (EIS), (ii) the diffusion coefficients D_0 and D_{eff} are commonly determined from steady-state numerical diffusion simulations applying an ionic concentration gradient across the separator membrane, and (iii) geometrical approaches are used to determine τ and ε directly from separator microstructures. Surprisingly, the MacMullin number of most separators as measured by EIS is a factor 2-4 larger compared to values determined by steady-state diffusion simulations or geometrical approaches [4-5].

Here, we characterize a commercially available polyethylene separator using EIS and FIB-SEM tomography and determine its MacMullin number based on its ionic conductivities (σ_0 and σ_{eff} by EIS), and by steady-state diffusion simulations [5-7]. We show that EIS and diffusion simulations probe the separator at different length scales, and that the two methods consider certain geometric features such as non-interconnected voids (dead ends) in different ways [7]. This way two different MacMullin numbers are obtained by the two methods for the same separator. We show that a MacMullin number extracted from a fractal analysis and random walks (RWs) of the 3D microstructure shows good agreement with the EIS-derived MacMullin number and can be used to reconcile the different values from EIS and geometric microstructural analysis. We also investigate how the surface properties of separators, such as their surface charge or specific functional groups, influence their performance. For this purpose, we modified commercially available polyethylene separators with ultrathin layers (~1 nm) of selected polyelectrolytes. While these coatings do not alter the separators' geometry, they considerably change their wetting behavior and ion transport properties as we confirm by EIS measurements. Testing the cycling performance of cells assembled with the modified separators, we also show that polyelectrolyte-modified separators improve a battery's cell potential and C-rate capability. We demonstrate through complementary finite element simulations that this effect is primarily caused by increased transference numbers.

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Lithium-ion pouch cell with LCO/NCA cathode: Development and experimental validation of a P3D model with blend electrodes

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The use of blend electrodes in lithium-ion cells allows to tune macroscopic properties such as rate capability, energy density and lifetime towards application requirement. Yet, the design-performance relationship of such electrodes becomes highly complex. Numerical simulations and mathematical modeling are useful techniques to help understand the nonlinear processes within the cells [1].

Here we present the modeling, parameter identification, and validation of a commercial 0.35 Ah high-power lithium-ion pouch cell with LCO/NCA blend cathode and graphite anode. The transport model is based on a 1D+1D+1D (pseudo-3D or P3D) multi-scale approach [2]. Heat transport in the through-cell direction (1D, macroscale) is modeled as conductive process, mass and charge transport on the electrode-pair scale (1D, mesoscale) as diffusion and migration, and intraparticle transport of lithium atoms (1D, microscale) as Fickian diffusion with concentration-dependent diffusion coefficient. The electrochemistry model allows to couple an arbitrary number of different active materials and their charge-transfer reactions, representing blend electrodes and/or electrodes with particle size distribution. The model is implemented in the in-house multiphysics software package DENIS, the electrochemistry is based on CANTERA [3].

Model parameters are identified by a combination of both literature data from similar cells (half-cell data, solid-state and liquid-phase transport coefficients) and own experimental analyses (electrochemical impedance spectroscopy, T over t, V over C during CCCV cycles). The validity of the model is tested over a wide range of parameters for CCCV charge/discharge curves with different C-rates (0.05…10) and temperatures (5 °C…50 °C) as well as impedance behavior of the cell with different SOC levels (0 %…100 %) and temperatures (5 °C…50 °C). The simulations allow to identify distinct discharge regimes for the two cathode materials (LCO and NCA) and to quantify their individual contributions to overall cell impedance.

Acknowledgements:
This work was supported by DFG through the Research Training Group GRK 2218 SiMET (Simulation of Mechanical, Electrical and Thermal processes in lithium-ion batteries). It was partially supported by the Federal Ministry of Education and Research (BMBF) through the STABIL project (13FH004PX5).

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Modeling evaporation cooled fuel cells

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While Polymer Electrolyte Membrane Fuel Cells (PEMFC) are considered a potential replacement for internal combustion engines (ICE) by many in the automotive industry, they are still penalized by their cost and their complexity. One source of complexity comes from the need to keep the membrane humidified and cooled enough that it does not dry, which would stop the electrochemical reaction [1]. To tackle simultaneously cooling and humidification of the cell, a compact evaporative cooling scheme for PEFC was developed using modified gas diffusion layers (GDLs). A synthesis method developed at PSI [2] transforms some portions of these hydrophobic GDL into hydrophilic lines, which are able to wick water at low capillary pressures [3]. These hydrophilic lines, parallel and equally spaced, define pathways for liquid water separated from the gases, which avoids flooding of the cell. In our design, shown in Figure 1, liquid water is brought into the cell through channels in the anode flowfields and is distributed over the entire area thanks to the hydrophilic lines of the anode GDL. Convection driven evaporation takes place on the anode at the contact of the water-filled hydrophilic lines and the hydrogen flow. Last, some water evaporates from the lines and diffuses through the membrane to be removed by the cathode air flow. This scheme has the advantage of not adding any new layers to the structure of the fuel cell, which means a reduction in complexity and in size for a fuel cell stack.

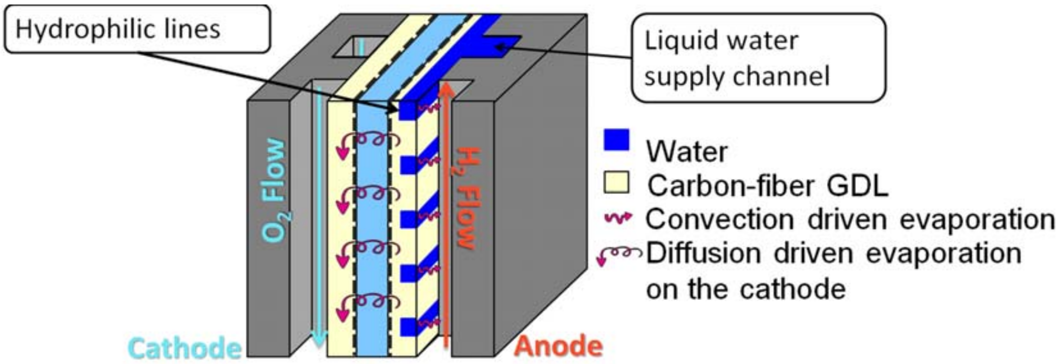

Figure 1: Evaporative cooling concept for PEFC developed at PSI

Previously, the evaporation in the fuel cell without electrochemical reaction was extensively studied thanks to a thermal test rig and with the help of neutron radiography. This allowed us to establish a simple 1D model to predict the evaporation rate as a function of the temperature, the anode and cathode mass flow rates, and the contact surface between the water in the hydrophilic lines and the gas mass flow [4] . However, the performances of the PEFC itself with evaporation cooling had not been extensively studied. Moreover the model was only tested for a small differential cell. Here we present how the evaporation acts on the performances of the cell itself and try to extrapolate on the workings of the evaporation cooling concept for a longer cell.

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Morphological and Topological Characterization of Porous Transport Layers for Proton Exchange Water Electrolysis

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Polymer electrolyte water electrolysis (PEWE) converts electrical energy in storable chemical energy by electrochemical splitting of water to hydrogen. PEWE technology allows for high pressure and dynamics, with high hydrogen purity at current densities up to more than 5 A/cm^2 [1]. For the energy storage application high efficiency is a key requirement.

To optimize the efficiency of electrolysis cells, the fundamental main losses of ohmic, kintic and mass transport have to be understood and quantified. The origin of mass transport losses are still not identified in the literature. The two phase flow of gas and water in the porous transport layers are expected to impact mass transport losses as it is reported that the structure of porous transport layers (PTL) affects the electrochemical performance [2].

This study aims to provide insight into the fundamental aspects of mass transport losses by systematic correlation of structural properties of PTLs with electrochemical performance. Two types of Titanium based PTL are characterized electrochemically and structurally. The morphological and topological properties of PTL are derived from X-ray tomographic microscopy (XTM) data. Tomographic microscopy was performed using a CT-scanner. Structural properties such as porosity and pore and particle size distribution (PSD) as well as surface properties are related to electrochemical performance with respect to ohmic and mass transport resistances.

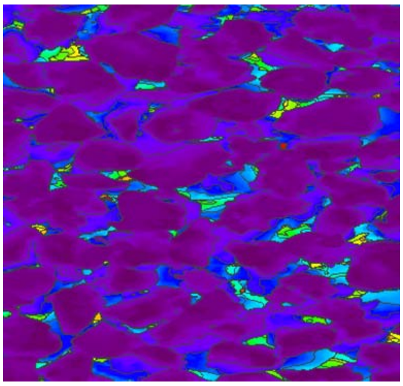

Figure 1: Surface topology of a porous transport layer based on X-ray tomographic microscopy.

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Perspectives of Thermal Recuperation for Fuel-Cell Vehicles

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Introduction

In recent years, there has been an increasing interest in alternative (i.e. non-fossil fuel) propulsion technologies. Basically, there are two major categories that can be distinguished: batteries and fuel cells, whereas each of them includes several subtypes. As there is currently no clear trend apparent, which of the two categories is the better one, each big car manufacturer develops his own solutions. Hence, there are currently many different systems with balanced amounts of advantages and drawbacks on the market.

Problem

Fuel-cell vehicles are a promising technology towards local zero-emission mobility. Some of the main advantages are:

- high efficiency
- carbon free when using H_2 and O_2
- can be refilled, does not need to be recharged
- no moving parts

The major disadvantages are:

- low density of fuel
- expensive materials
- safety concerns when transporting hydrogen
- high sensitivity on operating temperature and humidity

However, due to the high sensitivity on operating conditions, thermal management (especially cooling the fuel cells during operation) is vital for a secure and efficient operation of fuel cells. This also means that a lot of thermal energy is dissipated to the environment and that the energy is therefore irreversibly lost for the vehicle.

Method

This study examines the potential of using heat pipes and thermo-electric generators for the thermal management and for waste-heat recovery of PEMFCs (proton exchange membrane fuel cell). The thereby recuperated energy can be stored in an on-board LIB (lithium-ion battery) for later use.

The analysis is based on a multiphysical simulation model of an electric vehicle platform based on a VW GTE in Modelica. The vehicle is equipped with a hybrid energy storage, taking advantage of the benefits of both PEMFC and LIB technology. In normal operation, if the required power from the propulsion system is within a specific range, the vehicle is powered by the fuel cell only. If the target power is above the upper limit, the additional amount of power is withdrawn from the LIB. In contrast, if the power is below the lower limit, the LIB is either recharged by the PEMFC (if the state of charge of the LIB is low) or the vehicle is operated using only the LIB (if there is sufficient charge left). This operating strategy ensures that the propulsion system always works at the best possible efficiency.

The benefit of this simulative approach is that the mutual influence of each vehicle component, and especially of the PEMFC and LIB including thermal management, can be effectively investigated in a virtual environment.

Results

The results quantify the possible efficiency gain and thus, the increase in driving range, of an electric vehicle using the proposed hybrid energy storage and thermal management.

Determination of reaction kinetics for electrolysis cell models

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The potential of electrolyzers to exploit electricity excesses arising from renewable energy sources has led to an increased interest of researchers in electrochemical syntheses as power-to-chemicals concepts. During the development stage of such technologies, a model-based approach is more than a useful supplement to experiments, because numerical simulations can replace time- and cost-intensive experiments in many cases and moreover, they can be used to determine optimal points of operation for the final module. For this purpose, a mathematical model of an electrochemical cell is set up in this contribution. The model is spatially zero-dimensional, yet dynamic and the reaction kinetics is included in a detailed form.

The system of equations is based on molar and heat balances and the Butler-Volmer kinetics. It is implemented in the custom modeler of the Aspen Plus package for two reasons: First, this enables the use of Aspen's integrated activity coefficient models for thermodynamic consistency. Second, the model can be embedded as a unit operation into more extended flowsheet simulations this way, since commercial flowsheet simulators do not bring their own electrolyzer models.

Simulation results are only applicable if the underlying model is realistic in a sense that measured data has been used for validation and calibration. I.e. the model needs to be adjusted to experimental results before it can be used. In this respect, sensitivity analyses show, that the Butler-Volmer parameters are most influential and their accurate determination strongly improves the predictive quality. This is realized by direct fitting of the model equations to values of the product concentration measured as function of the feed rate. For this purpose, Aspen Plus is coupled to an external optimizer exploiting its COM interface. In a second approach, the reaction kinetics is determined from a combination of simulations and experiments on the rotating ring-disk electrode (RRDE) system [1], requiring the solution of a boundary value problem of the convection-diffusion equation to calculated local concentration profiles such as those in fig. 1. In both cases, the model is adjusted by minimizing the sum of squared differences between measured and simulated values for the same quantity while varying the kinetic parameters.

The methodology is demonstrated for the oxygen reduction reaction (ORR) mechanism. A pre-selection of the occurring chemical auxiliary reactions can be achieved using an analytical theory by Damjanovic et al. [2]. But in principle, it can be applied to arbitrary reaction mechanisms and catalyst systems.

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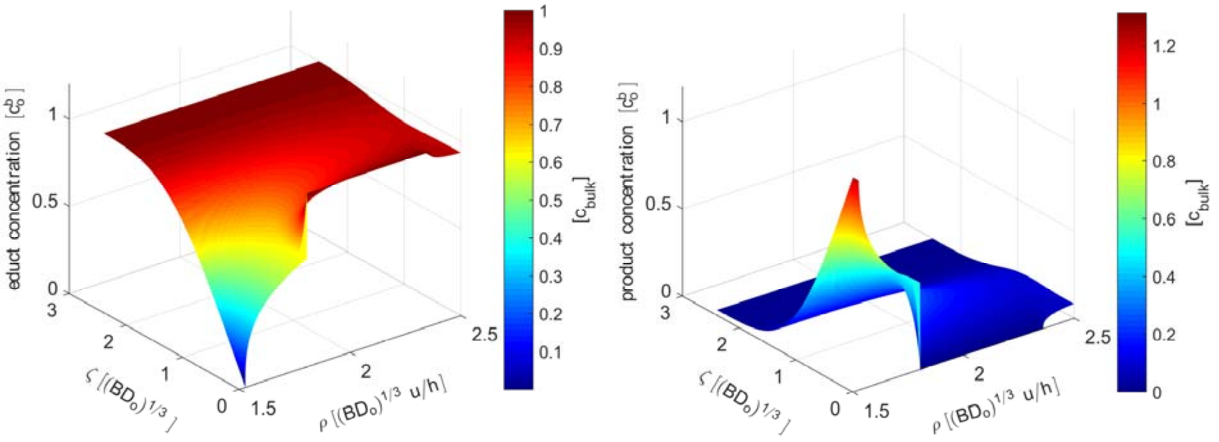

Figure 1: Spatial concentration profiles of the species to be reduced (left) and the reduced species (right) in cylindrical coordinates for the rotating ring-disk electrode (RRDE) system in dimensionless units. From the concentration gradient at z = 0, the electrical electrode currents are calculated, which are then set into relation to their experimental values.

Microscopic mass transport modelling for SOFC electrodes

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The kinetics of mass transport within the porous microstructure of solid oxide fuel cell (SOFC) electrodes are highly complex and consider multiple diffusion processes, such as ordinary diffusion, Knudsen diffusion and viscous fluid flow. In order to minimize the computational effort, the mass transport in the porous electrodes is described with homogenized modelling approaches in simplified geometries, namely dusty-gas model [1], binary friction model [2], or mean pore model [3]. One of the major challenges of the modelling approach is the need to characterize the complex microstructure by a set of homogenized parameters.

This study presents a numerical model describing the mass transport in a real porous microstructure of SOFC fuel electrodes. For this purpose, 3D microstructures were reconstructed by FIB-SEM tomography [4]. Subsequently, mass transport for a gas mixture of six components (H_2, H_2O, CH_4, CO, CO_2 and N_2) is simulated by spatially distinguishing between solid and gas phase. In order to take ordinary and Knudsen-diffusion into account, a novel model framework has been developed, which allows to variate diffusion coefficients in each finite element depended on wall distance.

Based on the model new insights into the (i) transport limitations within the porous microstructure due to pore shape and percolation of the pores can be obtained. Furthermore, this approach allows (ii) the approximation of the parameters needed for homogenized models and finally, the model can be employed (iii) to validate homogenized modelling approaches.

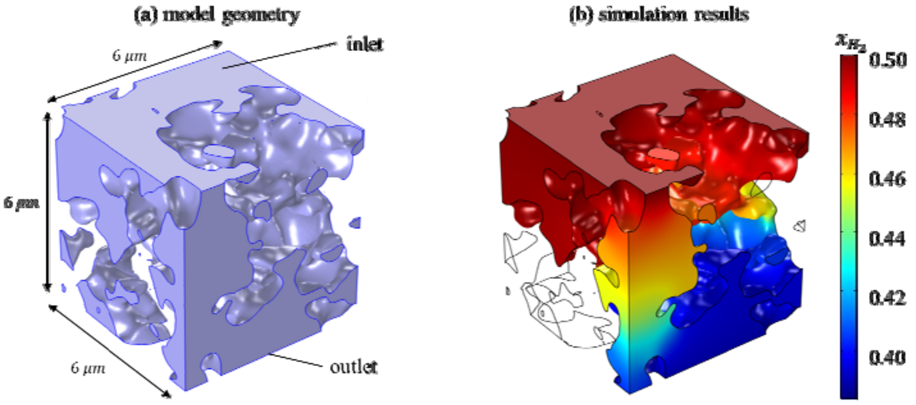

Figure 1: (a) Reconstructed porous microstructure of a Ni/YSZ anode substrate with an edge length of 6 µm. (b) Distribution of hydrogen within the pore phase. Simulation has been performed with a fixed gas composition of $xH_2 = 0.5$; $xH_2O = 0.3$ and $xN_2 = 0.2$ at the inlet and fixed molar in- and outflow of H_2 and H_2O at the outlet, respectively.

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Model-based performance analysis of Ni/8YSZ anodes

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The processes in Ni/8YSZ anodes, which limit the performance of solid oxide fuel cells (SOFCs), become accessible by Electrochemical Impedance Spectroscopy (EIS). Generally, we analyze the measured impedance spectra by the distribution of relaxation times [1] and with a subsequent Complex Nonlinear Least Square approximation we develop a physically motivated equivalent circuit model [2]. This approach enables us to identify and quantify all contributing loss mechanisms.

In most anode-supported SOFCs the anode consists of two porous Ni/YSZ layers, the supporting substrate (AS) with a thickness of 200 … 1000 µm and the anode functional layer (AFL) with a thickness of 5 … 20 µm (cf. Fig 1). The two layers are characterized by specified microstructure properties, which are volume fractions of nickel and YSZ, porosity, tortuosity and triple phase boundary length. These electrodes, especially the AFL, provide a large number of electrochemically active triple phase boundaries (TPB), where (i) the electrochemical oxidation of hydrogen couples (ii) the electronic conduction in the nickel matrix, (iii) the ionic conduction in the YSZ-matrix and (iv) the gas diffusion in the pores

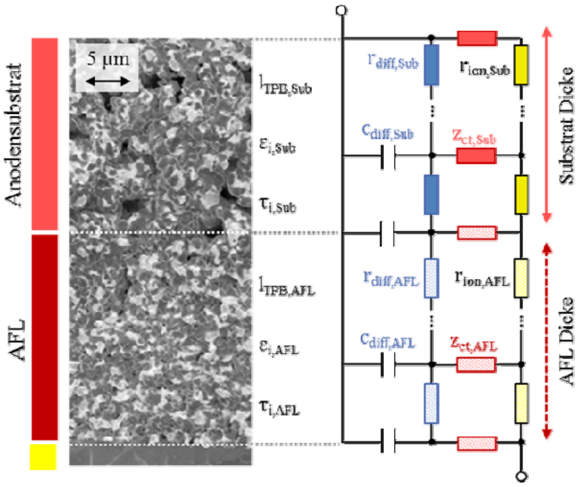

Figure 1. SEM-image of the anode functional layer and substrate and modelling scheme of the TLM.

In this study a physical meaningful modelling approach based on a three-channel transmission line model (TLM) was developed in order to describe all electrochemical and physical processes occurring in such a two-layer Ni/YSZ cermet anode (Fig. 1)). The required model parameters [3] are obtained from EIS measurements on patterned model anodes [4], 4-point DC conductivity measurements on electrolyte bulks and microstructure properties extracted from FIB-tomography for both layers [5]. This modelling approach is capable to correlate microstructure, cell geometry and material properties with the performance of Ni-based cermet anodes. As a consequence, a model based optimization of Ni/YSZ anodes comes into reach.

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Modeling the performance of Li-ion and Na-ion batteries

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Li-ion batteries (LIBs) are currently the most advanced technology for many energy storage applications because of their unrivalled energy density and reliable performance. Due to lower projected cost and environmental impact, Na-ion batteries (NIBs) are considered an adequate option to eventually complement the LIB technology.[1][2] Whereas it remains an open question whether NIBs will be able to compete with LIBs in terms of specific energy, they could be more suitable for applications with high power requirements. This is due to the fact that Na^+ has a smaller solvation shell than Li^+, which favours faster diffusion in the electrolyte and faster reaction kinetics at the electrode/electrolyte interface.[3][4] In this study, we employed a pseudo-two-dimensional (P2D) electrochemical battery model [5] to simulate discharge profiles of a LIB ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ vs graphite) and a NIB ($NaNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ vs hard carbon) for varying discharge rates. Ragone plots were obtained from the calculated discharge profiles using the below relationships for specific energy (E_s) and average specific power (P_s). J, w, and V(t) denote current density, battery cell weight, and discharge voltage, respectively.

$$E_s = \frac{J}{w}\int_{t=0}^{t_{cutoff}} V(t)dt \qquad (1)$$

$$P_s = \frac{J}{w t_{cutoff}}\int_{t=0}^{t_{cutoff}} V(t)dt \qquad (2)$$

Fig. 1 shows that the LIB displays superior specific energy at low power-to-energy (P/E) ratios, i.e. at low discharge rates. At higher P/E, the predicted NIB performance approaches the one of the LIB and at P/E ≈ 25 both batteries show similar specific energies. The presented work provides a critical evaluation of key parameters governing the performance of LIB and NIB cells.

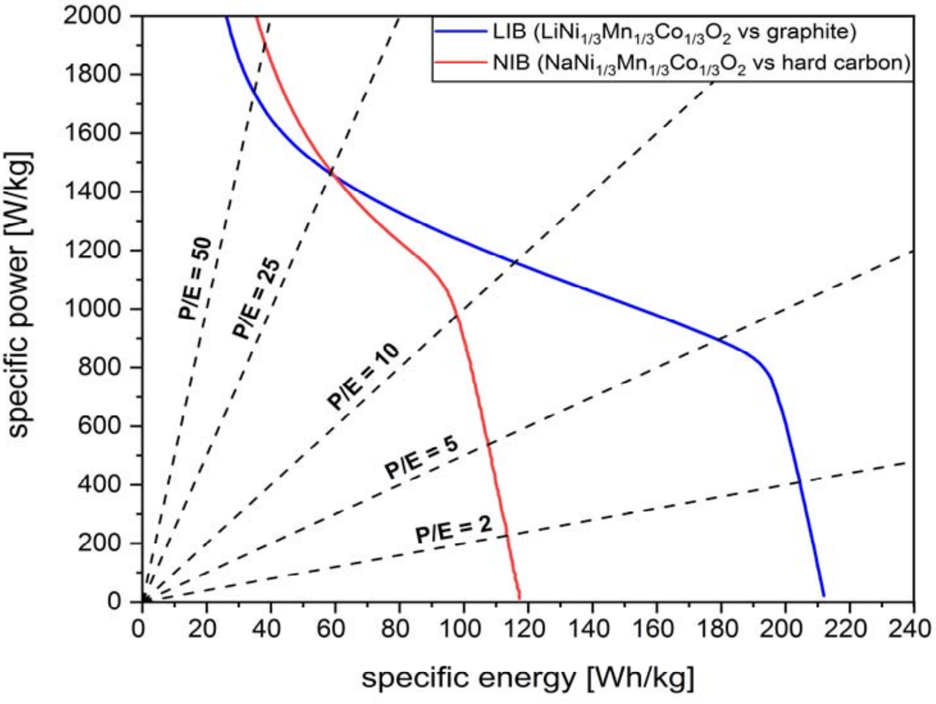

Figure 1: Ragone plots of LIB and NIB obtained with the P2D model. The anode thickness was set to 60 μm and the porosity of anode and cathode to 40%.

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XPEEM nanoscale surface spectroscopy applied to Li-ion battery electrodes: the case of NCA cycled vs. LTO

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Understanding the interactions between electrolyte and electrode for 5 V cathode materials is crucial for the further development of the next generation high energy density Li-ion (Li^+) batteries. Despite their enhanced capacity, such cathodes suffer from capacity fading during cycling, arising mainly from detrimental structural and surface changes, especially at potentials above 4.5 V vs. Li^+/Li [1]. A first undesired modification occurs when the active materials are in contact with air. The Li present in the near-surface reacts with atmospheric CO_2 to form Li_2CO_3 [2]. As a consequence, a surface structural reorganization occurs leading to a different structure with respect to the bulk. The evolution of the cathode surface continues upon cycling and further reactions are triggered as a function of the applied potential, including decomposition of Li_2CO_3, electrolyte oxidation, changes in oxygen content at the cathode surface, and dissolution of transition metals (TMs) in the electrolyte. These undesirable reactions affect the surface properties of the cathode and of the anode in the case of the presence of cross-talk between them. Despite all the significant efforts carried out to elucidate the nature and origin of the surface reactivity of the electrodes, a basic knowledge of the various reaction mechanisms occurring at the surface is still lacking. The scatter in the reported findings in literature is mainly caused by the surface complexity of the commercial electrodes (multiple particles, high roughness, and porosity) (Figure 1.a) and by the intrinsic limitations of the commonly used surface characterization techniques, especially the poor lateral resolution.

In this contribution we propose the use of X-Ray Photoelectron Emission Microscopy (XPEEM) in battery research as a surface sensitive technique, able to provide localized information on single particles of composite anode and cathode materials, while preserving their working environment as in commercial-like electrodes (Figure 1.b). The unique combination of high lateral resolution (below 70 nm) and X-ray absorption spectroscopy (XAS) capabilities will finally provide the missing piece to our understanding of the exact mechanisms of the electrolyte/electrode interactions.

The high voltage cathode material, $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) is investigated here, as a promising commercial material. The surface reactivity of NCA either after aging in air or upon cycling at potentials above 4.5 V is not fully understood yet. Moreover, the possible cross-talk between the cathode and the anode due to the migration/diffusion of TMs or organic/inorganic species is also not yet completely elucidated [3, 4]. Leanza et al. recently demonstrated that upon cycling only the surface of the $Li_4Ti_5O_{12}$ (LTO) particles is covered by a thin layer of electrolyte byproducts, while the conductive carbon remains surface layer free [5]. Thus, by cycling NCA vs. LTO (Figure 1.c) we will investigate the surface evolution on NCA as well the possible cross-talk by distinguishing species coming from the cathode (which will deposit all over the electrode) from the ones growing on LTO particles. *Post mortem* XPEEM measurements are performed on both cathode and anode by acquiring XAS on individual particles of the NCA, LTO and conductive carbon at different states of charge during the first cycle. The presence of electrolyte byproducts is monitored through the carbonate peak at 290.4 eV in the C K-edge spectra, while TMs oxidation states are evaluated by their respective L-edges. The C K-edge measured on the pristine electrode confirms the coverage of NCA particles with carbonated species (Figure 2.c), whereas the Ni and Co L-edges (Figure 2.a and 2.b, respectively) show the characteristic features associated to an oxidation state of +2, lower than the expected +3 state in the bulk. However, already at 3.78 V vs. Li^+/Li we find that all the surface species are decomposed, explaining the unexpected over potential “hump” observed in the galvanostatic curve (Figure 1.c). Additionally, we demonstrate that only Ni is oxidized to +4 at 4.9 V, while Co is not involved in the charge-compensation process. During the delithiation to 3V vs. Li^+/Li, Ni is reduced to +3 state and Co remain in +3. Similarly, we confirm the absence of any electrolyte oxidation byproducts deposited on the cathode surface after 3.78 V vs. Li^+/Li even after lithiation process, since no evolution is observed in the C K-edge (Figure 2.c). The C K-edge (Figure 3) and TMs L-edges (not shown) spectra measured on the LTO electrode are acquired separately on LTO and conductive carbon particles. Despite the expected surface layer on the LTO particles (Figure 3.a), no evolution can be observed on the conductive carbon (Figure 3.b), indicating that the cross-talk of oxidized electrolyte byproducts is not visible during the first cycle. Similarly, no traces of Ni or Co are detected in the first cycle. Further results will be presented for long cycling

In summary, we demonstrated the presence of a carbonate layer in the pristine NCA particles and its dissolution in the early stages of cycling. Thanks to the good lateral resolution of XPEEM we demonstrated that the surface layer does not reform on cycled NCA and that the oxidized electrolyte byproducts are not depositing on the anode during the first cycle. These results are determinant for obtaining a better insight on the mechanisms governing the electrolyte/electrode interface.

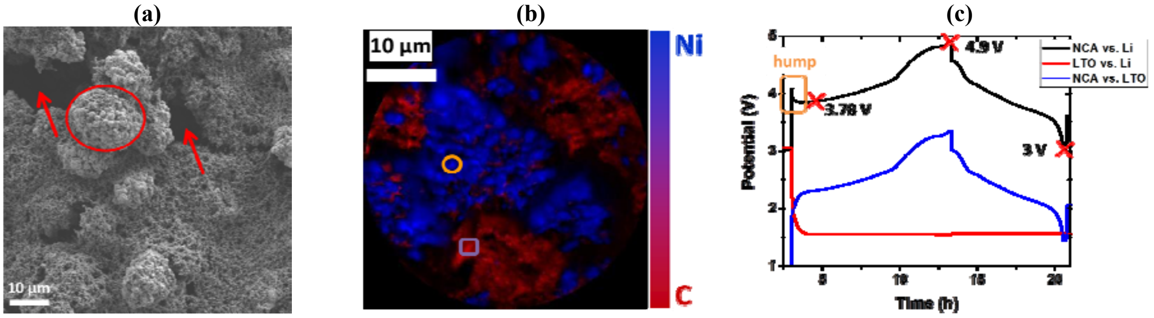
(a) (b) (c)

Figure 1: (a) SEM image of a pristine NCA electrode, showing the roughness and porosity of the surface as well as the active material particles (circle) and the conductive carbon. (b) XPEEM elemental contrast image performed on pristine NCA electrode at the Ni L-edge (blue, NCA particles) and the C K-edge (red, conductive carbon). (c) Galvanostatic profile performed in a 3-electrodes configuration, using metallic Li as reference. Red crosses show the potentials at which the *post mortem* analyses have been performed while the orange box shows the hump described in the text.

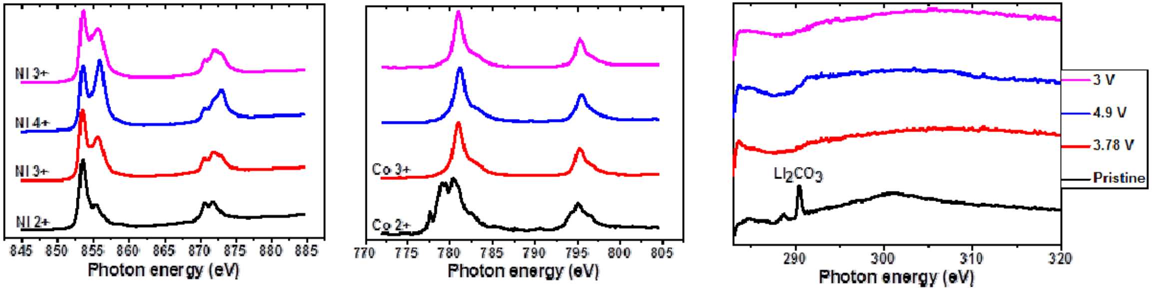
(a) (b) (c)

Figure 2: XAS spectra measured on NCA electrodes and acquired on NCA single particles (a) Ni L-edge, (b) Co L-edge and (c) C K-edge.

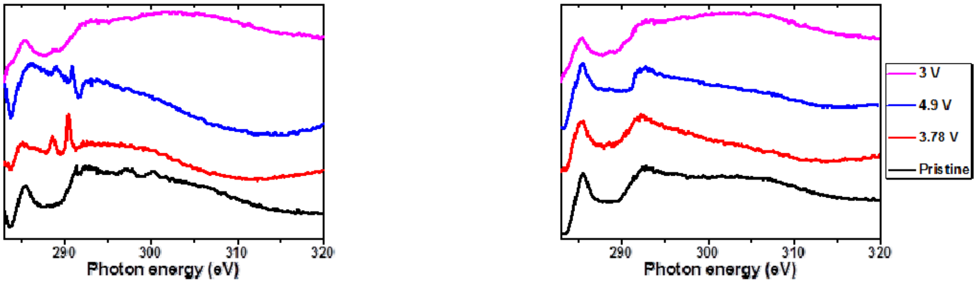
(a) (b)

Figure 3: C K-edge XAS spectra measured on LTO electrodes, acquired on (a) LTO and (b) conductive carbon particles.

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Thermodynamics and Electrochemical Impedance Spectroscopy - 1D Model of YSZ with blocking electrode

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Electrochemical impedance spectroscopy together with reliable models provides a powerful tool for analysing processes in solid oxide cells (SOC). Current state-of-the-art models [1, 2] describe the important underlying physical chemistry of the surfaces and the triple phase boundary. Despite their sophisticated structure, current models do not attempt to fully capture the impact of YSZ crystalline nature.

The presented model is derived within the framework of non-equilibrium thermodynamics [3, 4] which is a suitable tool for description of the fundamental processes in charged mixtures [5, 6, 7], especially on interfaces, such as surface adsorption, bulk and surface diffusion, electrochemical reactions and formation of charged double layers. Special attention is dedicated to the thermodynamically consistent derivation of the boundary conditions and to handling of the electrical double layer. Free energy function capturing crystalline structure of YSZ is constituted in order to obtain proper chemical potential of each component of considered system.

The contribution contains a derivation of 1D model for YSZ electrolyte with blocking electrode and also includes numerical solution of model partial differential equations with simulating electrochemical impedance spectroscopy.

The final aim of this research is to develop a thermodynamically consistent model of H2 | Ni | YSZ electrode in SOC. The created model will be implemented and validated due to numerical results which will be compared to currently known models for this type of electrode, and also to experimental data. During the comparison, physical model parameters will be found and therefore it will be possible to predict the behaviour of the electrode and determine the limiting processes in SOCs.

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Thermal-Electrochemical Modelling Approach to Study the Influence of Inhomogeneous Current Distributions

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Batteries in automotive applications have to meet multiple requirements that are often in conflict with each other, e.g. the ability to fast charge the battery in a couple of minutes without causing severe aging effects like plating. Hence, it is crucial for the development of battery systems to have knowledge of the underlying physical and chemical processes that are contributing to the degradation of lithium ion cells. In this work we present a modelling approach to simulate inhomogeneous temperature and current distributions using interpolation techniques to reduce the simulation time.

Modelling Approach

The highly nonlinear nature of the physical and chemical processes and the increasing amount of equations to be solved in a two-dimensional domain cause an exceeding number of degrees of freedom. These degrees of freedom need to be minimized to keep the simulation time in a reasonable range for daily simulation applications. At the same time, one would like to have the ability to simulate highly resolved models for validation purposes. To account for this, each physical domain can be assigned to an individual mesh. An electrochemical P2D-model for a graphite-NMC pouch cell based on the work of [1, 3] is coupled to an electrical FEM-triangular mesh created with the Matlab Tool DistMesh [2] as shown in Figure 1 and an individual thermal mesh with an underlying Krylov subspace reduced order thermal model originally built in ANSYS.

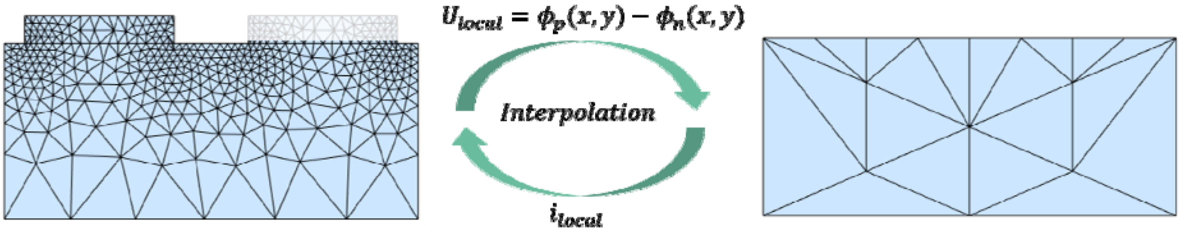

Figure 1: Highly resolved electrical mesh (left) and coarse electrochemical mesh (right). Interpolation of local potentials and current densities could e.g. be done via radial basis functions [4].

Implementation

The coupled nonlinear equation system is iteratively solved using the IDAS-Matlab interface sundials. Reasonable fast convergence is achieved by providing a partitioned functional jacobian for preconditioning using CasADi. Here the advantage is that it can be compiled to mex-code without the need of recompiling for a distinctive cell design later on as long as the parameters do not change.

Conclusion

Once set up, the model can be used in Simulink to evaluate different current and charging profiles in parallel. Compared to methods using numerically set up jacobians this approach is especially useful when many simulations of the same model with different initial and boundary conditions have to be run. It provides an insight into the electrochemical behaviour of large-scale pouch cells commonly used in automotive applications.

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Discrete Element Method for the modeling of lithium ion battery cathodes and the comparison with an analytical solution

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Discrete Element Method

In a multitude of engineering processes particles and their motion play a significant role. Lithium ion batteries (LIB) are composed of two electrodes consisting mainly of granular material. The static and dynamic behavior of such particulate structures is complex. However, for suitable designs, e.g. cathodes with determined mechanical or electrical properties, the knowledge of this behavior is of major importance.

An option for the simulation of the collective behavior of granular LIB cathodes is the so-called Discrete Element Method (DEM) [1]. For this method individual grain of active material and carbon black, the two main important components of the LIB electrode, are assumed as spherical particles with different sizes and differing mechanical properties, interacting with each other at contact areas mechanically and electrically.

In a first step of the simulation, a realistic initial structure has to be found. With the so-called Random Close Packing (RCP) [2] algorithm randomly distributed and overlap-free particle assemblies can be generated. Further, these initial structures are densified and arising percolated pathways are identified. For this densification process and the modelling of the occurring mechanical processes in the granular electrode the DEM has been proven as efficient tool. Treated as system of distinct interacting particles, each particle has its own mass, velocity, position and contact properties. Assuming a soft sphere approach, the total acting force on each particle can be determined in dependence of the existing contact properties and the overlap of two contacting particles. Further, from Newton's second law the acceleration of each particle can be gained and the motion of a particle can be tracked individually, updating its velocity and position.
For densified cathode structures the electrical resistance between particles can be calculated. Therefore, percolated pathways are identified and the electrical resistance is determined using the Resistor Network (RN) [3] approach. The resistance between particles is directly linked to the effective conductivity of the considered electrode structure.

Leap-Frog algorithm

Focusing on the mechanical DEM, the two main important parts are the choice of a realistic contact law as well as a proper numerical algorithm to solve the equation of motion. A common choice for the second task is the so-called *Leap-Frog* algorithm [4]. As special form of the *Verlet* algorithm, it calculates the positions for full time steps, whereas the velocity is directly calculated for the middle between time steps. To assure the accuracy of the numerical algorithm a comparison with an analytical solution can be used. Considering the impact of a frictional elastic sphere on a rigid wall, a suitable physical model can be found to describe the mechanical behavior. Solving the occurring differential equations of second order, an analytical formulation (cf. [5]) for the motion of the sphere can be gained.

Fig. 1 shows the results of the evolution of the tangential force calculated with the DEM code and the comparison to the analytically determined friction threshold in tangential direction. The good agreement of the two results shows that the used numerical algorithm works properly. The motion of the particle in normal and tangential direction, see Fig. 2, represents as well the high accuracy of simulation and analytical formulation.

Further, the comparison of the simulations with experimental tests (cf. [6]) is again in good agreement, see Fig. 3. This verifies that the analytical model is physically realistic. Thus, while the simulations fit to the analytically determined solution, the numerical code is also able to reproduce reality.

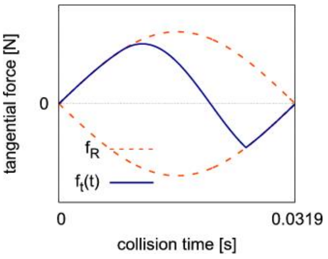

Figure 1: Development of tangential force (simulation) and comparison with friction threshold (analytical formulation), impact angle 10°

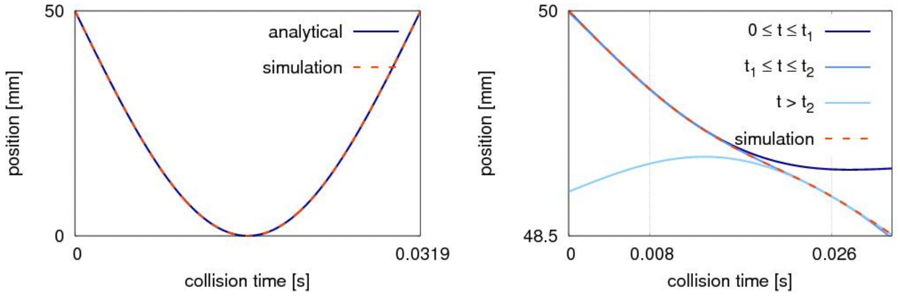

Figure 2: Evolvement of the position in normal (left) and tangential (right) direction of the impacting particle, impact angle 10°

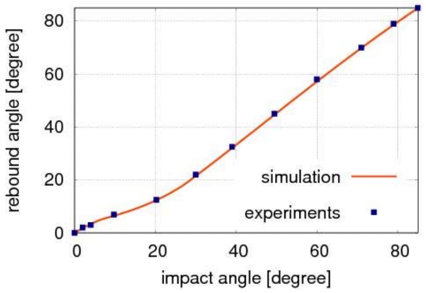

Figure 3: Tangential coefficient of restitution

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Cell Performance Determining Effects of the Anode Catalyst Layer Loading in Polymer Electrolyte Water Electrolyzers

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Water electrolysis is a key technology in future sustainable energy scenarios, since hydrogen as a universal energy carrier could promote the decarbonization of the energy economy, or even become its backbone in the context of a 'hydrogen economy'. Polymer electrolyte water electrolysis (PEWE) is a key technology in energy applications, where the possibilities of rapid start-up and dynamic operation with large differential pressures in compact units are of importance. The most prominent challenge for the market penetration of electrolyzers so far is its high costs, mostly associated with the cost of electricity. The fundamental understanding of the losses associated with PEWE is necessary to tailor the next generation of components for more efficient operation [1, 2].

The activation overpotential (η_{act}) is related to sustaining the redox reaction, specifically the sluggish oxygen evolution reaction (OER) in PEWE [3]. The largest contributing overpotential at high current densities ($j > 2$ A/cm^2) is the ohmic loss (η_{ohm}), stemming mainly from the limited proton conductivity of the polymer electrolyteproton exchange membrane (PEM) [4]. Reducing the PEM thickness is a viable path towards higher PEWE efficiency, but is limited due to higher gas crossover and increased susceptibility to mechanical failure. Besides the ohmic, mass transport overpotential (η_{mtx}) has been demonstrated to significantly contribute to the overall losses at high j in PEWE, in the range of 50 to 250 mV depending on the pressure and temperature [5].

The origin of the mass transport overpotential is still debated and unclear. In the fuel cell literature, a portion of the transport resistance has been attributed to the proton transport in the catalyst layers (R_{CLa}^{H+}). In this work we have systematically varied the anode catalyst layer (CL_a) loading in the range of 0.3 to 4.4 mgIr/cm^2 to determine its effects on the cell performance. Tafel breakdown of the polarization curve was conducted in accordance to the previous studies from Suermann et al. [4]. Increasing the loading resulted in lower η_{act}, but an overall lower catalyst layer utilization. The trend in decrease of the η_{mtx} is also observed with lower loadings, but only down to certain values. The cells were operated in H_2/N_2 mode [6] to quantify R_{CLa}^{H+} and a establish a correlation between R_{CLa}^{H+} , the loading and η_{mtx}.

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Phosphoric Acid Invasion in GDLs: Temperature and Concentration Dependence and Correlation to Phosphoric Acid Contact Angles

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High temperature polymer electrolyte fuel cells (HT-PEFC) use liquid phosphoric acid (PA) as the electrolyte which is imbibed in a polybenzimidazole membrane. PA is mobile within the pores of the membrane and, as was shown by Eberhardt et.al. [1], can also penetrate the pores of the gas diffusion layer (GDL) and be removed through the channels of the flow field under certain conditions. The consequential loss of electrolyte plays a significant role for fuel cell durability.

To examine the interaction between PA and GDL, an *ex-situ* experiment was developed, which allows injecting PA into GDLs under well-defined boundary conditions such as temperature, acid concentration and acid injection rate. The setup shown by Lamibrac et.al. [2] was adapted to be suited for PA invasion experiments at temperatures up to 160 °C.

The invasion of PA is performed by stepwise increasing the PA pressure. After each step, X-Ray tomographic microscopy imaging is performed at steady state. The resulting images are used to quantify the PA invasion in terms of PA saturation in the GDL as a function of the increasing capillary pressure. Results for PA invasion into a Toray GDL material, tested for different temperatures (room temperature to 160°C) will be presented and compared with the water invasion into the same GDL.

The study is supplemented with PA contact angle measurements on highly orientated pyrolytic graphite (HOGP) as well as on PTFE for different PA concentrations and temperatures. HOPG and PTFE were chosen to mimic materials present in the GDL.

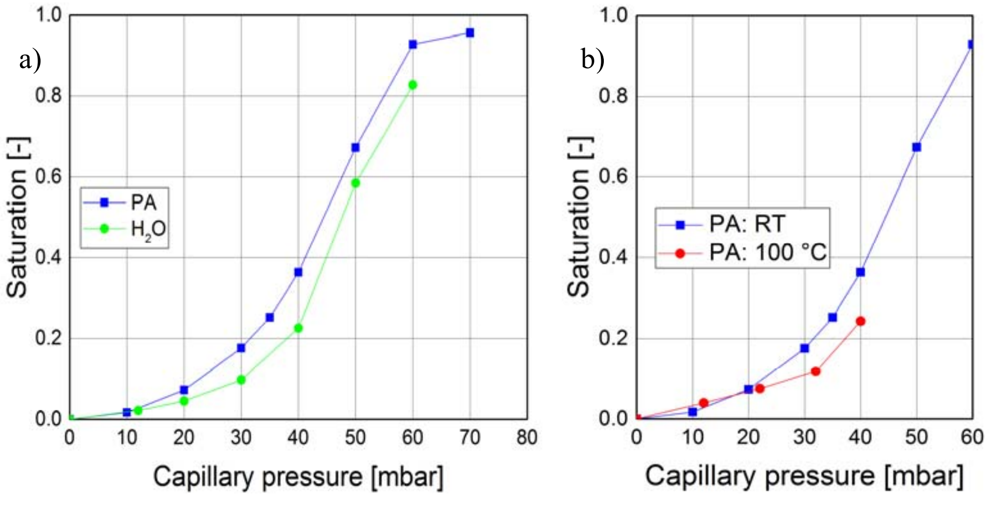

Figure 1a: Capillary pressure vs water and PA (85 w%) saturation at room temperature. Figure 1b: Capillary pressure vs PA (85 w%) saturation at room temperature and 100 °C.

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Coolant Induced Variable Temperature Flow Field for PEM Fuel Cells: Experimental Validation of the Developed CFD Model

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Performance of proton exchange membrane (PEM) fuel cells depends on water and heat management of the cell. High efficiency is only achieved if the proton conductive membrane is characterized by high membrane water content, which can be accomplished only if the relative humidity of the reactants is close to 100% along the anode and cathode side of the cell. Commercial PEM fuel cell stacks are operated in isothermal mode, i.e. the temperature gradient along the active area of the cell is minimized by relatively high mass flow rate of the coolant, therefore they require the addition of external humidifiers in order to achieve high efficiency. However, the implementation of external humidifiers results in occurrence of higher quantities of liquid water under transient operation and at higher currents in general, hindering the performance and limiting the operating range of the cell.

Newly developed concept presented in previous studies [1,2] termed "variable temperature flow field" is able to achieve high efficiency of the cell without the requirement for external humidification. The concept is illustrated in Figure 1. If isothermal temperature (60 °C) is set along the cell, and the reactants enter the cell at 0% relative humidity, 25 °C on the anode and 75% relative humidity, 30 °C on the cathode, the water produced inside the cell is not sufficient to achieve close to 100% relative humidity along the entire active area of the cell (Figure 1, left), therefore the performance of the cell is low. If the cell temperature is not isothermal, but instead resembles the water vapour saturation profile, it is possible to achieve close to 100% relative humidity along the entire active area of the cell (Figure 1, right).

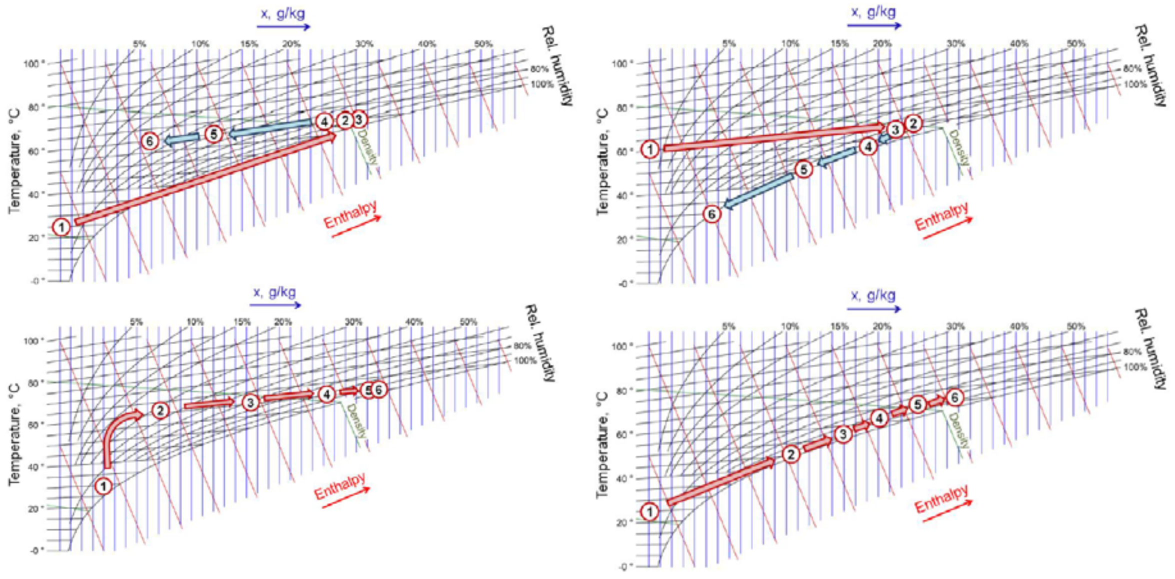

Figure 1: Mollier's h-x chart plot of relative humidity, temperature and enthalpy of reactants for isothermal (left: above anode side, below cathode side) and variable temperature flow field (right: above anode side, below cathode side) boundary conditions. Reactants are in counter-flow, 1 represents the inlet, 6 represents the outlet from the cell.

The concept was previously investigated using interactive combination of computational fluid dynamics (CFD) modelling and experimental validation on a segmented cell with capability of prescribing and maintaining the desired temperature of each segment via Peltier thermoelements. However, this concept was only applicable for laboratory size single-cell and simple flow field design.

This work presents a new method for establishing and maintaining the desired variable temperature flow field via coolant mass flow rate control. The method is developed using thoroughly calibrated and validated CFD model. The coolant enters the cell at ambient temperature, in co-flow with the cathode and counter-flow with the anode. The temperature of the coolant is gradually increased in the downstream direction as a consequence of internally produced heat. The resulting temperature profile, Figure 2, closely resembles the temperature profile extracted from Mollier's h-x chart.

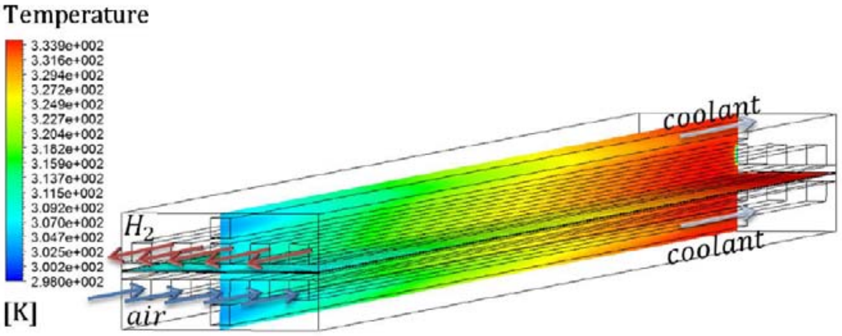

Figure 2: Temperature distribution along the cell for coolant induced variable temperature flow field.

The developed CFD model is validated in this work with experimental results for 3 different current densities, under isothermal operation and variable temperature flow field operation for 2 membrane-electrode assemblies with different membrane thicknesses (Nafion 212 and Nafion 115). The current density distribution along the cell and relative humidity profiles along the anode and cathode side of the cell obtained via CFD analysis are compared with the experimentally obtained data for all cases.

The method is able to prescribe and maintain the desired variable temperature flow field for different setups and outlines the importance of close monitoring of the temperature distribution inside the cell, as well as on the current collectors during operation. The application of coolant induced variable temperature flow field significantly minimizes the occurrence of liquid water inside the system, while the efficiency of PEM fuel cell operated with variable temperature flow field and completely dry reactants is higher than fully humidified isothermal operation, Figure 3.

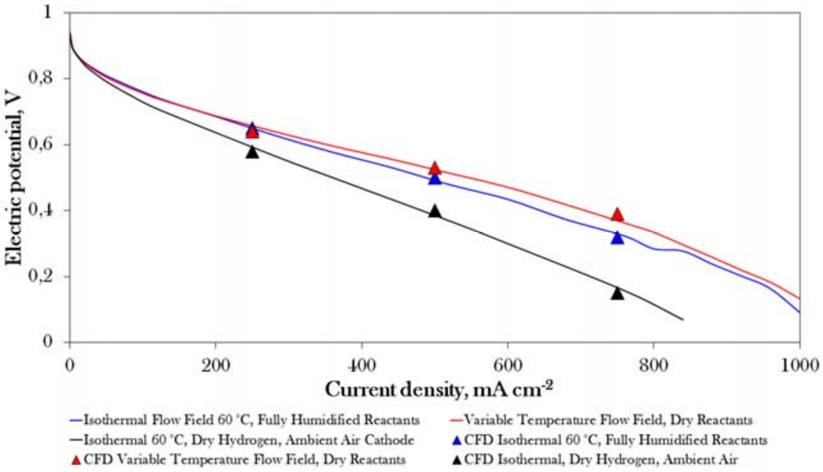

Figure 3: Comparison of polarization curves for different operating conditions, experimental data vs. CFD results.

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Sensitivity analysis of a stationary, macro-homogeneous, 1D through-plane membrane electrode assembly model for PEMFC

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A stationary, macro-homogeneous 1D through-plane model of a membrane electrode assembly (MEA) has been developed by Vetter and Schumacher [1]. In this work, a sensitivity analysis for various parameters of this MEA model is carried out. 48 parameters are identified that impact the model behaviour through the parameterization of transport properties, electrochemistry and through operating conditions. All parameters have been varied over a decade and compared to the initial value to study the impact on the simulated I-V characteristic. If the variation outranged physically reasonable limits, the latter are applied as variation boundaries.

In Fig.1 the variation of the electrical conductivity of the GDL σ_e is shown as exemplary simulation result. The value is varied between 130 and 1300 S/m to account for data of different products types, e.g. from SGL Carbon [2], Toray [3], Freudenberg [4] and Ballard [5]. Fig.1 (a) depicts the polarisation curve with cell voltage U in V plotted over the current density i in A/cm². Two reference points at static cell voltages of $U_{\mathrm{ref}} = 0.8$ V with $i_{\mathrm{ref}} = 0.3$ A/cm² (partial load) and $U_{\mathrm{ref}} = 0.6$ V with $i_{\mathrm{ref}} = 2.3$ A/cm² (full load) are used in order to evaluate the specific parameter sensitivity. The colour legend depicts the varied parameter values. It can be seen that a higher electrical conductivity leads to a higher current density at equal cell voltage. In Fig.1 (b), the relative deviation of the current density at static cell voltage $CCD = (i - i_{\mathrm{ref}})/i_{\mathrm{ref}}$ is plotted over the varied parameter range. Passing the 0-line indicates passing the default parameter value. Thus, positive deviation stands for an increase and negative deviation for a decrease in performance. The relative deviation at 0.6 V reaches from -0.1 to 0.2, indicating a high sensitivity of the model to σ_e at full load operation. For partial load conditions, the influence of σ_e is lower than at full load, as expected from the domination of activation losses over ohmic losses at low current densities.

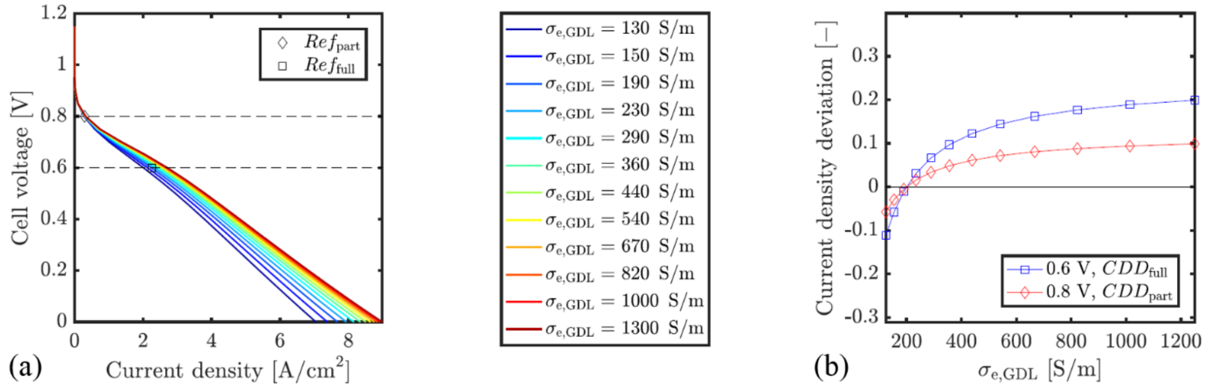

Figure 1: Sensitivity of the electrical conductivity σ_e at temperature $T = 65$ °C, pressure $p = 2.2$ bar and relative humidity $RH = 0.95$ at the anode and 0.9 at the cathode. The diagrams show the polarization curve (a) and the current density deviation (b). A diamond (◊) indicates the reference simulation at partial load (0.8 V) and a square (□) denotes the reference simulation at full load (0.6 V). An increase in σ_e leads to a performance gain.

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Influence of Porous Electrode Structure on Permeability – A Simple Study

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Hydrogen as energy carrier has received greater attention during recent times as growing number of countries are aiming to generate higher share of energy from renewable sources. Production of hydrogen by electrolysis of water using renewable energy involves different techniques. Polymer Electrolyte Membrane (PEM) water electrolysis is one of them. Research has been focused on optimizing the performance and reducing the cost of PEM electrolysers. According to Ayers et al. [1], for a 13kg/day electrolyser manufactured by Proton, 25% of the capital cost comes from flow field and separators. The porous transport layer (PTL), which is usually made from sintered titanium powder, plays a significant role in current flow and mass transport inside an electrolyser cell. To optimize the PTL it is necessary to understand how its structure influences the cell performance. To study this a simple pore network based model is used. Pore network model (PNM) represents porous materials as a network of connected pores and throats and it is usually employed for studying pore scale phenomena. In this work, using a simple cubic pore network to represent the PTL, the effect of pore and throat size distribution, porosity and connectivity on the hydraulic permeability is investigated.

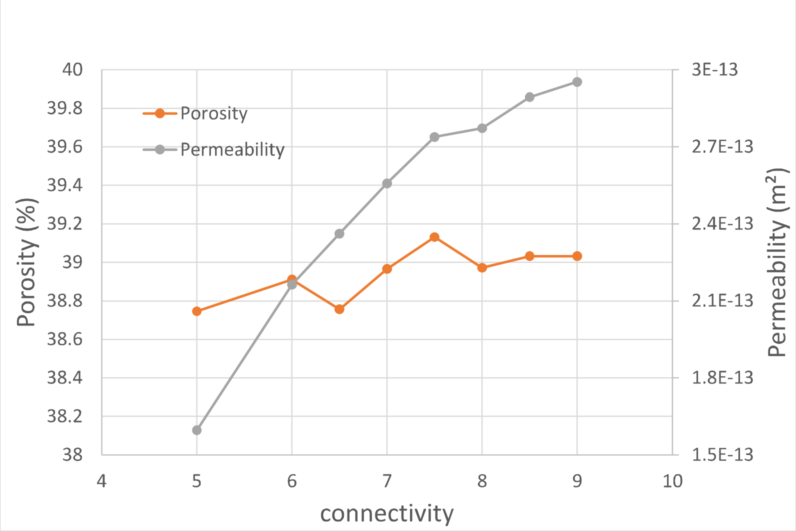

Figure 1: Change of permeability w.r.t. connectivity when porosity is kept constant

It is observed that even though permeability is directly related to porosity, pores and throats having higher sizes result in greater permeability for the same porosity. When porosity is kept constant the increase in permeability with respect to connectivity becomes gradual after certain range (Fig. 1). It is also observed that for the same range of porosity connectivity has a more prominent effect on permeability than the porosity of the sample. Relating this information with a combination experimental results and manufacturing process parameters can lead towards possibility of better PTL design.

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The inner and outer temperature distribution of Li-ion cells and modules with different thermal management applications

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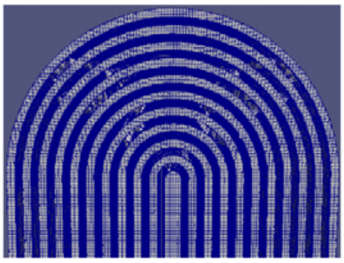
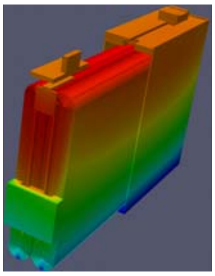
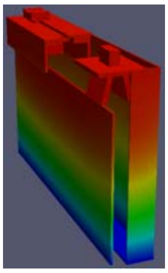
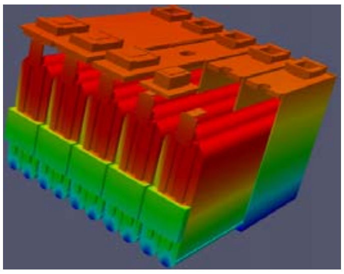
Increasing challenges for current Automotive Li-ion batteries, like fast charging capability, recuperation or charging at low temperatures, imply an increased complexity of the thermal management. The optimal design requires profound knowledge of the thermal processes within the batteries, since the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









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

Simulation of microstructure influences on the multi-physical transport processes in Li-ion cells

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The performance and lifetime of Li-ion battery cells are greatly determined by the individual and complex microstructure of their electrodes. Microstructure parameters like the active particle shape or size distribution, the binder distribution, the porosity or tortuosity, as a result of several different manufacturing steps, are crucial for the coupled electrical, electrochemical and thermal behaviour of a Li-ion cell. In addition, as the cell ages the microstructure itself changes along. Therefore, a profound knowledge of the influence of every aspect of the microstructure on the multi-physical coupled transport processes in the cell is necessary. Beside an experimental investigation of the electrode and cell behaviour the numerical simulation is an important tool to obtain a comprehensive understanding of the processes within the micro and meso scale of the cell and on this basis to analyse and predict the behaviour of Li-ion cells.

In this work a generic modelling approach is chosen to determine the individual impact of each modification parameter on the multi-physical transport processes and reactions on its own. Therefore, a Generic 3D Electrode Model (G3DEM) was developed to simulate the coupled electrical and electrochemical processes as well as the heat and mass transfer within the particle and electrode level of the cell.

The focus of this contribution is set on the behaviour of graphite based anodes, which show a strong deviation in their real microstructure from the often used modelling simplification of spherical particles with isotropic transport properties. A heterogeneous modelling resolution between the different solid phases and the liquid electrolyte phase of the anode were chosen to emulate the transport paths and limitations of the actual anode structure as accurate as possible. With the developed geometry creation routine a broad spectrum of anode structures can be automatically designed based on the desired microstructure parameters. Thereby, various particle shapes of the active material as well as different contact implementations between particles and the binder material can be considered. On the one hand, the developed model can be used to create generic replications of real microstructures based on experimental data. On the other hand, it can generate new microstructures resembling desired features and geometrical parameters for example defined particle size or binder distributions in the electrode.

An extensive simulation study is performed to investigate the influence of different microstructure aspects and crucial transport parameters (e.g. conductivity and diffusion) on the local and global cell behaviour. The individual impact of the most important variation parameters on the multi-physical transport processes will be shown. Based on these findings, limitations of the performance and critical conditions concerning degradation can be identified. Furthermore targeted optimisation approaches for the electrode structure can be investigated, resulting in an increased performance and lifetime of Li-ion cells.

3D-Simulation of thermal transport processes and characteristic heat sources in Li-ion battery cells

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Profound knowledge about the thermal behaviour of a battery cell is essential for improving the electrochemical performance, extending operational limits, e.g. maximum charge rate, and for better understanding of ageing phenomena. This is especially important for large-format automotive cells which have to face increasing challenges like inhomogeneous temperature distribution within the cells and fast charging applications. Experimentally, it is difficult to gain access to the inner temperature distribution and inhomogeneous heat generation. Therefore, thermal models are developed to provide important information about the cell behaviour and the complex interaction between heat transfer paths in the cell and various possible thermal management applications.

In literature, it is common to use 2D or 3D models with homogeneous material properties [1]. In this work, a 3D thermal model is developed where inner cell components like the metallic current collectors are heterogeneously resolved. Beside the main parameters for the heat equation (the anisotropic thermal conductivity and the heat capacity), the dynamic behaviour of the heat sources within the cell is determined. The heat sources are obtained by solving coupled simulations of the electrochemical and thermal processes. In the current level of the model development they are based on approaches from literature [2]. Therefore, information about the cell voltage, the open-circuit voltage and the change of the entropic heat, determined by experimental methods, are required. Further model refinement will address the local coupling of the inhomogeneous temperature field and the temperature sensitive electrochemical processes within the heterogeneously resolved inner cell geometry.

The model is used for investigations of the temperature distribution and the critical heat transfer paths as well as potential locations of hot spots. Moreover, the influence of different thermal boundary conditions, thus, various ways of managing the temperature inside the battery, are investigated.

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Experimental and numerical study on the effect of flow rate on the steady and transient response of all-vanadium redox flow battery

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All vanadium redox flow battery (VFB) is well-known as large-scale energy storage solution [1]. VFB research has been focused on performance improvement through component development [2]. However, there have been few studies conducted on VFB system characteristics. In this study, steady and transient responses of vanadium concentration, performance and efficiency according to flow rate variation are investigated both numerically and experimentally.

As the flow rate increases, the difference in vanadium ion concentration between reservoir and electrode is reduced, charging time is extended and storage capacity is increased. The non-dimensional flow rate, stoichiometric number (λ) is defined as the ratio of actual flow rate and theoretical flow rate. When λ is increased from 1 to 6, the changes in charge-discharge voltage, vanadium concentration in reservoir and electrode, SOC, efficiencies and overpotentials are investigated. V^{3+} and V^{4+} are increased due to self-discharge. This tendency becomes more dominant as flow rate increases. The charges in charge-discharge behavior and vanadium ion concentration caused by flow rate variation in transient operating state are studied and explained physically. The energy efficiency contours are plotted according to SOC and λ. The empirical equation for the maximum energy efficiency is suggested as a function of SOC, λ and current density.

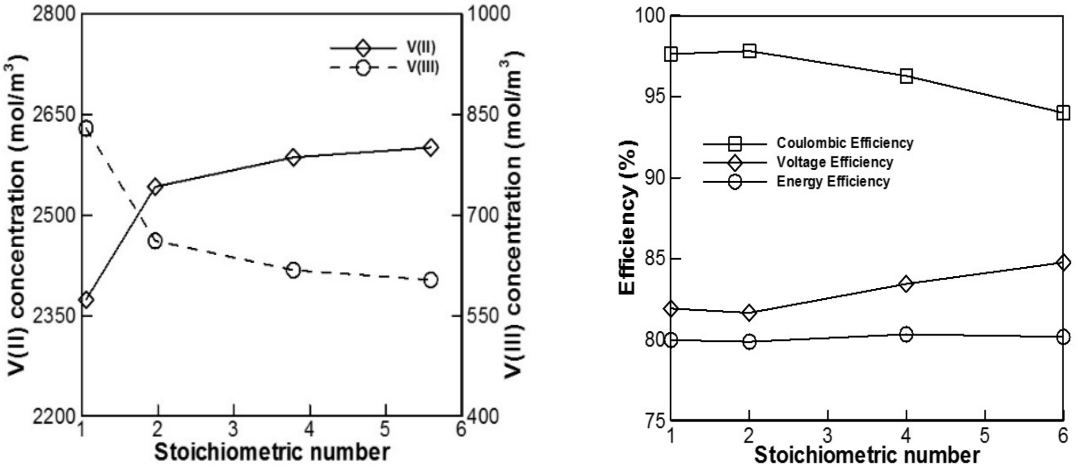

Figure 1: Variation of vanadium species concentrations and efficiencies depending on flow rate, charge and discharge current density = $75 mA/cm^2$.

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Engineering toolbox for flowfield plates with automated mesh generation

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Introduction

This work presents the development of an engineering tool for the evaluation of flowfields. The example application is the design of a flowfield plate for electrochemical hydrogen purification. Electrochemical hydrogen purification cells are membrane reactors that work like a combination of a fuel cell and an electrolyser. The goal of this device is to extract pure hydrogen from a gas mixture [1,2]. For this purpose the gas mixture is provided at the anode side where hydrogen is electrochemically converted to protons and electrons. The protons are transported to the cathode side by a suitable polymer membrane (e. g. Nafion). At the cathode side pure hydrogen is obtained by recombining protons and electrons. This process allows also to build up a pressure difference between anode side and cathode side. Thus, such an device can act as a gas separator and compressor for hydrogen [3,4].

Generation of the computational mesh

For the overall layout flow fields consisting of single or multiple serpentine channels are considered. The computational mesh is generated within the free software SALOME [5]. The geometry and mesh are constructed from generic building blocks which are able to create a wide range of serpentine flowfields. The object oriented coding in the programming language PYTHON allows to couple these small building blocks. The final script allows to freely choose parameters like width of flowfield, number of channels, channel width and mesh resolution.

First step: fast evaluation of overall flow characteristics

For the screening of different design options only the flow channels and the porous transport layer (gas diffusion layer, GDL) of a half cell are generated. The computational fluid dynamics simulations are performed by using the free software OpenFOAM [6]. A simple fluid mixture model is applied, where one component can be added or removed from the catalyst interface at the bottom of the porous transport layer. At this stage a homogeneous current density distribution is prescribed. An example of different flow field configurations is shown in Figure 1.

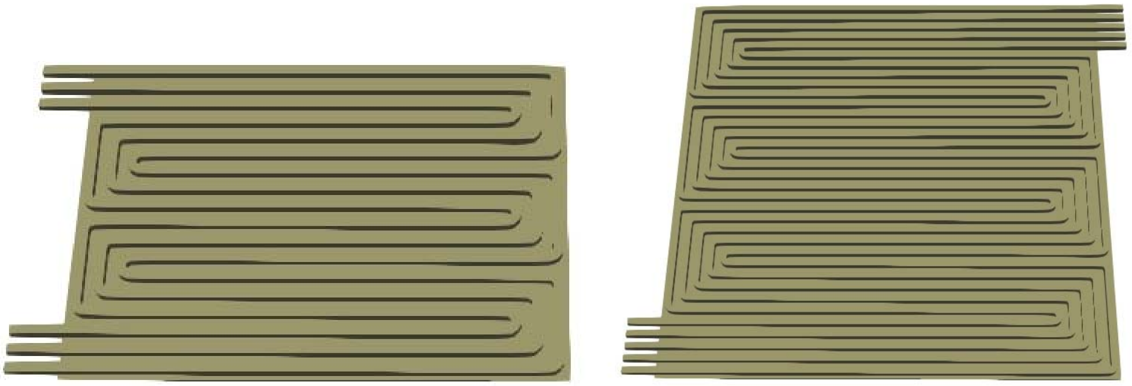

Figure 1: Serpentine flow fields with channels and ribs of 1 mm x 1 mm
Left: 3-fold serpentine (U confirguration) with an active area of 17 cm^2
Right: 5-fold serpentine (Z confirguration) with an active area of 49 cm^2

Second step: full electrochemical cell performance

For the computation of the electrochemical performance an existing fuel cell model for OpenFOAM is used [7], which is modified to simulate an electrochemical purification cell. This model requires the cell to consist of two flowfield plates (solid part), channel and GDL (fluid part) and membrane electrode assembly (solid part). The PYTHON script allows to generate the mesh for the complete cell with conformal meshes. The resulting mesh is used by the fuel cell model in OpenFOAM, where it is splitted into four different child meshes. Figure 2 shows an example for a small serpentine cell.

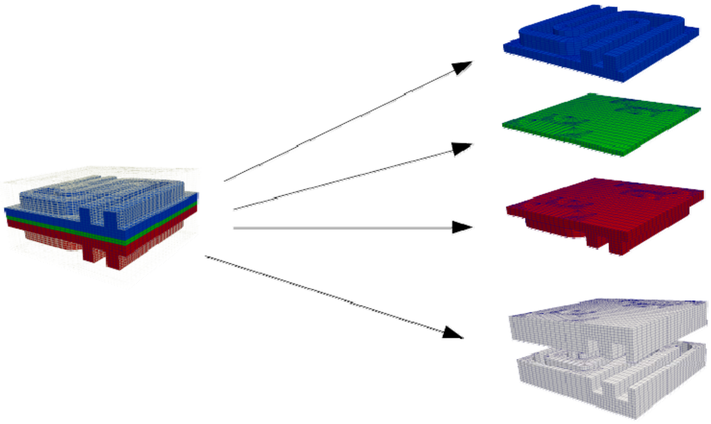

Figure 2: Computational mesh for the existing fuel cell model and internal splitting into four conformal child meshes

Acknowledgment

Financial support through the project MEMPHYS (membrane based purification of hydrogen systems) is acknowledged. This project is part of the European Union's Fuel Cells and Hydrogen Joint Undertaking (FCH2JU - Horizon 2020).

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Optimal selection of design points for power-to-methane system with solid-oxide electrolyzer swept by oxygen

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Converting renewable power to easy-to-store chemicals (particularly methane) for long time and large-scale storage, can potentially address the increasing penetration of intermittent renewable power. The performance of the electrolyzer used in power-to-methane (PtM) technologies largely determines the system performances. Therefore, solid-oxide electrolysis (SOE) with high electrical efficiency and good durability is promising to realize PtM systems with high efficiency.

Currently, durability testing and practical operation of SOE introduces air to the anode channel for sweeping the produced oxygen and cooling the cell/stack. The amount of air fed to the SOE affects the electrochemical performance and the overall system performance. As intensively discussed in our recent publication [1], by reducing the sweep-air feed, the system efficiency is continuously improved, but at the same time the methane production rate is decreasing; this is due to the fact that the operating current density of SOE must be lowered when stack cooling (by sweep air) is insufficient. When the sweep air is reduced to zero (SOE equivalent to pure oxygen production), the system achieves the highest efficiency but the lowest methane production, indicating that such a pure oxygen production mode of a SOE without any sweep gas may not be economically viable.

Therefore, in this paper, we investigated the optimal selection of design and operating points of a PtM system with the SOE swept by pure oxygen and delivering pure oxygen as a valuable by-product. For both steam- and co-electrolysis, we comprehensively and comparatively investigate several critical design issues: (1) system-level heat integration, (2) the impacts of operating variables (operating voltage, reactant utilization, anode/cathode feed ratio, and operating pressure of the methanation reactor and membrane) on system performances, and (3) the possibility of avoiding electrical heating, which so far is necessary in thermoneutral operating mode in order to close the heat balance (heat up the electrolyzer feeds to the required temperature). The results are expected to bring new system designs of a high efficiency SOE-based PtM system achieving high methane production even with pure oxygen production, which may further promote the integration of SOE-based PtM technologies with other pure oxygen- consuming industrial processes.

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Optimising lithium-ion cell design for plug-in hybrid and battery electric vehicles

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Increased driving range and enhanced fast charging capabilities are two immediate goals of transport electrification. However, these are of competing nature, demanding increased energy and power densities respectively. Finding the optimum trade-off between increasing the number of pouch-cell electrode pairs and maintaining sufficient electrode thickness can help in achieving application-specific design of power vs energy cells. Achieving this trade-off through iterative empirical testing of multiple layer choices is expensive and often produces sub-optimal designs.

We report a modelling methodology to rapidly and inexpensively design cells optimised for energy-density for electric vehicles – supplanting traditional, empirical methods. Our work is analogous to the computational screening of materials, wherein instead of materials, we efficiently screen pouch cell layer configurations at different initial and ambient temperatures for given load demands. The methodology is centred around a physics-based pseudo-two-dimensional electrochemical model that accepts inputs from vehicle simulations enabling battery pack engineers to maximise vehicle range. We exemplify the use of this methodology for a highly topical study, namely for predicting an optimum cell design to avoid lithium plating during fast charging, which can be the most challenging criterion to be met in battery design. Moreover, we present a novel, hybrid finite volume-spectral implementation of a pseudo-2D electrochemical model of a lithium-ion cell with the ability to directly accept input power densities, facilitating rapid and accurate searching of layer configurations.

The results, highly relevant to battery engineers and the wider automotive industry, illustrate the potential of application-tailored cell designs, and the importance of partnerships between automotive and cell manufacturers in producing efficient energy storage solutions. We show how thermal management system design can limit driving range for high charging temperatures. Of particular importance to materials scientists and cell manufacturers, we indicate that cell energy density can be increased by designing electrodes with better transport properties as an alternative strategy to pursuing materials with higher capacity.

An X-ray tomography investigation and modelling the effect of non-uniform cell compression of polymer electrolyte membrane fuel cell membrane electrode assemblies

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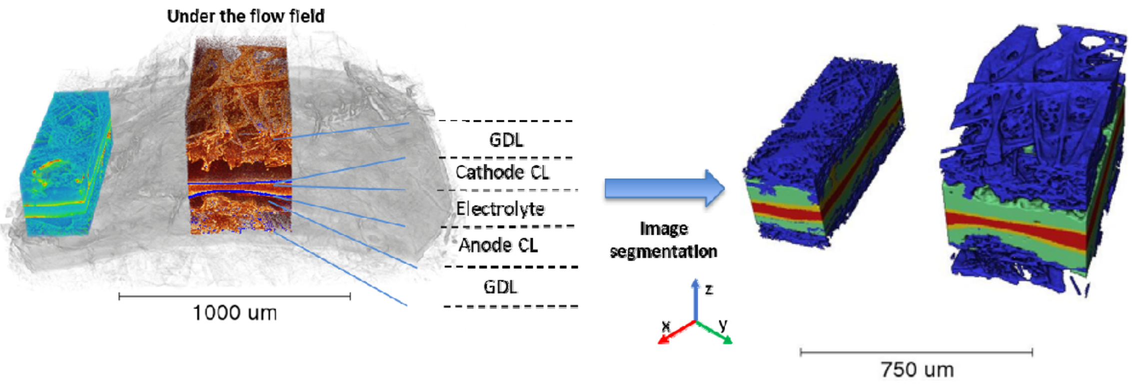
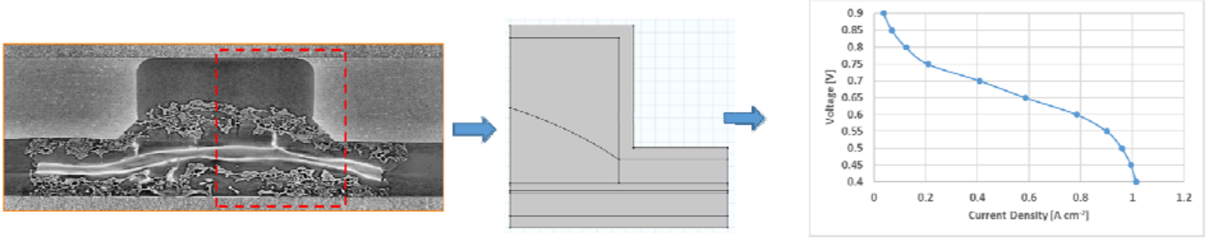
Polymer Electrolyte Membrane Fuel Cells (PEMFC) offer clean energy generation for a range of applications, including the stationary and automotive sectors. However, to accelerate large scale commercialization, further development work is required that will benefit from improved understanding of the processes occurring within operational fuel cells and optimizing cell design. The cell compression is one of the key parameters to be considered in deciding the optimal design of the fuel cell.

In order to optimize the cell performance it is important to investigate and understand the morphological structure of the different layers of a membrane electrode assembly (MEA) when under non-uniform compression. The cell compression process not only changes the morphological properties, such as porosity, tortuosity, and effective permeability, but also results in potential blocking of the flow-field. This poster reviews 3-D imaging techniques that quantifies microstructural properties of the MEA under variable inhomogeneous compression. This work also discusses the use of 'Representative Volume Analysis' (RVA) to generate effective parameters for modelling studies [1–3]. The developed finite element model discusses the effect on inhomogeneous cell compression on PEMFC performance, reactant distribution and water accumulation[4].



Figure

Figure 1: X-ray tomography investigation of inhomogeneous compression of the MEA and image segmentation to analyse effective parameters for an individual phases that can be used in the modelling



(a) (b) (c)

Figure 2: FEA model solving for partial blocking of the active channel using effective parameters derived from x-ray tomography analysis

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Multiphysics Modelling and Experimental Validation of a Segmented Microtubular SOFC: A Study of Interconnect Configuration

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Microtubular Solid Oxide Fuel Cells (μ-SOFC) are suited to a broad spectrum of applications with power demands ranging from a few watts to several hundred watts. μ-SOFC's possess inherently favourable characteristics over alternate configurations such as high thermo-mechanical stability, high volumetric power density and rapid start-up times. Computational modelling at the design level minimises cost and maximises productivity, giving critical insight into complex SOFC phenomena and their interrelationships. To date, models have been limited by oversimplified geometries, often failing to account for oxidant supply complexities, gas distribution within pores and radiative heating effects [1-3].

Here, a multiphysics Computational Fluid Dynamics (CFD) model of electrodes, electrolyte, current collectors and furnace is considered using COMSOL Multiphysics. The distribution of temperature, current density, electrical potential, pressure and gas concentrations throughout the cell are simulated.

The model is used to determine the effect of interconnect position and number of interconnects on the cell performance. The model is validated with a mirroring experimental setup using a segmented μ-SOFC. Results show good correlation with experimental data and the model is reliable for prediction of fuel cell performance within set parameters.

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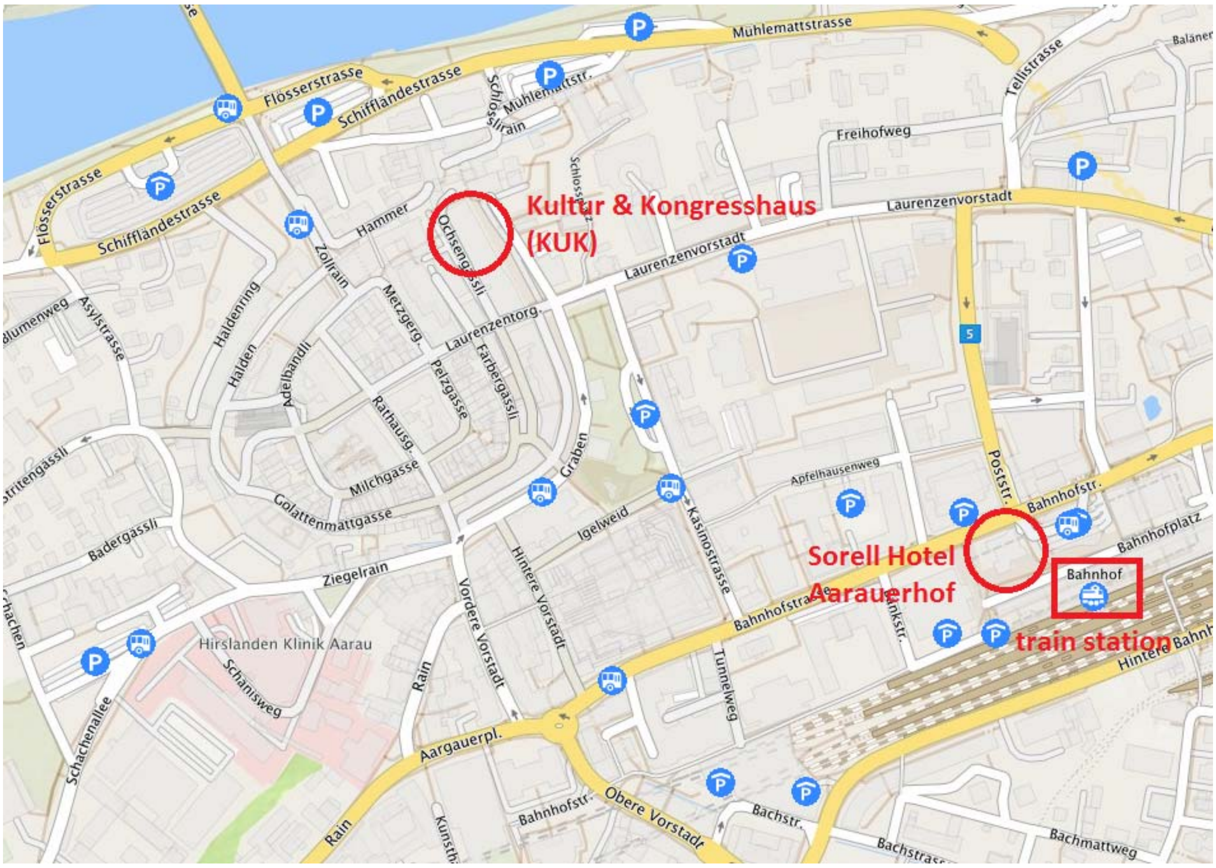

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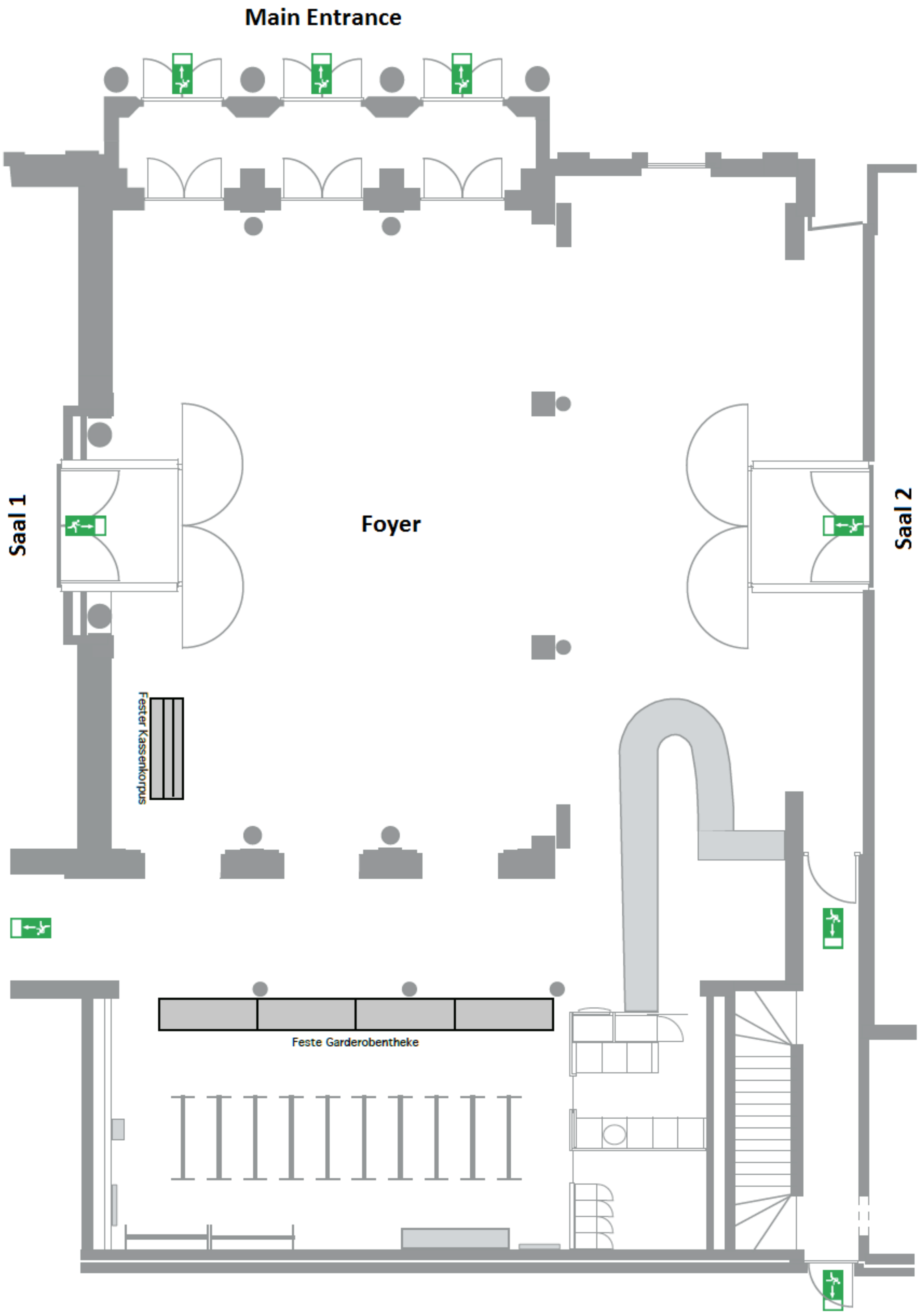

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