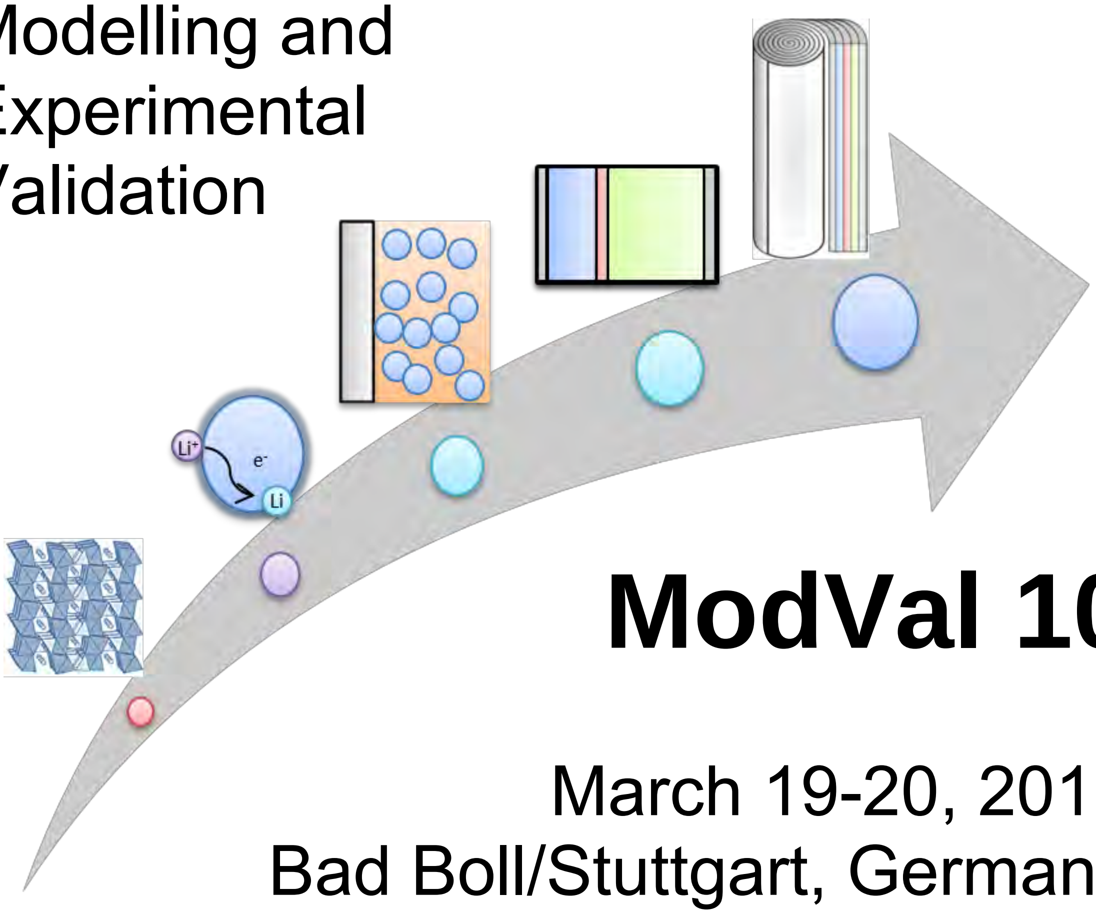
10th Symposium on Fuel Cell and Battery Modelling and Experimental Validation



ModVal 10

March 19-20, 2013
Bad Boll/Stuttgart, Germany

Hochschule Offenburg
University of Applied Sciences

ulm university universität uulm

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

Welcome to Bad Boll!

Welcome to the 10th Symposium on Fuel Cell and Battery Modelling and Experimental Validation – the ModVal 10. This year, ModVal celebrates its 10th anniversary, and to this occasion we are especially happy to have you as attendees in Bad Boll. The first symposium took place at ETH Zürich in 2004, followed by symposia at various locations in Germany and Switzerland ever since.

The aim of the symposium is to present and discuss recent advances that are related to the mathematical modelling of electrochemical cells, as well as experimental techniques for model validation. Having started as a symposium for fuel cells only, the vastly growing activities in battery research, together with the methodological similarities, have in the past two years attracted a significant amount of battery researchers to the symposium. This year's meeting has 120 registered participants, sharing a total of 57 oral and 19 poster presentations. These numbers show the continuously growing interest of both academia and industry in fuel cell and battery modelling as well as in validation techniques.

We thank the Helmholtz-Institute Ulm for Electrochemical Energy Storage (HIU) for financial support of this event.

We warmly welcome you to Bad Boll and wish you a pleasant and successful symposium!

Prof. Dr. Wolfgang G. Bessler	Prof. Dr. Axel Groß	Prof. Dr. Timo Jacob
Offenburg University of Applied Sciences	Ulm University	Ulm University
	Helmholtz-Institute Ulm (HIU)	Helmholtz-Institute Ulm (HIU)

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Monday, March 18, 2013

From 15:00	Hotel rooms available
From 18:00	Light dinner buffet and get-together

Tuesday, March 19, 2013

08:30-08:40	**Welcome from the organizers** W. Bessler, T. Jacob, A. Groß	
08:40-09:30	**Plenary lecture** **Measurement and modelling of solid oxide fuel cell and lithium battery electrode microstructure in three dimensions** **N. Brandon,** F. Tariq, K. Rhazaoui, V. Yufit, R. Clague, S. Cooper, F. Marquis, C. Adjiman, P. Shearing, Q. Cai, D. Eastwood, P. Withers, R. Bradley, P. Lee, J. Gelb Dept. Earth Science and Engineering, Imperial College London, UK; Dept. Chemical Engineering, UCL, UK; Dept. Chemical Engineering, Surrey University, UK; School of Materials, University of Manchester, UK; Xradia Inc, Pleasanton, CA, USA	
	Microstructure of fuel cells and batteries	**PEM fuel cell degradation**
09:40-10:00	**Microstructure degradation in SOFC anodes: Relationship between topological parameters and transport properties** **L. Holzer,** L. Keller, T. Hocker, O. Pecho, B. Münch,P. Gasser, B. Iwanschitz, M. Neumann, G. Gaiselmann, V. Schmidt Zurich University of Applied Sciences, Winterthur, Switzerland; Empa Dübendorf, Switzerland; ETH Zurich, Switzerland; Hexis SA, Winterthur, Switzerland; Ulm University, Germany	**Validation of membrane degradation mechanisms at defects by synchrotron based methods** S. Kreitmeier, A. Wokaun, **F. N. Büchi** Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
10:00-10:20	**Microstructural modelling for prediction of effective properties in porous SOFC electrodes** **A. Bertei,** C. Nicolella University of Pisa, Department of Civil and Industrial Engineering, Pisa, Italy	**Dead spot in a PEM fuel cell anode** **A. Kulikovsky** Research Centre Juelich, IEK-3, 52425 Juelich, Germany
10:20-10:40	**Solid oxide fuel cell effective conductivity modelling** **K. Rhazaoui,** Q. Cai , C. S. Adjiman, N. P. Brandon Imperial College of Science, London, UK; University of Surrey, Guilford, UK; Ulm University, Institute of Electrochemistry, Ulm, Germany	**Long-term test of PEM fuel cells with a dry cathode supply and daily EIS analyses** **S. Gößling,** P. Beckhaus, A. Heinzel ZBT GmbH, Duisburg, Germany
10:40-11:10	**Coffee break**	
	Microstructure of fuel cells and batteries	**PEM fuel cell degradation**
11:10-11:30	**Modeling of electrical and ionic transport properties in granular electrodes considering composition and mechanical loading** **J. Ott,** B. Voelker, Y. Gan, R. McMeeking, M. Kamlah Institute for Applied Materials (IAM-WBM), Karlsruhe Institute of Technology (KIT); Department of Mechanical and Environmental Engineering, University of California, Santa Barbara, USA; School of Civil Engineering, The University of Sydney, Australia	**PEMFC predictive modelling function of the operating mode and local conditions** **M. Gerard,** P. Schott, C. Robin CEA, DRT/LITEN, 17 rue des Martyrs, 38000 Grenoble, France
11:30-11:50	**Thermodynamically derived model and simulation of intercalation currents and overpotentials in Li Ion batteries** **A. Latz,** J. Zausch Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany; Institute for Technical Thermodynamics, DLR, Stutgart; Fraunhofer Institute for Industrial Mathematics, Kaiserslautern, Germany	**Elementary kinetic modeling for the investigation of direct-methanol fuel cell degradation** **T. Jahnke,** W. G. Bessler German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany; Offenburg University of Applied Sciences, Offenburg, Germany

11:50-12:10	**Graph-based simulated annealing: A hybrid approach to stochastic modeling of uncompressed graphite electrodes used in Li-ion batteries** **O. Stenzel,** D. Westhoff, I. Manke, M. Kasper, D. P. Kroese, V. Schmidt Ulm University, Institute of Stochastics, Ulm, Germany; Helmholtz Center Berlin, Institute of Applied Materials, Berlin, Germany; Centre for Solar and Hydrogen Research Baden-Württemberg (ZSW), Ulm, Germany; University of Queensland, Department of Mathematics, Brisbane, Australia	**Determination of catalyst layer resistance in alkaline fuel cell** **P. S. Khadke,** U. Krewer Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstraße 1, 39106 Magdeburg, Germany; Technische Universität Braunschweig, Institut für Energie- und Systemverfahrenstechnik, Franz-Liszt-Straße 35, D-38106 Braunschweig
12:10-12:30	**Phase-field model for the interplay of diffusion and stresses in electrode particles of lithium ion batteries** **M. Huttin,** M. Kamlah Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany	**A quasi 2D AC model for analysis of degradation of a high temperature proton exchange fuel cell** **A. Baricci**, G. Vendrami, S. Galbiati, A. Casalegno Politecnico di Milano, Department of Energy, Milano, Italy
12:30-13:40	**Lunch**	
	Microstructure of fuel cells and batteries	**Solid oxide fuel and electrolyzer cells**
13:40-14:00	**Modeling and simulation of fracture in active electrode particles of Li-Ion batteries using a phase field approach** **M. Klinsmann,** C. Miehe, M. Kamlah Robert Bosch GmbH, CR/ARM, Gerlingen-Schillerhöhe, Germany; KIT Karlsruhe, Institute for Applied Materials (IAM), Karlsruhe, Germany; Stuttgart University, Institute of Applied Mechanics, Stuttgart, Germany	**Oxygen exchange mechanism on mixed-conducting perovskites: Insight from experiment and theory** **R. Merkle,** L. Wang, Y. A. Mastrikov, E. A. Kotomin, M. M. Kuklja, J. Maier Max Planck Institute for Solid State Research, Stuttgart, Germany; Institute for Solid State Physics, University of Latvia, Riga, Latvia; Materials Science and Engineering Dept., University of Maryland, College Park, USA
14:00-14:20	**Synchrotron tomographic study on the inhomogeneous compression of gas diffusion layers in fuel cells** **C. Tötzke,** G. Gaiselmann, I. Manke, A. Hilger, T. Arlt, H. Markötter, F. Wieder, M. Osenberg, J. Bohner, W. Lehnert, V. Schmidt, A. Kupsch, B.R. Müller, J. Banhart Technische Universität Berlin, Department of Materials Science and Technology, Germany; Helmholtz-Zentrum Berlin für Materialien und Energie, Institute of Applied Materials, Germany; Ulm University, Institute of Stochastics, Germany; Forschungszentrum Jülich, Institute of Energy and Climate Research, Germany; BAM Federal Institute for Materials Research and Testing, Germany; RWTH Aachen University, Germany	**Current-voltage behaviour of SOFCs considering anode degradation** **V. Yurkiv,** J. Neidhardt, W. G. Bessler German Aerospace Center (DLR), 70569 Stuttgart, Germany; University of Stuttgart, 70550 Stuttgart, Germany; Offenburg University of Applied Sciences, 77652 Offenburg, Germany
14:20-14:40	**Stochastic modeling of fiber-based materials for varying degrees of compression** **G. Gaiselmann,** C. Tötzke, I. Manke, W. Lehnert, V. Schmidt Ulm University, Institute of Stochastics, Germany; Helmholtz Centre Berlin for Materials and Energy, Institute of Applied Materials, Germany; Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-3, Germany; RWTH Aachen University, Germany	**Computational modelling and simulation of a single micro tubular solid oxide fuel cell and stack for unmanned aerial vehicles** **B. Hari,** A. Dhir, W. Bujalski, R. Steinberger-Wilckens The University of Birmingham, School of Chemical Engineering, Edgbaston, Birmingham, United Kingdom
14:40-15:00	**Predicting effective transport properties in PEM fuel cells using pore-network simulations** E. Medici, V. Konduru, **J. S. Allen** Michigan Technological University, Houghton, Michigan, USA	**Electrochemical impedance modeling of gas transport and reforming kinetics in Ni/YSZ anodes for SOFCs** A. Kromp, **H. Geisler,** A. Weber, E. Ivers-Tiffée Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruher Institut für Technologie (KIT), Adenauerring 20b, D-76131 Karlsruhe / Germany; DFG Center for Functional Nanostructures (CFN), Karlsruher Institut für Technologie (KIT), D-76131 Karlsruhe / Germany
15:00-15:20	**Refinement on post-processing of 3D transport simulations in fibrous microstructure, using the lattice boltzmann method** **D. Froning,** J. Hofmockel, J. Brinkmann, G. Gaiselmann, U. Reimer, V. Schmidt, W. Lehnert Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-3, Jülich, Germany; Ulm University, Institute of Stochastics, Ulm, Germany; Modeling in Electrochemical Process Engineering, RWTH Aachen University, Germany	**Modeling and experimental validation of solid oxide electrolysis cells for hydrogen production** **V. Menon,** V. M. Janardhanan, S. Tischer, O. Deutschmann Institute for Chemical Technology and Polymer Chemistry; Helmholtz Research School, Energy-Related Catalysis; Institute for Catalysis Research and Technology; Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany; Department of Chemical Engineering, IIT Hyderabad, Andhra Pradesh 502 205, India
15:20-15:40	**Numerical Determination of Transport Properties of Catalyst Layer, Microporous Layer and Gas Diffusion Layer** **Jürgen Becker** Math2Market GmbH, Kaiserslautern, Germany	**Hybrid CFD and EIS model for SOFC and SOEC cell simulations** **V. Novaresio,** C. Graves, H. L. Frandsen, M. Santarelli Politecnico di Torino, Energy department, Turin, Italy; Riso DTU, Energy conversion and storage department, Roskilde, Denmark

15:40-17:10	Poster session with coffee break
	Computer aided material engineering of porous transport layers with GeoDict **J. Becker**, E. Glatt, A. Wiegmann Math2Market GmbH, Kaiserslautern, Germany; Fraunhofer ITWM, Kaiserslautern, Germany
	Opportunities for the validation of fuel cell modeling studies through the H2FC transnational access activities **P. Boillat**, P. Oberholzer, E. H. Lehmann Electrochemistry Laboratory, Paul Scherrer Institut (PSI), 5232 Villigen PSI, Switzerland; Neutron Imaging and Activation Group (NIAG), Paul Scherrer Institut (PSI), 5232 Villigen PSI, Switzerland
	Mass transport in gas diffusion electrodes with aqueous electrolytes for Li-O$_2$ batteries: Modeling and experiments **T. Danner**, B. Horstmann, D. Wittmaier, N. Wagner, W. G. Bessler German Aerospace Center, Institute of Technical Thermodynamics, Stuttgart, Germany; University of Stuttgart, Institute for Thermodynamics and Thermal Engineering, Stuttgart, Germany; Offenburg University of Applied Sciences, Offenburg, Germany; Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany
	Analysis of starvation and degradation effects in PEFCs under dynamic operating conditions **S. Enz**, M. Messerschmidt, J. Scholta Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Helmholtzstraße 8, Ulm, Germany
	Electrochemical impedance modeling of gas transport in Ni/YSZ anodes and associated gas channel for SOFCs **H. Geisler**, A. Kromp, S. Hirn, A. Weber, E. I. Tiffée Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruher Institut für Technologie (KIT), Adenauerring 20b, D-76131 Karlsruhe / Germany; DFG Center for Functional Nanostructures (CFN), Karlsruher Institut für Technologie (KIT), D-76131 Karlsruhe / Germany
	Time-dependent 3D impedance simulation formixed conducting SOFC cathodes **A. Häffelin**, J. Joos, M. Ender, A. Weber, E. I. Tiffée Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruher Institut für Technologie (KIT), Adenauerring 20b, D-76131 Karlsruhe / Germany; DFG Center for Functional Nanostructures (CFN), Karlsruher Institut für Technologie (KIT), D-76131 Karlsruhe / Germany
	Understanding the effects of the polysulfide shuttle in Li/S batteries: A one-dimensional continuum model **A. F. Hofmann**, A. Latz, W. G. Bessler German Aerospace Center (DLR), Institute of Technical Thermodynamics, Pfaffenwaldring 38-40, 70579 Stuttgart, Germany; Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage3, 89081 Ulm, Germany; Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany; Offenburg University of Applied Sciences, 77652 Offenburg, Germany
	Accurate calculation of tortuosity from velocity fields of transport simulations in porous media **J. Hofmockel**, D. Froning, J. Brinkmann, U. Reimer, W. Lehnert Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-3, Jülich, Germany; RWTH Aachen University, Germany
	Ab-initio study of processes on Li$_2$FeSiO$_4$ surfaces **N. Hörmann**, A. Groß Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, Albert-Einstein-Allee 11, 89069 Ulm, Germany; Ulm University, Institute of Theoretical Chemistry, Albert-Einstein-Allee 11, 89069 Ulm, Germany
	Investigation of the influence of membrane parameters on PEMFC performance using the CFD code AVL FIRE **L. Karpenko-Jereb**, C. Sternig, A. Theiler, C. Fink, R. Tatschl, P. Prenninger Graz University of Technology, Institute of Physical & Theoretical Chemistry, Graz, Austria; AVL List GmbH, Advanced Simulation Technology, Graz, Austria
	Modelling and simulation of the electrohydrodynamic equilibrium shape of nanochannels in PEM **S.-J. Kimmerle**, P. Berg, A. Novruzi University of the Federal Armed Forces at Munich, Neubiberg, Germany; NTNU, Department of Physics, Trondheim, Norway; University of Ottawa, Ottawa, Canada
	Case-specific adaptions of the DIRECTT algorithm to neutron and electron tomography of fuel cell components **A. Kupsch**, M. P. Hentschel, A. Lange, B.R. Müller, T. Arlt, C. Tötzke, H. Markötter, R. Grothausmann, I. Manke, S. Lück, V. Schmidt BAM Federal Institute for Materials Research and Testing, Berlin, Germany; Helmholtz Centre Berlin, Berlin, Germany; Ulm University, Institute of Stochastics, Ulm, Germany
	Microstructure influence on effective transport properties investigated by means of a stochastic simulation model **M. Neumann**, G. Gaiselmann, O. Pecho, L. Holzer, V. Schmidt Ulm University, Institute of Stochastics, Ulm, Germany; Zurich University of Applied Sciences, Institute of Computational Physics, Winterthur, Switzerland
	Mathematical modelling of direct ethanol fuel cells including free and adsorbed intermediate species **J. Sánchez-Monreal**, P. A. García-Salaberri, M. Vera Dept. de Ingeniería Térmica y de Fluidos, Universidad Carlos III de Madrid
	Structural and dynamical properties of Li-Ion batteries studied by various NMR techniques **M. Scheuermann**, R. Heinzmann, S. Indris Karlsruhe Institute of Technology, Karlsruhe, Germany; Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany
	A simplified model for O$_2$ transport and reduction kinetics in porous cathodes of Li-O cells **T. Schied**, F. Scheiba, H. Ehrenberg Technische Universität Dresden, Fakultät Maschinenwesen 01062 Dresden, Germany; Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e. V., Helmholtzstraße 20, 01069 Dresden; Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany; Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage 3 , Albert-Einstein-Allee 11, 89081 Ulm, Germany
	Simulation and modelling in a SOFC/GT hybrid power plant **M. Steilen**, M. Henke, C. Willich, J. Kallo, K. A. Friedrich German Aerospace Center, Institute of Technical Thermodynamics, Germany

	Numerical simulation and experimental validation for thermal runaway on lithium-ion cells **N. Tanaka**, J. Mehne, W. Nowak, M. A. Danzer, H. Döring, W. G. Bessler German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany; University of Stuttgart, Institute for Modeling Hydraulic and Environmental Systems, Stuttgart, Germany; Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Baden-Württemberg (ZSW), Ulm, Germany; Offenburg University of Applied Sciences, Offenburg, Germany
	Preliminary physical model of DMFC anode impedance **M. Zago**, A. Baricci, F. Bresciani, A. Casalegno Politecnico di Milano, Department of Energy, Italy
	Simulation and parametric analysis of a power system equipped with a SOFC stack **B. Zakrzewska**, P. Pianko-Oprych, Z. Jaworski West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Institute of Chemical Engineering and Environmental Protection Processes, al. Piastow 42, 71-065 Szczecin, Poland
	Mathematical Modeling Tools for Improving Lithium-Ion Battery Technology **T. G. Zavalis**, M. Behm, G. Lindbergh KTH Royal Institute of Technology, Stockholm, Sweden
17:10-18:00	Plenary lecture Mathematical modeling of lithium-Ion batteries R. E. White University of South Carolina, Dept. of Chem. Engineering, Columbia, SC 29206
19:00	Conference dinner

Wednesday, March 20, 2013

		Lithium-ion and post-Li-ion batteries
08:30-08:50	***Invited lecture*** **Model validation for model development in electrochemistry** **A. Badinski**, T. J. Schmidt, R. Lee, S. Bräuninger BASF SE, Scientific Computing, Carl Bosch Straße, Ludwigshafen, Germany; Paul Scherrer Institut, Electrochemistry Laboratory, Villigen, Switzerland	**From conventional vanadium redox flow batteries to vanadium oxygen fuel cells – modeling and simulation** **F. Wandschneider,** P. Fischer, J. Tübke, H. Nirschl Fraunhofer Institute for Chemical Technology, Department of Applied Electrochemistry, Karlsruhe, Germany; Karlsruhe Institute of Technology, Institute for Mechanical Process Engineering and Mechanics, Karlsruhe, Germany
	Microstructure of fuel cells and batteries	
08:50-09:10	**Influence of feed gas humidity and current density on the 3D water distribution in PEFC** **J. Eller,** J. Roth, R. Gaudenzi, S. Irvine, F. Marone, M. Stampanoni, A. Wokaun, F.N. Büchi Electrochemistry Laboratory, Paul Scherrer Institut, Villigen, Switzerland; Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland; Swiss Federal Institute of Technology, Zürich, Switzerland	**Modeling crystallization in lithium-oxygen batteries** **B. Horstmann,** T. Danner, W. G. Bessler German Aerospace Center, Institute of Technical Thermodynamics, Stuttgart, Germany; University of Stuttgart, Institute for Thermodynamics and Thermal Engineering, Stuttgart, Germany; Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany; Offenburg University of Applied Sciences, Offenburg, Germany
09:10-09:30	**2-Phase fuel cell model based on discrete water path network model** **R. Alink**, D. Gerteisen Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany	**3D CFD simulation of lithium-air batteries based on electrochemical models** **C. Fink,** T. Traußnig AVL List GmbH, Graz, Austria
09:30-09:50	**Distinction of liquid water and ice based on dual spectrum neutron imaging** **J. Biesdorf,** P. Boillat, P. Oberholzer, F. Bernauer, A. Kästner, P. Vontobel, E. Lehmann, T. J. Schmidt Electrochemistry Laboratory, Paul Scherrer Institut (PSI), 5232 Villigen PSI, Switzerland; Neutron Imaging and Activation Group (NIAG), Paul Scherrer Institut (PSI), 5232 Villigen PSI, Switzerland	**Low-temperature charging of lithium-ion cells part I: Electrochemical modeling and experimental investigation on degradation behavior** **S. Tippmann,** D. Walper, B. Spier, W. G. Bessler Deutsche ACCUmotive GmbH, Neue Str. 95, D-73230 Kirchheim/Teck; Offenburg University of Applied Sciences, Offenburg, Germany
09:50-10:10	**Modified PNP-Stokes equations for electro-kinetic flow in PEM nanopores** **P. Berg,** B. E. Benjaminsen NTNU, Department of Physics, Trondheim, Norway	**Low-temperature charging of lithium-ion cells part II: Model reduction and application** **J. Remmlinger,** S. Tippmann, M. Buchholz, K. Dietmayer Ulm University, Institute of Measurement, Control, and Microtechnology, Ulm, Germany; Deutsche ACCUmotive GmbH & Co. KG, Kirchheim/Teck, Germany
10:10-10:40	**Coffee break**	
	Fuel cell stacks and systems	**Lithium-ion batteries**
10:40-11:00	**3D model of a SOFC stack using porous media approach** **G. Ganzer,** J. Schöne, A. Pönicke, W. Beckert Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany	**From micro to macro – modeling and simulation of lithium ion batteries on multiple scales** **J. Zausch,** V. Taralova, M. Taralov, O. Iliev, A. Latz Fraunhofer Institute for Industrial Mathematics, Kaiserslautern, Germany; Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany; DLR, Institut für Technische Thermodynamik, Stuttgart, Germany
11:00-11:20	**Cr_2O_3 scale growth rates on metallic interconnectors derived from 40'000 hours solid oxide fuel cell stack operation** **M. Linder,** T. Hocker, L. Holzer, B. Iwanschitz, A. Mai, J. A. Schuler Zurich University of Applied Sciences, Winterthur, Switzerland; Hexis AG, Winterthur, Switzerland	**Critical review of parameterisation methods for equivalent circuit based, spatially resolved models of lithium-ion cells** **S. Stumpp,** L. Kostetzer, C. Günther, E. Rudnyi, M. A. Danzer Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg, Ulm, Germany; CADFEM GmbH, Grafing bei München, Germany
11:20-11:40	**One dimensional modeling of an SOFC system with discretisation in flow direction** **S. Wahl,** A. G. Segarra, P. Horstmann, M. Carré, W. G. Bessler, A. K. Friedrich, F. Lapicque Robert Bosch GmbH, Schwieberdingen, Germany; Offenburg University of Applied Sciences, Offenburg, Germany; German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany; LRGP, CNRS – Université de Lorraine, Nancy, France	**Electrochemical impedance spectroscopy on complete Li-ion-battery cells: Internal interfaces and influence of state-of-charge and cycle number** **S. Indris,** N. Schweikert Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany; Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany

11:40-12:00	**Development of HT-PEFC stacks supported by modelling and simulation** **W. Lehnert,** L. Lüke, M. Kvesić, D. Froning, U. Reimer, H. Janßen Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-3: Electrochemical Process Engineering, D-52425 Jülich, Germany; Modeling in Electrochemical Process Engineering, RWTH Aachen University, Germany	**Towards a computational method for advanced battery systems supported by experimentally determined parameters** **A. Ehrl,** J. Lee, N. Tsiouvaras, H. A. Gasteiger, V. Gravemeier, W. A. Wall Technische Universität München, Institute for Computational Mechanics, Munich, Germany; Technische Universität München, Chair of Technical Electrochemistry, Munich, Germany
12:00-13:10	**Lunch**	
13:10-14:00	**Plenary lecture** **Modeling and diagnostics of low Pt loading polymer electrolyte fuel cells** **C.-Y. Wang** Electrochemical Engine Center, The Pennsylvania State University, USA	
	PEM fuel cells	**Lithium-ion battery thermal behavior**
14:10-14:30	**Water transport through an anion exchange membrane used in alkaline direct methanol fuel cells** **C. Weinzierl,** U. Krewer Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany; TU Braunschweig, Institute of Energy and Process Systems Engineering, Braunschweig, Germany	**Measuring entropy profiles of commercial Li-ion batteries – separating influences of time and temperature** **P. J. Osswald**, S. Schlueter, H. E. Hoster Technische Universität München, TUM CREATE, Singapore
14:30-14:50	**Investigating bistability in the polarization curve of a segmented PEM fuel cell** **N. Zamel,** A. Bhattarai, D. Gerteisen, C. Hebling Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany	**Modelling and measurement of uneven heat generation in lithium-ion battery packs** **B. Wu,** V. Yufit, M. Marinescu, D. A. Howey, G. J. Offer, R. F. M. Botas, N. P. Brandon Department of Earth Sciences and Engineering, Imperial College London, UK; Department of Mechanical Engineering, Imperial College London, UK; Department of Engineering, University of Oxford, UK
14:50-15:10	**Characterization of O_2 diffusive losses in the gas diffusion layer (GDL) of the PEFC by means of simplified flow field patterns** **P. Oberholzer,** P. Boillat, A. Kaestner, E. H. Lehmann, T. J. Schmidt, A. A. Wokaun Paul Scherrer Institut, Electrochemistry Laboratory, Villigen, Switzerland; Paul Scherrer Institut, Neutron Imaging and Activation Group, Villigen, Switzerland	**3D Thermal-Electric Li-Ion battery model** **W. Beckert,** C. Freytag, T. Frölich, M. Schneider Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany
15:10-15:30	**Multiphase multicomponent flow through multilayers of thin porous mediums: Conservation equations** **C. Qin,** S.M. Hassanizadeh Department of Earth Sciences, University of Utrecht, Utrecht, The Netherlands	**Effect of temperature spatial non-uniformity on electrochemical impedance in lithium-ion cells** **R. R. Richardson,** D. A. Howey, P. Ireland Department of Engineering Science, University of Oxford, Oxford, UK
15:30-15:50	**Local EIS studies in PEM fuel cells - distinguishing between through-plane mass tansport limitations and convective in-plane oxygen effects** **D. Gerteisen,** A. Bhattarai, N. Zamel, C. Hebling Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany	**The effect of temperature gradients on the performance of Li-ion batteries** **M. Marinescu,** Y. Troxler, Y. Patel, B. Wu, V. Yufit, A. J. Marquis, N. P. Brandon, G. J. Offer Imperial College London, Department of Earth Science and Engineering, London, UK; Imperial College London, Department of Mechanical Engineering, London, UK
15:50	**Closing and announcement of ModVal 11**	
16:00	**End of symposium**	

Plenary lectures

Tuesday, March 19, 2013

Measurement and Modelling of Solid Oxide Fuel Cell and Lithium battery electrode microstructure in three dimensions
N. Brandon 8:40 – 9:30

Session Chair: Wolfgang Bessler

Mathematical Modeling of Lithium-Ion Batteries
R. E. White 17:10 – 18:00

Session Chair: Axel Groß

Wednesday, March 20, 2013

Modeling and diagnostics of low Pt loading polymer electrolyte fuel cells
C.-Y. Wang 13:10 – 14:00

Session Chair: Timo Jacob

Measurement and Modelling of Solid Oxide Fuel Cell and Lithium battery electrode microstructure in three dimensions

Nigel Brandon*[1], Farid Tariq[1], Khalil Rhazaoui[1], Vladimir Yufit[1], Ralph Clague[1], Sam Cooper[1], Fred Marquis[1], Claire Adjiman[1], Paul Shearing[2], Qiong Cai[3], Dave Eastwood[4], Phil Withers[4], Rob Bradley[4], Peter Lee[4], Jeff Gelb[5]
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[2] Dept. Chemical Engineering, UCL, UK
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The presentation will discuss work on the use of Focussed Ion Beam and X-ray Tomography techniques to characterise electrode microstructures for both Solid Oxide Fuel Cells and Lithium-Ion Batteries. This includes recent studies moving towards the *in-situ* characterisation of these structures, which offers the prospect of resolving the time dependent changes in electrode microstructure seen during operation of these devices. These experimental studies are coupled with simulation studies on both synthetically generated electrodes, and the experimental data sets, with the aim of linking resolved microstructural characteristics with functional performance. The latest progress in this area will be reported.

Mathematical Modeling of Lithium-Ion Batteries

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Abstract

Lithium-ion batteries are now being used in electric vehicles and satellites. These batteries have been designed and developed primarily by empirical processes. Typically these batteries are larger than desired to insure that the required performance is met. There is a strong desire to reduce the size and cost of these batteries while maintaining the required service life through computer aided engineering (i.e., mathematical modeling). A review of some of the techniques being used to realize this objective will be presented. In particular, some reduced order modellilng for lithium ion cells will be presented. Newman's psuedo two dimensional model will be used for individual cells that are used to develop a battery model. Lithium depostion on the anode will be included in the model. Also, the dissolution of manganese from a lithium manganese oxide cathode will be discussed.

Modelling and Diagnostics of Low Pt Loading Polymer Electrolyte Fuel Cells

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Despite tremendous progress made in the last decade in reducing platinum loading in polymer electrolyte fuel cells, further reduction by a factor of 5 on the cathode is required for viable commercialization. Recent efforts have discovered a significant oxygen-transport limitation in low Pt loading electrodes that severely limits high current density performance.[1-5] However, its fundamental cause remains unclear and elusive. In this talk we shall describe diagnostic and modelling efforts to understand and characterize the O_2-transport resistance in electrodes of various architectures. In addition, we discuss our initial studies on electrodes without Nafion ionomer in order to assess its role in the O_2-transport resistance in low Pt loading electrodes[6] as well as to develop future generation electrodes without O_2-transport limitation.[7] Figure 1 shows such an example where polypyrrole is used both as catalyst support and proton conductor. Finally, we will discuss recent advances in modelling and diagnostics of water flooding in fuel cells, which is becoming a more acute issue in low Pt loading systems.

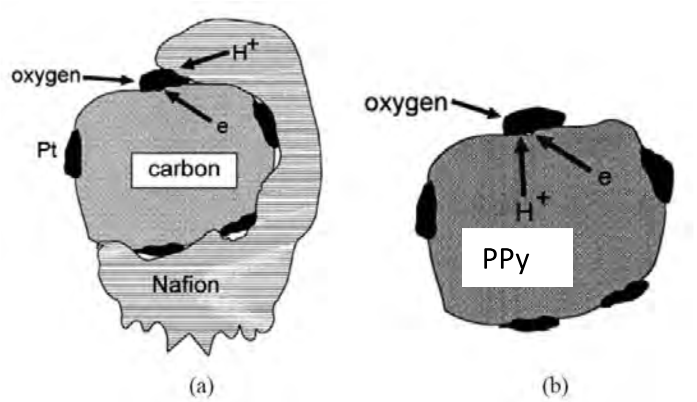

Figure 1. Schematic of a Nafion-based and a polypyrrole (PPy)-based electrode[7]

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Microstructure of fuel cells and batteries

Tuesday, March 19, 2013

Session Chairs: Arnulf Latz, Volker Schmidt, and Dietmar Gerteisen

Microstructure degradation in SOFC anodes: Relationship between topological parameters and transport properties

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The performance of SOFC electrodes is strongly depending on effective transport properties (i.e. ionic and gas diffusivities as well as electronic conductivity). In historical papers going back to Carman, Kozeny, Archie, Clenell, van Brakel, and others (e.g. [1, 2]) basic relationships between microstructure parameters and effective transport properties were postulated. The most important parameters in this context are tortuosity, constrictivity and percolation factor. The relationships were postulated based on theoretical and semi-empirical considerations a long time ago. However, in the past, a rigorous validation of the postulated relationships was not possible due to a lack of suitable techniques. With the recent improvement of 3D-imaging techniques (e.g. with FIB-tomography [3]) and of the associated image analysis tools (see e.g. [4], [5]) transport relevant parameters can now be determined, which opens new possibilities to test the postulated relationships and to study microstructure effects, e.g. in SOFC electrodes. In this context we also refer to a test of these relationships by means of a stochastic simulation framework, which was done at Ulm University (see their contribution in the present abstract volume [6]).

In our contribution we will first discuss the relevant morphological parameters (size distributions, bottleneck dimensions, geometric tortuosity, percolation factor) and the corresponding analytical methods, including basic statistical aspects (i.e. local porosity theory, percolation theory, determination of REV [7]). Some examples are then presented where the techniques are used to study microstructure effects in SOFC anodes. New insight is gained how redox cycling of cermet anodes influences the effective transport properties and which topological features are responsible for the corresponding drop of the anode performance [8-12]. Finally, the presentation also includes a short discussion how the topological information from 3D analysis can be used as input for FE modeling of the electrode performance.

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Microstructural modelling for prediction of effective properties in porous SOFC electrodes

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A modelling framework for the prediction of effective properties in porous SOFC electrodes is presented. The model consists of: i) a packing algorithm to numerically reconstruct the microstructure, and ii) a Monte Carlo method to calculate the effective transport properties. This modelling technique improves the accuracy of the prediction of effective properties beyond percolation theory estimates. In addition, the numerical reconstruction does not rely on existing samples and complex instrumentations (for example, X-ray tomography, FIB-SEM analyses) required by other reconstruction methods.

The packing algorithm enables to numerically generate a representative sample of the electrode microstructure with the desired particle size distribution, composition and porosity. Sintering phenomena are simulated by increasing the overlap among the particles, pore-former particles are accounted for during the packing generation [1]. The model is capable to simulate packings of spherical particles as well as of agglomerates of spheres.

The reconstructed samples are then analyzed with a Monte Carlo method [2]. Random walk simulations are used to determine the transport properties in gas and solid phase, such as the effective diffusivity and the effective electric conductivity. Other geometric quantities can be evaluated, such as the pore size distribution, the surface area exposed to the gas phase, the three-phase boundary length.

In this study, effective properties as a function of porosity and particle size for random packings of spherical particles are calculated. The results are compared with independent experimental data, revealing a good agreement for both gas and solid phase properties. Effective properties of agglomerates of particles are also presented and compared with the results obtained for spherical particles. The comparison highlights that particle agglomeration significantly increases the mean pore size while reducing the effective gas diffusivity and the specific surface area exposed to gas phase (Figure 1).

The presented modelling technique can be used to improve SOFC electrode design and to support the interpretation of experimental data.

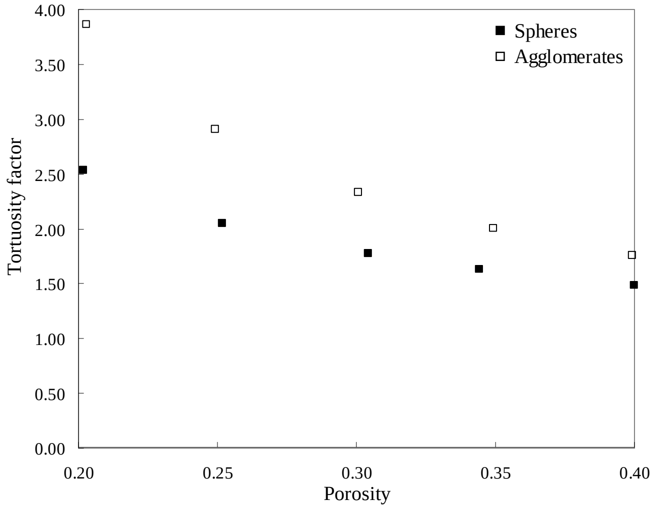

Figure 1 - Tortuosity factor in random packings of spherical particles and agglomerates.

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Solid Oxide Fuel Cell Effective Conductivity Modelling

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Abstract

The effective conductivity of a thick-film solid oxide fuel cell (SOFC) electrode is an important characteristic used to link the microstructure of the electrode to its performance. With the development of increasingly accurate three dimensional (3D) imaging methods of fuel cell microstructures by destructive (e.g. focused ion beam) and non-destructive (e.g. X-ray tomography) techniques, we are now capable of analyzing more effectively the relationship between microstructural characteristics and overall cell performance. A 3D resistance network model has been developed to determine the effective conductivity of a given SOFC electrode microstructure. This work presents a brief overview of the functionality of the 3D resistance network model alongside a comparison of resistance data with analytical results from literature and commercial software packages. A validation with experimental results is investigated alongside the introduction of the aggregation of the voxels into volume elements. A given 3D SOFC anode microstructure reconstructed from imaging processes is initially discretized into voxels, typically 1/25th the size of a nickel particle, based on which a mixed resistance network is drawn. A potential difference is then applied to the network which yields by mathematical manipulation the corresponding current, finally allowing for the equivalent resistance of the entire structure to be determined.

Modeling of electrical and ionic transport properties in granular electrodes considering composition and mechanical loading

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Besides others, Solid Oxide Fuel Cells (SOFC) and Lithium-Ion Batteries (LIB) are attractive solutions for clean energy conversion and storage. In order to make them competitive to state of the art solutions, efficiency and durability need to be improved further. Due to their similarity in electrode structure the same modeling approaches are applicable to investigate morphological influences on transport properties closely related to efficiency.

A mixture of spherical particles represents the granular electrode structures containing ionic and electrical conducting material in SOFC respectively active material and carbon black in LIB. A tracking algorithm (Hoshen-Kopelman) was adapted for non-lattice environments with periodic boundaries to specify the percolation threshold for binary mixtures. Based on that, a network analysis method is implemented to determine the effective conductivity of various structures.

In general, these methods enable us to investigate the influence of microstructural and compositional properties such as size ratio and volume fraction on percolation threshold and effective conductivity of spherical systems.

In SOFC, percolating of both species is crucial for the system. For various compositions percolation probability, effective conductivity and other relevant transport properties have been determined. The results obtained in this way can be used as input for one-dimensional cell models to determine the influence on cell power and efficiency.

In LIB, intercalation processes lead to volume change and therefore internal stresses. To investigate this, the methods mentioned above for determination of conductivity were combined with discrete element modeling (DEM), which allows simulating interparticular forces and rearrangements in granular structures during loading. In this way the impact of mechanical stress on transport properties can be determined.

Thermodynamically derived model and simulation of intercalation currents and overpotentials in Li Ion batteries

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We recently presented a thermodynamically consistent transport model for Li ion batteries [1] and a finite volume based implementation of this model [2], which allows simulating detailed transport phenomena in the microstructure of secondary Li-ion batteries. One important ingredient for simulating the transport is the model for the intercalation flux at the interface of active particles and electrolyte. A commonly used model for Li – ion intercalation is a version of the Butler-Volmer theory which is mainly applied to porous electrode theory [3]. In the usual macroscopic derivation of this model the intercalation current is driven by overpotential between the active material and electrolyte and depends also on the concentration of Li –ions in the electrolyte and in the active particle. The actual form of the concentration dependence varies between different models and is chosen mostly independently from the dependence on the overpotential and the thermodynamic properties of the electrolyte. To obtain a fully thermodynamic consistent theory, it is necessary to derive intercalation currents and transport theory using the same theoretical concepts. Starting from our thermodynamically consistent microscopic transport equations for active particles and electrolyte, we therefore derive the expression for the intercalation current from nonequilibrium thermodynamics. The derivation shows conclusively how the overpotential has to be modeled to obtain a thermodynamically consistent theory for the intercalation coupled transport of ions and the spatio-temporal variation of the electrical potential in active particles and electrolyte. The new intercalation model is implemented in ITWM owns three dimensional simulation code BEST (Battery and Electrochemistry Simulation Tool). The results of the simulation for currents, potentials, SOC etc. are compared with the ones obtained with the usual form of the Butler-Volmer model for intercalation batteries.

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Graph-based simulated annealing: A hybrid approach to stochastic modeling of uncompressed graphite electrodes used in Li-ion batteries

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A stochastic model is presented for the efficient simulation of complex 3-dimensional microstructures consisting of two different phases. [1] The model is fitted to tomographic image data describing the microstructure of uncompressed graphite electrodes used in Li-ion batteries.

In general, the microstructures of advanced functional materials are closely related to their physical properties. Mathematical models - as presented in this talk - are useful tools providing methods to quantitatively elucidate the correlation between microstructure and functionality. Moreover, systematic modifications of model parameters, in combination with numerical transportation models, offer the opportunity to identify morphologies with improved physical properties by model-based computer simulations, i.e., virtual materials design.

The proposed stochastic 3D model combines two well-established stochastic approaches: Spatial stochastic graphs and simulated annealing. More precisely, a spatial stochastic graph model is developed which describes the main structural features of the microstructure and is then combined with simulated annealing. The spatial graph modeling leads to an improved initial configuration of the simulated annealing - enhancing runtime - and offers a better control on the resulting microstructure. The simulation model is validated by comparing relevant image characteristics of experimental and simulated data, where a good agreement is found, see also Figure 1.

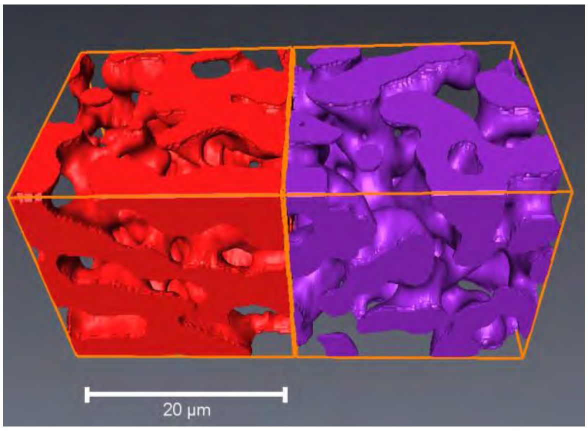

Figure 1: Left: 3D uncompressed graphite electrode (cutout) gained by synchroton tomography; right: corresponding simulation by graph-based simulated annealing.

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Phase-field model for the interplay of diffusion and stresses in electrode particles of lithium ion batteries

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Many cathodic materials in lithium ion batteries show capacity fade due to particle crackings, especially cathodes made of LixMn2O4 particles present, even at low applied charge and discharge current, mechanical failure.

On the one hand, during lithium (de-)intercalation, the gradient of the hydrostatic stresses contributes, together with the concentration gradient, to the diffusion of the lithium ions into the cathodic particle.

On the other hand, an inhomogeneous concentration profile gives rise to mechanical stresses that may cause failure. Here we have to distinguish between two cases: First, mechanical stresses increase with the magnitude of the lithium flux applied at the surface of the particle. This may explain the particle crackings that arise at large applied charge and discharge current only. Second, LixMn2O4 material exhibits phase segregation on the 4V-plateau, when the state of charge $0<x<1$. In this talk we introduce a phase-field model coupled with mechanics. This model accounts for phase segregation and demonstrates the relationship between phase segregation and large values of the mechanical stresses even at negligible applied charge and discharge current.

Modeling and Simulation of Fracture in Active Electrode Particles of Li-Ion Batteries using a Phase Field Approach

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Fracture of active electrode particles is considered to be one of the major reasons for capacity fade and increasing power losses in many commercial Lithium-Ion batteries due to emerging effects as the growth of a so called solid electrolyte interface (SEI), loss of contact to conductive pathways or complete disintegration of the electrode. The appearance of fracture and cracks in the active particles is commonly ascribed to mechanical stresses, which evolve from inhomogeneous swelling and shrinkage of the material when Lithium is inserted or extracted.

In our work, we approach the problem of fracture in active particles by joining a coupled model of mechanical stresses and diffusion of Lithium-ions with a phase field description of an evolving crack. While the mechanics of the particle is described by a linear, elastic and isotropic constitutive law, the diffusion equation is derived from fundamental thermodynamics and valid beyond the dilute limit. Furthermore, not only the appearance of stresses due to an inhomogeneous Lithium concentration is considered, but also the stresses themselves are taken into account as a driving force for the Lithium diffusion. The phase field is then coupled to the stress equation by a Griffith type minimization principle of the total energy increment, compromised by the surface energy to create the crack surface and the elastic bulk energy due to the occurring stresses.

This novel approach allows us to simultaneously study the evolution of the Lithium concentration together with the initiation and growth of a crack in an arbitrary geometry, in two and three dimensions, and without presuming a specific crack path.
We investigate how the formation of cracks depends on the geometry of the particle, as well as the material parameters, such as Young’s modulus or molar volume of the Lithium, and the applied boundary conditions, e.g. Lithium flux at the surface. Further, different scenarios for the Lithium diffusion along and across the crack are assumed.

Synchrotron tomographic study on the inhomogeneous compression of gas diffusion layers in fuel cells

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The water transport properties of gas diffusion layers (GDLs) are of substantial importance for the water management of proton exchange membrane fuel cells (PEFCs) [1]. The transport behaviour of a GDL is closely linked to its microstructure. We used synchrotron X-ray tomography to study the morphology of various GDL materials three-dimensionally at high resolution in order to determine basic structural parameters, such as porosity or tortuosity. These data are needed for the detailed understanding and simulation of water transport phenomena. When mounted in a fuel cell at usual clamping pressure conditions, the mechanical interaction with the channel-rip pattern of the flow field results in different local compression rates of the porous GDL material. Therefore, some transport-relevant morphological parameters, such as local pore size distribution or fiber orientation, vary between regions located underneath flow field channels and land areas. We used a dedicated compression device to produce highly resolved tomograms (voxel size ~1µm^3) of the GDL morphologies at increasing compression rates. The application of a stamp with a channel-rip profile provides realistic pressure conditions. The tomographic data is used to develop and validate stochastically derived geometry models of GDL materials [2] and can serve as input for mass and heat transfer simulations, e.g. with the Lattice-Boltzmann method.

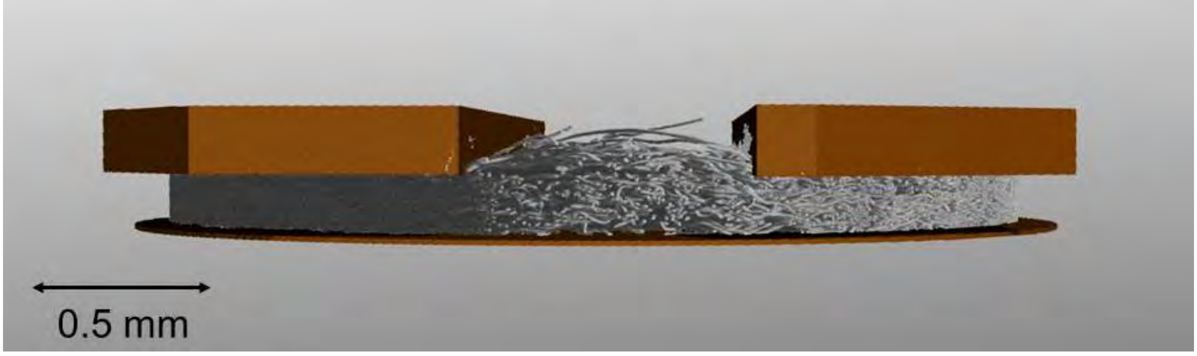

Figure 1. Perspective view on a compressed GDL sample (Freudenberg H2315)

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Stochastic modeling of fiber-based materials for varying degrees of compression

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The micro-structure of complex porous materials is closely related to their physical properties, in particular with transport processes of gases and fluids. Thus, the systematic development of new 'designed' morphologies with improved physical properties is an important task. Simulation models from stochastic geometry can help to solve this problem. They can be used to provide a detailed, quantitative description of complex microstructures in existing materials [1, 2]. Then, by systematic modifications of parameters of the stochastic simulation model in combination with numerical transportation models, virtual 3D morphologies and virtual transportation processes in these morphologies can be simulated. In this way, it is possible to elucidate the correlation between the micro-structure of porous materials and its physical properties and thereby to detect optimized morphologies. We present a parameterized stochastic model which describes the micro-structure of (strongly) curved fiber systems under varying degrees of compression. The compression model distinguishes between two different kinds of compression. The first kind compresses the material with a flat stamp, whereas the second one uses a stamp with a channel-bar profile. As an example of application, the compression model is used for a non-woven gas diffusion layer (GDL) in polymer membrane fuel cells, see Fig. 1. Finally, the compression model is validated by comparing several structural characteristics computed for a sequence of 3D synchrotron X-ray data with varying degrees of compression and for corresponding realizations of the compression model. An excellent agreement of experimental and simulated data has been found.

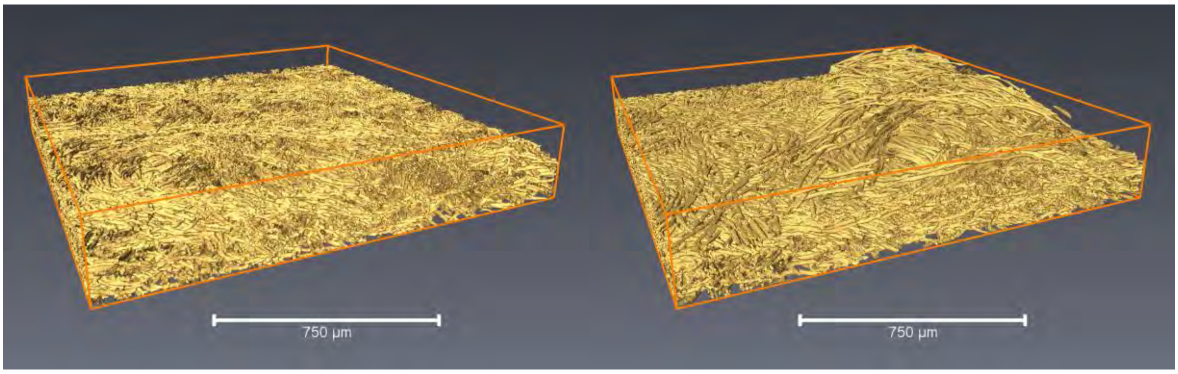

Fig. 1: Compressed GDL sample by a flat stamp (left) and by a stamp with channel-bar profile (right).

References:
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Predicting Effective Transport Properties in PEM Fuel Cells Using Pore-Network Simulations

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Modelling of mass and thermal transport in proton exchange membrane (PEM) fuel cells is a complex, conjugate problem due in part to the stochastic nature of the porous gas diffusion layer (GDL). Cell-level models capture the kinetic and electrochemical reactions, but rely upon empirically-derived effective transport properties through the porous media. [1] In contrast, pore-network models may be used to capture spatial and temporal gradients in transport through porous media without resorting to bulk effective properties, but this approach becomes computationally intensive for large domains. [2] Coupling the two modeling approaches could enable robust cell-level models that need not rely upon empirical approximations for effective thermal and mass transport properties.

To that end, a pore-network model that resolves two-phase transport and thermal transport, including evaporation and condensation, has been developed for PEM fuel cell porous media. [3] The effective gas-vapor diffusivity and thermal conductivity have been determined for a range of operating conditions, pore size distributions, water content, and porosities. Effective diffusivity is often approximated using a Bruggeman-type approximation that attempts to correct binary diffusivity using porosity, but does not include relative humidity. [1,4] Experimental results indicate effective diffusivity is relatively insensitive in dry GDL samples having different porosities. [4] The value of effective diffusivity exhibits greater sensitivity to pore size distribution and relative humidity at the channel. The role of pore-size distribution and the effect of operating conditions on effective transport properties will be discussed.

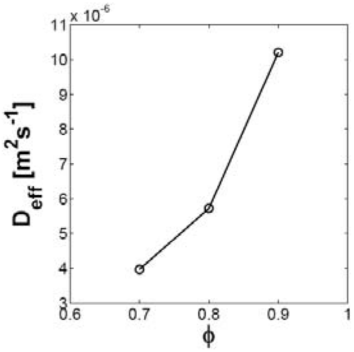

Figure 1. Effective vapor diffusivity as function of the relative humidity.

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Refinement on post-processing of 3D transport simulations in fibrous microstructure, using the Lattice Boltzmann method

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The gas diffusion layer (GDL) is a key component of fuel cells based on polymer electrolyte membranes (PEFC, DMFC and HT-PEFC). The efficient operation of fuel cells requires good transportation properties of GDL which allow educts to reach the electrodes out of the gas channels as well as to transport products from the electrodes back to gas channels.

A stochastic model creates virtual 3D structures representing the real geometry [1][2]. Because of the stochastic nature of the geometry, transport simulations using the Lattice Boltzmann method are applied on ensembles of the geometry. To characterize the GDL material, tortuosity is one prominent value which can be taken from the results of the transport simulations. The result of two different methods of calculating the tortuosity [3] are discussed on an ensemble of virtual structures of fiber based GDL material. The tortuosity is calculated through-plane and in-plane in two directions because the particular material might be non-isotropic in planar directions.

The general objective of our research is the construction of microstructures of GDL which are favorable for mass transport in fuel cells. Preliminary investigations of GDL microstructures with respect to transport relevant structural properties have been reported in [4]. We investigate transport properties of GDL not only by considering structural characteristics, but incorporating numerical models for transport processes. Simulations of transport processes by means of the Lattice Boltzmann method are applied, where the stochastic model for the microstructure mentioned above is used in order to generate the underlying geometric structures.

This research is funded by the German “Federal Ministry of Education and Research“ grant 03MS507. Simulations are running on hardware of the Jülich Supercomputing Centre.

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Numerical Determination of Transport Properties of Catalyst Layer, Microporous Layer and Gas Diffusion Layer

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The performance of a PEM fuel cell depends essentially on the transport properties of the porous layers that form the MEA. Therefore, the connection between 3D pore structure and transport property needs to be understood and can then be exploited to create optimal layers. For this, two things are necessary:

A) To determine the effective transport properties based on 3D images.
In this talk, I will shortly summarize which methods were used to determine the transport properties of GDL [1] and MPL [2]. Then, I will show how transport properties can be determined from FIBSEM images of catalyst layers [3].

B) To create 3D structure images virtually.
This ability can be used to study systematically the connection between 3D pore structure and transport property, e.g. how does the MPL porosity and thickness influence the diffusivity of the layer? In this talk, I will present results from a recent design study [4] performed with GeoDict [5].

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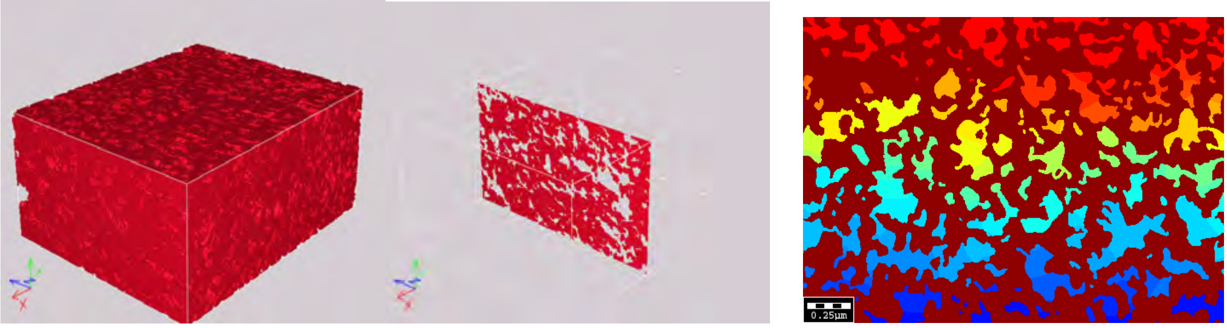

Figure: Left: 3D structure of a catalyst layer, reconstructed from FIB/SEM images[3]. Right: diffusion in the catalyst layer pores: numerically determined concentration distribution.

PEM fuel cell degradation
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Solid oxide fuel and electrolyzer cells

Tuesday, March 19, 2013

Session Chairs: N.N, Rotraut Merkle, and Andrei Kulikovsky

Validation of membrane degradation mechanisms at defects by synchrotron based methods

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Polymer electrolyte membranes undergo chemical, mechanical and thermal degradation during fuel cell operation. Gas crossover is the key element of membrane degradation, triggering two out of the three degradation mechanisms. Hydrogen and oxygen crossover is the primary source of oxygen radical species that chemically decompose the polymer via the unzipping reaction mechanism, as described by Curtin *et al.* [1]. The carboxyl group (COOH) is a key function of this mechanism and therefore often used as an indicator for chemical polymer decomposition. For chemically stabilized perfluorosulfonic acid membranes, the main reason for the loss of the gas separation is not membrane thinning, but rather the mechanical formation of pinholes induced by humidity fluctuations and imperfections of the gas diffusion electrode [2]. However, the initiated degradation processes at pinholes leading to cell failure remain unclear.

In order to gain a better understanding of the degradation mechanism at membrane defects, MEAs with artificially implemented membrane defects (10 µm in diameter) were degraded using different accelerated stress tests. Degradation at membrane defects was investigated post mortem using synchrotron based X-ray tomographic microscopy (XTM) and FTIR spectro-microscopy.

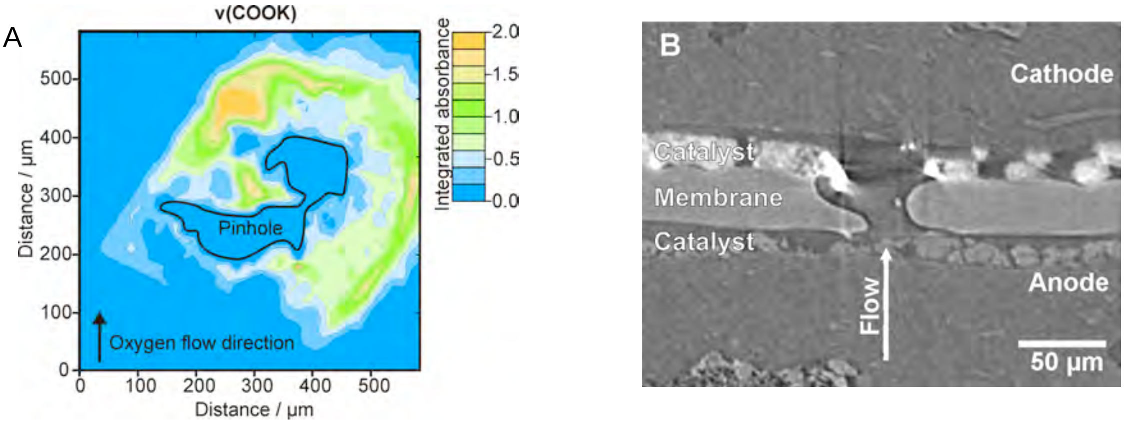

Figure 1. *A) 2D-FTIR map of the integrated COOK absorbance for a degraded Nafion 111 membrane at a defect;B) XTM cross-section of a degraded MEA.*

Polymer decomposition is highest at the oxygen downstream side of the defect, and the maximum intensity is not at the pinhole edge (Figure 1A). The partially decomposed polymer fractures induced by mechanical stress, and the pinhole size increases. When the defect exceeds 30 to 50 µm, thermal degradation of the polymer starts, further increasing the defect size and finally leading to cell failure (Figure 1B).

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Abstract for oral presentation

Dead spot in a PEM fuel cell anode

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CO poisoning, catalyst agglomeration etc. may cause significant *local* lowering of the exchange current density of the hydrogen oxidation reaction (HOR) in the anode catalyst layer of a PEMFC. In transmission X—ray absorption spectroscopy studies of a fuel cell cathode, the anode catalyst is deliberately removed in a small spot to provide transparent non—Pt window for X—rays targeting the cathode.

We report a model for the distribution of local currents in and around the ‗dead” spot in the anode catalyst. We start with a Laplace equation for the membrane potential Φ in the cylindrical domain encompassing the dead spot. The 2D Laplace equation is transformed to 1D radial Poisson equation with the right side being the difference of the local HOR and ORR current densities entering and leaving the membrane; the approach is similar to that of [1].

The model reveals formation of the current double layer (CDL) at the interface between the spot and the regular cell domain (Fig.1). As protons in the anode spot are not produced, local ORR current in the cathode catalyst layer (CCL) in front of the spot is strongly reduced (Fig.1b). This reduction is supported by lowering of the membrane potential and ORR overpotential toward the spot axis (Fig.1a). However, radial gradient of Φ inevitably means radial proton current j_r in the membrane. A peak of the HOR current at the spot boundary forms to provide protons for j_r in the region of spot (Fig.1b). Note that the peak HOR current density is nearly 2.5 times higher, than the mean current density in the regular domain (Fig.1b).

Calculations show that the CDL parameters are independent of the spot radius, provided that this radius greatly exceeds the membrane thickness. The CDL is thus an autonomous structure, which serves as an electrochemical connector between the spot and the regular domain. High HOR current around the spot may accelerate local cell aging.

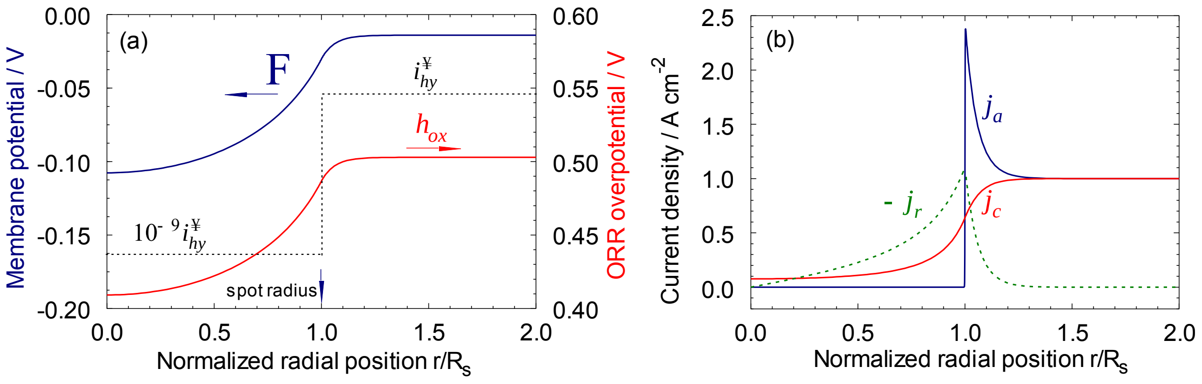

Figure 1. (a) Potentials and (b) ORR j_c and HOR j_a current densities, and radial proton current density j_r in the membrane. Note a peak of the HOR current just outside the spot boundary. The shape of the HOR exchange current i_{hy} is depicted schematically in (a). Current in the regular domain is fixed at 1 A cm^{-2}. The spot radius R_s is 0.025 cm.

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Long-term test of PEM fuel cells with a dry cathode supply and daily EIS analyses

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In scientific publications long term performance of PEM fuel cell components is usually presented on the basis of highly sophisticated test environments. Nevertheless real life stability of the individual components is dependent on system architectures, media supply, operational strategies and further materials both of the fuel cell stack itself and all peripheral elements within the balance of plant.

The main focus of long-term tests at ZBT is the simulation of real operating conditions in portable and mobile applications. Therefore the tests are being performed without cathodic humidification and using anode recirculation of hydrogen. Furthermore for secured test results short stacks of 5 cells are used and always three short stacks are being tested in parallel (Figure 1). This allows verified results for long term tests e.g. comparing stack components (MEA, gaskets, bipolar plates) or operational topics like media supply independently from any outside influences.

This talk will give an overview on the design and iterative optimization of the implemented EIS (Electrochemical Impedance Spectroscopy) test architecture and its influence on the measured impedance spectra. The results of multiple test series, including continuous and various loads and start/stop cycles, are presented. A strong influence of start/stop cycles on the cell performance has been detected.

FIGURE 1 Long-term parallel operation of three short stacks.

PEMFC predictive modelling function of the operating mode and local conditions

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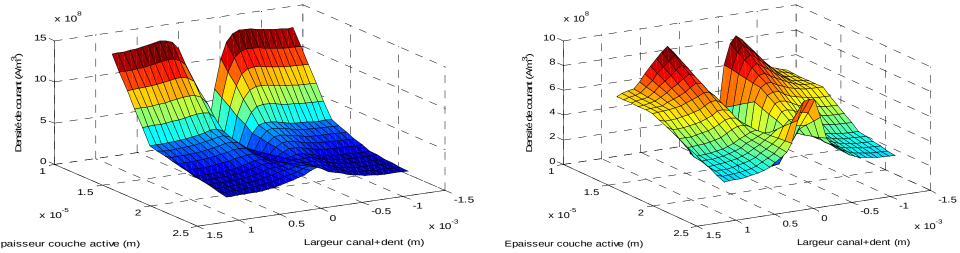
The strong coupling between the mechanisms of degradation in the MEA (Membrane Electrode Assembly) (as the platinum dissolution/oxidation, Ostwald ripening and carbon support corrosion) and the local conditions in the MEA (in the active layer and also along the MEA surface) must be understood to improve fuel cell system command strategies and the operating conditions.

In this work, two PEMFC models are coupled with degradation mechanisms. The first model is a 2D MEA model computing the local conditions in the active layer thickness. The difference between rib and channel is made. This model is developed under Comsol-Multiphysic® environment. The second model is a 2D cell model (1-2). The local conditions along the MEA surface are calculated function of the operating mode of the fuel cell system (nominal power, peak power). This model is developed under Matlab/Simulink® environment.

Both model are indirectly coupled with a degradation bottom-up model (3). This model describes the degradation mechanisms in the active layer. As a first step, only the platinum oxidation/dissolution is implemented. With this model a degradation rate of the active surface of platinum function of temperature, hygrometry, pressure and current density, is performed (4). This law is introduced on both MEA and cell model.

With this complementary approach, the evolution of the active layer local conditions and MEA surface conditions are calculated function of ageing. For example the figure below describes the current density evolution function of platinum surface dissolution during nominal conditions. The operating modes of the fuel cell system are also a strong impact on degradation and the evolution of the current density distribution on the cell surface.

These approaches are useful to understand the interactions between the MEA local conditions and also to optimize the fuel cell system management and control.



Current density distribution in the cathode CL (left) and after 1000h (right).. The left axis represents the thickness of the CL, whereas the front axis represents the position in the rib-channel cross-section of the MEA. The channels are on the sides and the rib is in the middle of the axis.

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Elementary kinetic modeling for the investigation of direct-methanol fuel cell degradation

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In order to become competitive to conventional energy conversion systems, the lifetime of direct-methanol fuel cells (DMFCs) still has to be increased. Therefore it is important to get a deeper understanding of the mechanisms responsible for cell degradation.

We present a detailed one-dimensional model of a direct-methanol fuel cell, based on the in-house modeling framework DENIS[1,2], including gas diffusion layers, catalyst layers and membrane. Two-phase transport for the methanol-water mixture within GDL and CL is taken into account. Within the membrane methanol crossover due to diffusion and electro-osmotic drag is considered. The electrochemistry (methanol oxidation and oxygen reduction reactions) is described by means of an elementary kinetic approach including the most relevant surface-adsorbed intermediate species on the anode (Pt-Ru) and cathode (Pt) catalysts. The kinetic coefficients are parameterized using quantum chemical data available from literature. The model allows for steady state, transient as well as impedance simulations.

Based on this cell model, degradation mechanisms which cause changes in catalyst active surface area are studied in detail. A mechanism which is considered to be crucial for lifetime of DMFC is ruthenium dissolution. We demonstrate a model for this degradation mechanism implemented into the cell model and discuss its effect on the cell performance. In the elementary mechanism, ruthenium is responsible for activating water molecules that inhibit poisoning of the Pt surface due to adsorbed CO molecules. The feedback on Ru dissolution on this mechanism is quantified.

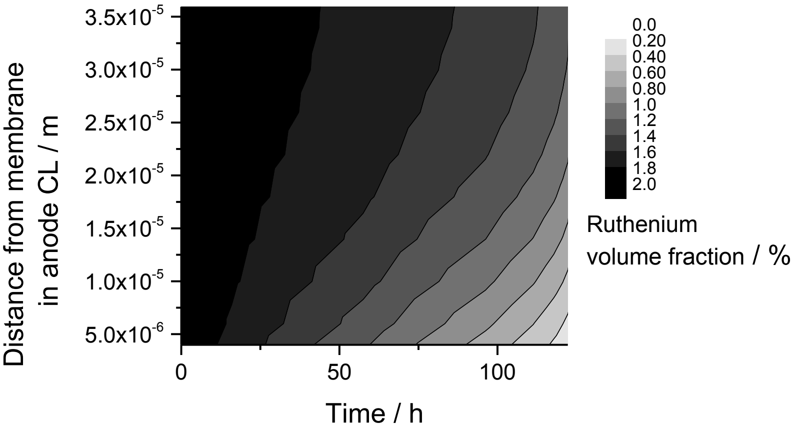

Figure 1. Spatially resolved analysis of ruthenium dissolution in the anode catalyst layer

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Determination of catalyst layer resistance in Alkaline Fuel cell

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The earliest fuel cells which were developed rigorously and made generation of electricity from hydrogen feasible were Alkaline Fuel Cells (AFCs). Despite its early success AFC has been surpassed by Proton Exchange Membrane Fuel Cell (PEMFC) technology due to high power density, simpler design and low maintenance. However, with new recent material developments, availability of commercial solid alkaline electrolyte membrane and ionomer which prevent precipitation of carbonates, and the possibility to use non-precious metal as catalyst [1], the interest in AFC has been renewed. Yet the performance of these fuel cells (H_2-O_2 or MeOH-O_2 without liquid electrolyte) employing commercial membrane and ionomer is low due to insufficient knowledge about the electrochemical processes inside catalyst layer (CL). CL resistance is one of the important parameter for assessing the performance. The study on CL resistance in AFC has been not reported yet.

In this work, studies were conducted in order to find the percentage contribution of catalyst layer resistance to the overall polarization loss. Due to presence of ionomer and catalyst particles in CL, the CL exhibits mixed conductivity during the reaction. It is often difficult to separate the contribution of electronic and ionic resistance to the total resistance by conventional impedance spectroscopy. Therefore a modified Membrane Electrode Assembly (MEA) [2] was prepared by sandwiching an inert layer (reaction-less) of carbon-ionomer composite between the cathode and membrane to form Anode-Membrane-Inert layer-Cathode assembly. The inert layer comprised of electronically conducting carbon particles and ionically conducting anion exchange ionomer. The inert layer adds resistance to the ionic conduction path between cathode and anode in the modified MEA, whereas the carbon's function is to establish a similar structure and porosity as in the catalyst layer. The effect of inert layer thickness on the performance is evaluated and CL resistance is determined from various polarization curves. With obtained results performance loss in AFC due to CL resistance is projected and compared with CL comprised of Nafion ionomer.

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A quasi 2D AC model for analysis of degradation of a high temperature proton exchange fuel cell

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In 1996 phosphoric acid doped polybenzimidazole was first proposed and successfully demonstrated as a polymer electrolyte suitable for application in high temperature proton exchange fuel cells (HT-PEMFC). In the last decade, large efforts have been dedicated to fuel cell testing and to the development of electrochemical fuel cell models. For a complete review on HT-PEM modeling we suggest the work of Siegel et al [1]. Basically, HT-PEMFCs suffer mainly two issues: electrocatalysis is affected by the presence of phosphoric acid within the electrode and the degradation rate in continuous operation is still not satisfactory. Further modeling is necessary in order to deepen the understanding of the phenomena involved and thus to suggest actions which could mitigate them. In particular, electrochemical impedance spectroscopy could contribute significantly because it succeeds in separating the different phenomena occurring within a PEMFC, e.g. mass transport, proton conduction, kinetics. What's more, impedance can be measured without interrupting the operation and thus is suitable for diagnostic purposes. AC models able to reproduce impedance spectra of PEM fuel cells where proposed in the 90's by Springer et al [2]. To the authors knowledge, there is still lack of phenomenological AC models able to reproduce the impedance spectra of HT-PEMFCs.
In this work we present a quasi 2D isothermal phenomenological AC model and we perform the fitting of the electrochemical parameters on experimental data obtained during a degradation test of the duration of 6000 hours on a commercial HT-PEMFC.
The model solves the continuity equation along the channel in order to account for change in reactant composition along the channel and orthogonally, along the through-MEA coordinate, each component is solved in 1D approximation: the gas diffusion layers are described by means of Stefan-Maxwell diffusion and the electrode is modeled by means of the pseudo-homogeneous porous model. The numerical solution of the equation system is carried out in Matlab environment in both steady and AC mode and the unknown parameters are fitted on a polarization curve performed in reference condition (temperature 160°C, anode/cathode stoichiometry 1.2/2) and six impedance spectra performed at different current density. The fitting parameters are the charge transfer coefficient, the oxygen diffusion coefficient and the exchange current density.
Once the calibration is performed on the data available at the beginning of life of the HT-PEM, the fitting is thus performed on the polarization curve and spectra recorded at five different times up to 6000 hours of operation. Degradation in continuous operation it was shown in the literature to affect mainly the nanoparticle size and the catalyst active area, thus appearing as a reduction in the exchange current density. On the contrary, a change in exchange current density only, even though can fit the polarization curve, it does not cause any change in the spectra, which experimentally shows an increase in the kinetic arch. An acceptable fit of the spectra can be performed by changing the oxygen diffusivity of the electrode in addition to the exchange current density. The change of these parameters in time was found to reproduce the same change shown experimentally by the catalyst active area measured by cyclic voltammetry.

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Oxygen exchange mechanism on mixed-conducting perovskites: insight from experiment and theory

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Mixed-conducting perovskites are key functional materials, e.g. for solid oxide fuel cells or oxygen permeation membranes. A detailed insight into the oxygen exchange reaction mechanism is decisive for recognizing further performance improvements as well as device limitations. The ABO_3 perovskites investigated as SOFC cathode materials range from $(La,Sr)MnO_{3-\delta}$ (LSM) to $(La,Sr)(Co,Fe)O_{3-\delta}$ (LSCF) and $(Ba,Sr)(Co,Fe)O_{3-\delta}$ (BSCF). Measurements on pore-free PLD films on YSZ substrates (= model cathodes with well-defined morphology) allow us to obtain the effective rate constants *k* for the oxygen surface exchange reaction. The correlations of *k*, varying by 5 orders of magnitude at 750°C, with (bulk) materials properties emphasize the importance of ionic conductivity - i.e. both a high oxygen vacancy concentration as well as a high vacancy mobility - as a key factor for fast surface oxygen exchange [1].

DFT calculations are a complementary tool for understanding the oxygen exchange kinetics, yielding energies of bulk and surface defects, intermediates and transition states, and migration and reaction barriers. For LSM perovskites [2] extensive calculations indicated that the migration of an oxygen vacancy towards oxygen intermediates adsorbed on the surface is the rate-determining step. The BSCF and LSCF perovskites with different cation compositions were investigated by means of DFT calculations, to understand the reasons for the exceptionally low oxygen migration barrier of 0.45 eV for Ba- and Co-rich compositions [3,4]. In BSCF the barrier does not only depend on geometric criteria (inter-ionic distances in the "critical triangle"), but also on the oxygen vacancy formation energy which is a measure of the reducibility of the transition metal ion. A closer inspection shows that in the transition state some electro density is transferred from the migrating oxygen to the neighboring transition metal ion. This process – decreasing the oxygen ion size and thus the migration barrier - is more favorable for materials with low vacancy formation energy. Unfortunately, the size mismatch between large Ba^{2+} and smaller Co ions causing the low vacancy formation energy decreases also the structural stability of the BSCF cubic perovskite lattice, leading to the detrimental hexagonal perovskite phase formation.

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Current-voltage behaviour of SOFCs considering anode degradation

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Solid oxide fuel cells (SOFC) are promising alternative energy sources for a wide application range from mobile technology to stationary power plants due to their high energy efficiency and low pollutant emission. One of the biggest advantages of an SOFC is its ability of direct utilization of various fuel types, i.e. H_2/H_2O, CO/CO_2 and hydrocarbons. It is, however, well known that operation of an SOFC based upon various fuels could cause various types of cell degradation. Therefore, understanding the origin and evolution of degradation processes on micro(nano)-scale is essential to develop long-term operating SOFC technology.

We present a modeling and simulation study of secondary-phase formation in porous Ni/YSZ, which leads to anode degradations. Specifically, we investigate the formation of solid nickel oxide formation (re-oxidation) in the case of high fuel utilization or low cell voltages, as well as the formation of solid carbon (coking) in the case of internal reforming. The model is based on a multi-phase framework [1], that allows the introduction of arbitrary solid and gas phases, where reactions between the bulk phases occur via interface-adsorbed species and they are described by an elementary kinetic approach. Published experimental data are used for parameterization and validation.

Regarding nickel oxide formation, thermodynamic calculations are used to predict the local conditions for the formation of nickel oxide. Simulation results reveal a big gap between local condition inside the cell and global operating parameters. For example, cell operation far below the limiting voltage of 0.704 V (at 1073 K) is possible without re-oxidation as long as the fuel utilization is low.

In the case of solid carbon formation, the simulation results show that the cell performance degradation are influenced significantly by the operation temperature and applied potential. Specifically at OCV, high temperature (~1000 K), mainly, provokes the formation of surface and/or subsurface carbon and at low temperature (~700 K) carbon mostly blocks pores, which significantly influences fuels diffusion. However, under applied potential the amount and type of carbon change drastically due to higher hydrogen content in carbon phase.

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Computational Modelling and Simulation of a Single Micro Tubular Solid Oxide Fuel Cell and Stack for Unmanned Aerial Vehicles

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Fuel cells are important clean converters of energy with potential for high efficiency. They possess the advantages of direct conversion of chemical energy into electrical energy, low emission, almost no moving parts and quiet operation with low operational costs. Fuel cells can utilise conventional hydrocarbon fuels or hydrogen to produce electricity, for instance for auxiliary and portable power devices or propulsion energy for transport, marine, unmanned aerial and space exploration vehicles.

The aim of this work is to develop a Computational Fluid Dynamics (CFD) model of a single micro tubular Solid Oxide Fuel Cell (mSOFC) and a mSOFC stack for an unmanned aerial vehicle in order to assist the mSOFC Balance of Plant (BoP) system design development. The single mSOFC analysed here consists of four layers: Ni-YSZ cermet anode, YSZ electrolyte, SDC diffusion barrier and LSCF cathode. A detailed single mSOFC macroscopic computational model is developed based on continuity, momentum, species mass, electric charge and energy conservation equations to accurately capture complex phenomena inside the anode and cathode channels, gas diffusion and catalyst layers and electrolytes of this particular fuel cell type. The knowledge gathered from the single mSOFC computational model is used to scale up, design, optimise and build a 200 W mSOFC stack prototype, fuelled by propane reformate coming from a catalytic partial oxidation fuel reformer. Variation of tube arrangements inside the stack, different air and fuel flow distributions and a heat transfer analysis based on CFD results are studied to develop and optimise the mSOFC stack prototype for the best operating and heat management performance.

Acknowledgement

The SOFC Unmanned Aerial Vehicle (SUAV) research project “Microtubular Solid Oxide Fuel Cell Power System Development and Integration into a Mini-UAV” is part-funded by the Fuel Cell and Hydrogen Joint Undertaking (FCH JU) under the Grant Agreement Number 278629. The information contained in this work reflects the views of the authors only. The authors gratefully acknowledge the support from the SUAV partners: HyGear Fuel Cell Systems BV (Netherlands), Adelan Ltd (United Kingdom), Catator AB (Sweden), CNR-ITAE (Italy), EADS Deutschland GmbH (Germany), EADS UK Ltd (United Kingdom), efceco (Germany), SURVEY Copter (France) and Zachodniopomorski Uniwersytet Technologiczny w Szczecinie (Poland).

Electrochemical Impedance Modeling of Gas Transport and Reforming Kinetics in Ni/YSZ Anodes for SOFCs

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Due to the remarkable fuel flexibility, solid oxide fuel cells (SOFC), particular with nickel-based anodes, are very attractive for energy conversion systems that require reformate fuels. However, the polarization processes which are related to gas transport phenomena, exhibit a high complexity [1-2]: the low-frequency impedance response is observed to consist of multiple arcs (Fig. 1), presumably linked to the complex coupling of multi-component diffusion and reforming chemistry.

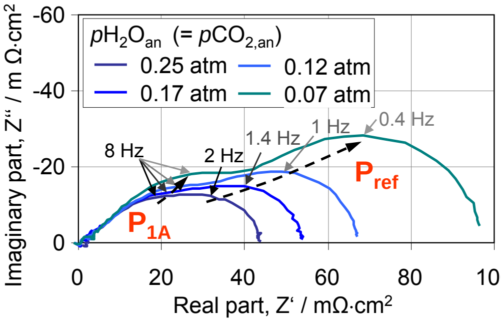

Fig 1: Measured impedance spectra for reformate fueled SOFC, T = 800°C.

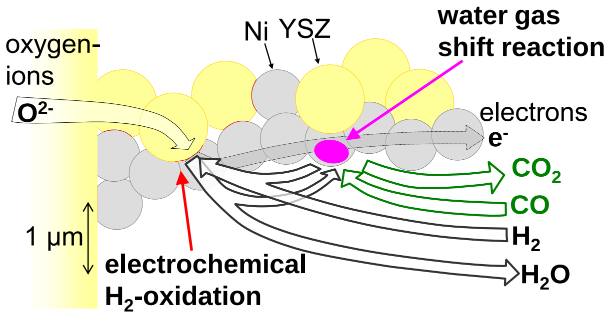

Fig 2: Reaction and transport processes for anode supported SOFC operating with reformate fuel.

In our previous results on Ni/YSZ anodes, we showed that only H_2 is electrochemically oxidized at the triple phase boundary (TPB) and thus CO is subsequently thermally converted via the water-gas shift reaction on the catalytically active Ni surface [2]. As a consequence, gas transport must accommodate two transport pathways which are coupled by the water-gas shift reaction [3]. An implementation of this schematic model (Fig. 2) in FEM simulation is promising to contribute to the understanding of the measured low-frequency polarization processes (Fig. 1). Therefore, in this work, a transient FEM model is set up representing the reaction and gas transport processes for anode-supported SOFC operating with reformate fuels. The isothermal model accounts for the porous-media gas transport within the anode substrate. A global rate expression is applied to model for the gas conversion caused by the heterogeneous reforming chemistry.

As the model is capable to coherently calculate the complex species transport phenomena and the kinetics of the reforming chemistry, the multiple semicircles of the measured gas-transport impedance can be reproduced with the model. The results are used to explain the origin of the measured semicircles.

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Modeling and experimental validation of solid oxide electrolysis cells for hydrogen production

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Solid oxide fuel cells can be operated in “reverse” mode at high temperatures as solid oxide electrolysis cells (SOECs) for production of hydrogen by means of H_2O electrolysis. Unlike low temperature electrolysers (LTEs), which are divided based on the type of electrolyte (alkaline or acidic), the energy required for high temperature SOECs is lower because a part of the energy required for gaseous steam electrolysis is in the form of supplied heat. This makes LTEs commercially incompetitive. Thermodynamically, operation at high temperature decreases the change in Gibbs free energy, i.e., this results in a decrease in electrical energy demand that helps decrease the cost of hydrogen production.

This paper presents a quasi-two-dimensional model to numerically study the performance of a SOECs. The computational framework, independent of the specified geometry, encompasses a detailed multi-step reaction model for heterogeneous chemistry in the H_2 electrode, modified Butler-Volmer formalism to represent charge transfer chemistry and Dusty Gas Model (DGM) for the porous media transport. Electrochemical parameters are adjusted to reproduce experimentally observed data using the B-V equation and its approximations, namely, the hyperbolic sine approximation and the low-field approximation. Simulations are carried out under isothermal/adiabatic conditions to infer the distribution of adsorbed surface species, local current densities, overpotentials, temperature profiles and gas concentrations in the channels. The results indicate that the operating SOEC potential could be notably lowered by increasing operating temperature and steam molar fraction. The concentrations of surface adsorbed species - $H_2O_{(s)}$, $O_{(s)}$, $H_{(s)}$ and $OH_{(s)}$ are shown to be significantly affected by variations in operating temperature, fuel composition and cell voltage. Furthermore, it is found that the exit cathode gas composition is a strong function of temperature, cathode thickness and current density. Simulations are performed to elucidate the effectiveness of the tool for performance and design optimization.

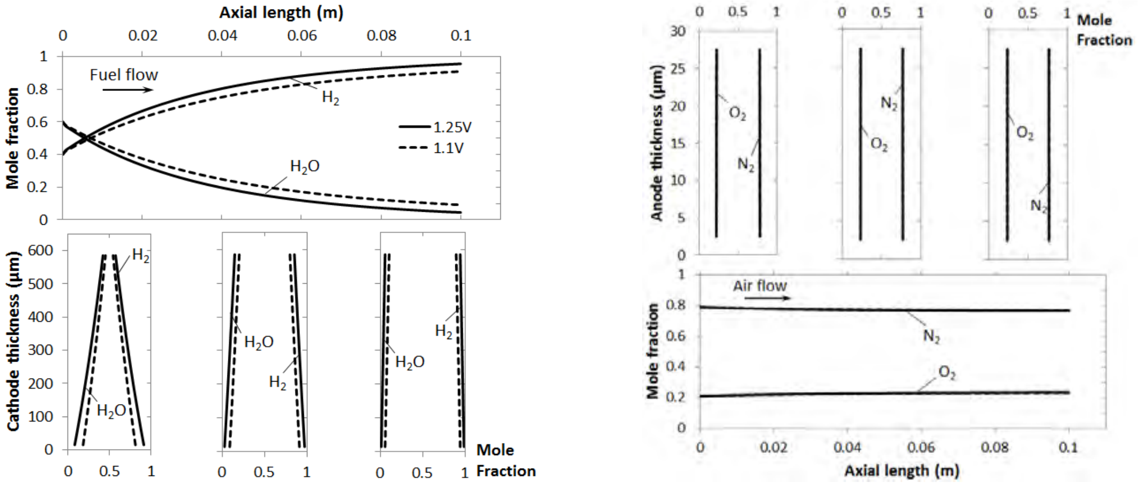

Figure 1: Gas concentration distribution through the SOEC system

Hybrid CFD and EIS model for SOFC and SOEC cell simulations

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EIS analysis of solid oxide fuel and electrolytic cells (SOFC and SOEC) are extensively used for understanding the influence of each process (kinetic activation, gas transport, gas conversion…) and degradation phenomena. Many detailed models are been proposed and most of them show a good agreement with experiments. Two main drawbacks characterize classical EIS models: a) they are usually zero dimensional and use bulk condition for setting the parameters and b) they don't fit experimental data under load conditions mainly because mass transport process are not well modelled. In fact an equivalent circuit element is typically adopted for mass transfer that is based on one dimensional linearization and simply considers Fickian diffusion model.

In present work SOFC anode-supported (and SOEC cathode-supported) cells are studied by electrochemical impedance spectroscopy. Impedance due to mass transfer is obtained from fully three dimensional CFD simulation. Multispecies mass transport and Navier Stokes transient equations are solved both for fuel and air side. Impedance between current density and applied voltage is computed as a function of frequency using an open source tool based on OpenFOAM®. Furthermore Maxwell-Stefan diffusion model and dusty gas model are been implemented for diffusion fluxes. The code is reversible and allows to simulate both SOFC and SOEC operation mode. These improvements show relevant differences in mass transport processes spectra at medium/high current density.

High frequency processes are simulated using classical EIS models. The code can provide local value to compute EIS parameters. This aspect allows to simplify high frequency equivalent circuits reducing the number of parameters and giving them a more physical meaning. More accurate interpretations of processes and degradation phenomena are so possible.

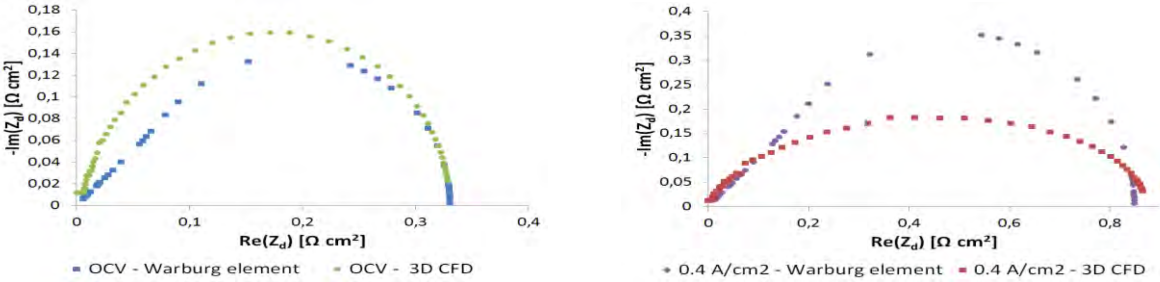

Fig. 1: "Mass transport spectrum computed with classical EIS Warburg element and present work model at OCV (left) and with applied current density (right)"

R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y. Liu, P. V. Hendriksen, *"Detailed Characterization of Anode-Supported SOFCs by Impedance Spectroscopy"* J. Electrochem. Soc. 154 (4), B371-B378 (2007).

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Poster session

Tuesday, March 19, 2013

Computer Aided Material Engineering of Porous Transport Layers with GeoDict

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The membrane-electrode assembly of a PEM fuel cell consists of various porous layers: gas diffusion layer (GDL), micro porous layer, and catalyst layer. Improving the performance of the cell is possible by optimizing each of the layers to its requirements. Optimization includes improving the micro-structure of each layer as material connectivity and pore-morphology have a major impact on the transport properties. Computer simulations help to reduce costs as they allow to determine the transport properties of a layer without the need to produce it first.

On this poster, we will show how the software tool GeoDict[1] can be used to virtually create and analyze porous layers used in PEM fuel cells. GeoDict allows to create pore-scale models by

i. importing a tomography image of a GDL,
ii. importing a FIBSEM image of MPL or CL,
iii. creating a 3D model of a nonwoven carbon paper GDL or
iv. creating a 3D model of a microporous layer or catalyst layer.

Once a model is created or imported, GeoDict can determine the effective transport properties of the material, i.e. pore size distribution, diffusivity, conductivity, permeability and flow resistivity. Also, saturation dependent properties like capillary pressure curve and relative permeability can be determined with a pore morphology approach.

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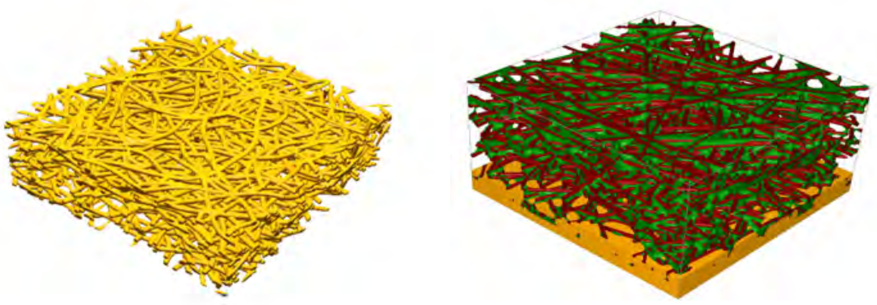

Figure: Gas diffusion layer models, on the left hand side with curved fibers, on the right hand side with binder and microporous layer.

Opportunities for the validation of fuel cell modeling studies through the H2FC transnational access activities

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The H2FC European Infrastructure Project (http://www.h2fc.eu) aims at integrating the existing and future research infrastructures in the field of hydrogen and fuel cells. The project is divided in three parts: joint research activities, networking activities and transnational access activities. This last part provides the opportunity for researchers from academy and industry to obtain access to unique research facilities (e.g. neutron imaging at the NEUTRA [1] and ICON [2] beam lines). A total of 15 partners offer free of charge access through this program to more than 50 installations.

In this presentation, the opportunities opened to researchers active in fuel cell modeling in terms of experimental validation will be exposed through the example of the infrastructures provided by the Paul Scherrer Institute. The combination of water distribution measurement using neutron imaging with advanced performance analysis techniques including helox/O_2 pulse analysis [3] and electrochemical impedance spectroscopy (EIS) can provide a much stronger validation data base than the simple recording of current-voltage characteristics. Studies which imply variations of materials and/or flow channel dimensions could also benefit from the newly designed multi-cell setup [4] allowing the simultaneous operation and imaging of up to 6 small scale fuel cells. A brief overview of the research installations provided by other project partners will also be given.

Besides the technical possibilities of the offered installations, information about the process for obtaining access will be given. This information includes the conditions which the user or user group must meet in order to be eligible for transnational access within the H2FC project, as well as the procedure to be followed.

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Mass transport in gas diffusion electrodes with aqueous electrolytes for Li-O_2 batteries: Modeling and experiments

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The lithium-oxygen (Li-O_2) battery is an interesting candidate to substitute conventional combustion technologies in the mobility sector [1]. However, the development of Li-O_2 cells is still at an early stage and a list of challenges has to be addressed. A relevant aspect is the need to deliver high power densities during discharge. Therefore, good oxygen supply in the cathode is a crucial factor in the design of this battery concept [2]. Gas Diffusion Electrodes (GDEs) offer fast oxygen transport, a high specific surface area, and therefore high discharge rates. Although GDEs are already used in various applications like electrolysis or fuel cells [3], they have not been studied in detail in the context of lithium-oxygen cells.

We develop a continuum model of Li-O_2 batteries describing the coexistence of solid, liquid, and gaseous phases in the GDE [4]. Oxygen dissolution in the aqueous electrolyte, oxygen reduction and lithium oxidation at the two electrodes are taken into account, as well as precipitation of solid $LiOH \cdot H_2O$ that occurs at concentrations above the solubility limit [5]. Kinetic parameters for the oxygen reduction reaction have been extracted from experimentally obtained polarization curves in one molar solution.

For the validation of the proposed model half-cell experiments using silver electrodes have been carried out for various temperatures and concentrations. Experiments include cyclic voltammetry and electrochemical impedance spectroscopy. The combination of experimental techniques and our model approach allows detailed insight into the transport and saturation behavior of the GDE. The validated model agrees reasonably well with experiments and can be used to improve the design of future electrodes.

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Analysis of starvation and degradation effects in PEFCs under dynamic operating conditions

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The dynamic operation of polymer electrolyte fuel cells (PEFCs) is investigated by experimental measurements as well as computational fluid dynamics (CFD) simulations. Especially in automotive applications, transient operation conditions like load changes or start up / shutdown cycles lead to starvation effects on anode as well as cathode side which are closely connected with degradation effects like carbon corrosion. From the electric potential range, carbon corrosion is more likely expected at the cathode side. At events as start up / shutdown cycles, the oxidation of the carbon catalyst support on cathode side induced by a local fuel starvation on anode is described in literature [1] and is known as „reverse current decay mechanism" [2]. Furthermore, the local fuel starvation on anode side provokes a massive cell reversal in which the carbon catalyst support on anode side is oxidized in order to maintain the current [3].

The correlation of local starvation effects and carbon corrosion was investigated by load change experiments on a test bench for dynamic measurements which has been developed by ZSW. The sampling rate of the test bench was in the range of 1–3 milliseconds (ms) and in order to analyze the current density distribution during the load change, a current scan shunt with 144 measurement segments and a reaction time of about 10 ms was used. The availability of different flow controllers inside the test bench enabled the set up of different operating conditions according to different current densities at the same time. The load changes were performed by opening or closing the magnet valves of the respective pathways within 10 ms. For the detection of carbon dioxide due to the carbon corrosion, an in-situ measurement of the cathode exhaust was examined by using a non-dispersive infrared (NDIR) analyzer.

The dynamic measurements as well as the transient simulations were performed with a PEFC single cell with meander-shaped flow field channels and an active area of 100 cm^2. Load changes from 0.2 to 1.0 A cm^{-2} were investigated by varying the adaptation of mass flow rate according to 1.0 A cm^{-2} before, simultaneous and after the load change in order to investigate the fuel cell operation under a brief starvation as well as under a sufficient media supply. In addition, these kinds of mass flow adaptations were performed on both sides as well as on anode and cathode side while the other side had a sufficient media supply. Regarding the load changes with starvation on anode side, a massive cell reversal, an increase in the cell resistance and an amount of carbon dioxide release of greater than 1 µmol were obtained. At load change with starvation on both sides, the highest amount of CO_2 was 2.35 µmol inside the cathode exhaust. Due to the massive impact of fuel starvation on cell degradation, only measurements with adaptation of mass flow rate before the load change were possible without accelerated cell damage. In comparison to the fuel starvation on anode, the oxidant starvation on cathode side had a minor impact on cell degradation. The maximum amount of CO_2 was 0.9 µmol at all load changes with adaptation in the range of 7 s in front of and 2 s afterwards the load change.

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Electrochemical impedance modeling of gas transport in Ni/YSZ anodes and associated gas channel for SOFCs

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Solid oxide fuel cells (SOFC) are very attractive for energy conversion systems due to their high efficiency and their remarkable fuel flexibility. In the past, the loss processes occurring during operation have been characterized thoroughly and can be distinguished into ohmic loss mainly due to the low conductivity of the electrolyte, activation polarization resistance based on the electrochemical reaction and into diffusion polarization, which arises from the species concentration gradient inside of the porous electrodes [1].

However, due to the fuel consumption the water vapour partial pressure increases under operation towards the gas outlet in the gas channels and therefore influences the gas transport in the porous electrodes and lowers the harvestable power. This additional loss can be observed via electrochemical impedance spectroscopy notably for lower anodic fuel flow rates in terms of an additional low frequent arc in the impedance spectrum. In literature [2-3] this loss is called generally gas conversion, but its influence or coupling with the species transport in the porous electrode remains not completely certain. A detailed analysis via multi-dimensional FEM-modelling of application-specific cell geometry including the porous anode substrate is desirable to understand the origin of the additional loss and the coupling with the gaseous species transport itself.

In this work, a time-dependent finite element model (FEM) is set up representing the reaction and transport processes for anode-supported SOFC operating with H_2/H_2O. With the developed FEM model, it is aimed to investigate the relation between the reported characteristics of measured impedance response and the underlying gas transport within Ni/YSZ anodes during the operation with low anodic flow rates. The isothermal model accounts for the mass transport phenomena within the anode substrate and the corresponding gas channel and uses a rate step determine expression to model the partial pressure depending electrochemical reaction.

As the model is capable to calculate the complex species transport phenomena spatially and time resolved, the increased overall resistance linked to lower anodic flow rates can be reproduced with the model. Furthermore the model has the ability to reproduces qualitatively the 2 low frequent arcs of the measured impedance response. The results are used to gather deeper knowledge about the coupling of the gaseous species transport phenomena and the fuel consumption.

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Time-dependent 3D Impedance Simulation for mixed conducting SOFC Cathodes

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The performance of porous mixed ionic-electronic conducting (MIEC) $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathodes is predominantly determined by the material properties like the oxygen surface exchange and bulk diffusion coefficient, as well as the microstructural properties including porosity, tortuosity and surface area. Electrochemical impedance spectroscopy (EIS) is an established method for the analysis of complex electrochemical systems such as solid oxide fuel cells (SOFC) enabling a deconvolution of individual electrochemical processes at the electrodes [1]. In combination with appropriate impedance models such as the Gerischer element [2] the cathode performance can be determined and degradation as well as information about material properties of the cathode come into reach [3].
Unfortunately these models assume a cathode with a homogeneous microstructure and transport processes in the electrode such as gas diffusion in the porous electrode and electronic conduction in the mixed conductor as well as nonlinear effects, inhomogeneous microstructures and the impact of the electrode thickness are not considered.

In this work, we present a time-dependent 3D finite element method (FEM) model for mixed conducting cathodes to overcome these disadvantages. The model is based on our formerly published stationary 3D cathode models [4,5], which are extended to perform simulations in the time-domain of the rate-determining processes i) gas diffusion in the pores, ii) oxygen exchange between the gas phase and the mixed conductor, iii) oxygen ion diffusion in the mixed conductor and iv) charge transfer between the MIEC cathode/electrolyte. The space- and time-resolved simulations of the current response due to a sinusoidal voltage signal or an appropriated voltage step [6] enable the calculation of the impedance data.
The time-dependent 3D impedance model was validated by performing low-level signal simulations on simplified microstructures and comparing them with the results calculated according to the homogenized model [2] and measured impedance data of LSCF-cathodes [1]. The simulation results enabled us to understand the impact of different loss contributions on the impedance spectra and provided guidelines for the design of MIEC cathodes.

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Understanding the effects of the polysulfide shuttle in Li/S batteries: A one-dimensional continuum model

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Lithium-Sulfur (Li/S) cells are promising candidates for a next generation of safe and cost-effective high energy density batteries for mobile and stationary applications. At present, Li/S cells still suffer from poor cycleability, capacity loss under high current densities and self-discharge. Furthermore, the underlying chemical mechanisms of the general discharge/charge behavior as well as Li/S-specific phenomena like the polysulfide shuttle-effect during charging (i.e., the continuous oxidation and reduction of polysulfide intermediates associated with transport from one electrode to the other) are not yet fully understood.

Here we present a thermodynamically consistent and fully reversible continuum model of a Li/S cell with simplified four-step electrochemistry, based on a multi-phase modeling framework developed previously [1]. The model reproduces experimentally obtained discharge curves from literature [2] at various current densities with fairly high accuracy. In contrast to previously published, similar Li/S cell models [3,4], our model allows for polysulfide redox reactions and the precipitation of solids on the anode side. While being instructively simple, the presented model can still reproduce distinct Li/S-cell operational features and degradation phenomena like seemingly infinite charging at low charge current-densities (shuttle effect), voltage spikes before the plateau-phases of the charging process, as well as voltage drops and capacity loss due to cycling. This not only fosters understanding of possible mechanisms for the shuttle effect, but also makes the presented model a suitable tool for investigation and interpretation of Li/S cell experimental data and a powerful base model for further, more complex model studies focusing on specific details of Li/S cells.

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Accurate calculation of tortuosity from velocity fields of transport simulations in porous media

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The gas diffusion layer (GDL) is a key component of fuel cells based on polymer electrolyte membranes (PEFC, DMFC and HT-PEFC). The efficient operation of fuel cells requires good transportation properties of GDL which allow educts to reach the electrodes out of the gas channels as well as to transport products from the electrodes back to gas channels.

Transport simulations on the microstructure of porous media require three steps. The first is the pre-processing step of creating the geometry, either the real structure or a virtual structure generated by a model. The most prominent step is the transport simulation itself. The result is in any case a detailed field of velocity vectors. In the post-processing step the desired outcome is calculated. One prominent result is an effective tortuosity. We focus on two different methods [1] of calculating the value of the tortuosity, both of them based on a capillary model. We present characteristics of the two methods and their applicability on particular microstructures.

The general objective of our research is the construction of microstructures of GDL which are favorable for mass transport in fuel cells. Preliminary investigations of GDL microstructures with respect to transport relevant structural properties have been reported in [2][3][4]. The appropriate method of post-processing is applied to the results of transport simulations in fibrous GDL material by means of the Lattice Boltzmann method. The underlying fine structure was generated by a stochastic model of the geometry.

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Ab-initio study of processes on Li_2FeSiO_4 surfaces

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In addition to the low production costs and safety, Li_2FeSiO_4 has a high theoretical capacity of up to 300 mAh/g[1], when used as cathode material in rechargeable Li ion batteries. In synthesis Li_2FeSiO_4 typically crystallizes in the orthorhombic space group $Pmn2_1$, with the cations located at the tetrahedral interstitials of a hexagonally close packed framework of oxygen atoms [2].

Materials properties such as diffusion barriers [3] or redoxpotentials [4] that are relevant for the electrode performance in Li ion batteries might be different at the surface compared to bulk. Here theoretical tools can help to elucidate the differences by, e.g., determining the influence of adatoms or chemical substitutes at the surface on diffusion through the surface.

In this study we present results obtained by ab initio electronic structure calculations via density functional theory (DFT). Surface energy calculations for Li_2FeSiO_4 reveal the composition and structure of the most stable Li_2FeSiO_4 surfaces. These calculations give insights in the different chemical bonding mechanisms that come into play in Li-transitionmetal-oxides. Application of a simple model that combines ionic and covalent behavior shows that indeed both kinds of bonds contribute to the surface energy. Furthermore the energetically most favorable shape for nanosized particles is determined – the dominant surfaces are of type {010}, {110} and {001}. In addition to that we show the influence of the applied voltage V against a Li/Li^+ counter electrode on the surface composition of these predominant surfaces. Furthermore, aspects, concerning the impact of different surfaces on Li extraction and incorporation voltages [4] are adressed. We also address Li diffusion on the surface with regard to possible pathways and energetic barriers and compare these to bulk references.

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Investigation of the influence of membrane parameters on PEMFC performance using the CFD code AVL FIRE

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The goal of the work was to investigate the influence of characteristics of the polymer electrolyte membrane on PEMFC performance. The simulations of PEMFC behaviour were carried out using the CFD code AVL FIRE [1-2] for different water sorption isotherms, water diffusion and electro-osmotic coefficients. The calculations were performed on a single channel of the fuel cell, for 70°C, symmetric humidification RH=90% and pressure 1 atm. The description of the membrane water transport [3-4] takes into account the dependence of water diffusion and electro-osmotic coefficients on the membrane water concentration and temperature. The membrane over-potential is calculated from Ohm´s law, the membrane conductivity as a function of the membrane water concentration is described by the equation of percolation theory [5]. The membrane water concentration is determined from the water sorption isotherm.

The simulations have shown that changes in water sorption of the membrane significantly influence the total water flux through the membrane and the polarisation curves of the fuel cell. The increase of the water sorption of the membrane of 25-30% leads to increasing the current density of 15-17%. The variations of the water diffusion as well as of the electro-osmotic coefficients result to the changes of the total water flux, but do not lead to some visible changes in the mean water concentration of the membrane and consequently influence the current density of the fuel cell insignificantly.

In the further work we plan to study the influence of other characteristics of the membrane (thickness, membrane conductivity, permeability of gases etc.) as well as the parameters of catalyst and gas diffusion layers on PEMFC performance.

The work has been financially supported by Austrian Promotion Foundation (FFG), Project A3 FALCON, No.835811 (Advanced 3D Fuel Cell Analysis and Condition Diagnostics).

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Abstract for poster presentation

Modelling and simulation of the electrohydrodynamic equilibrium shape of nanochannels in PEM

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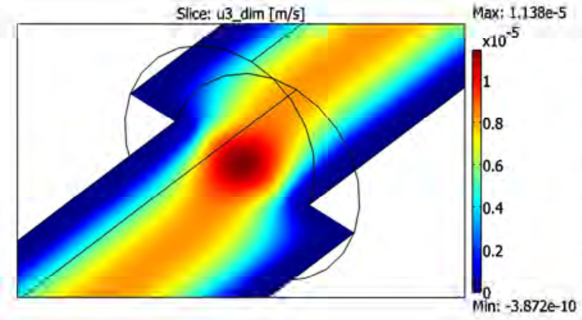
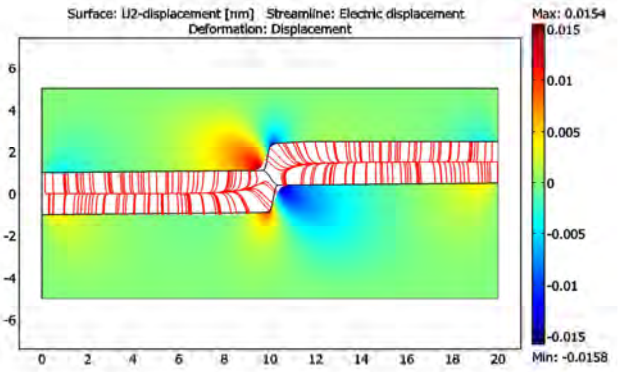
Polymer-electrolyte membranes (PEM) are assumed to consist of many cylindrical nanochannels [4], which may connect, open or close under operation [1]. It is important to understand the change of the channel network morphology with time in order to understand and design better material properties of PEM. We focus on the situation when one nanochannel joins another nanochannel.

We present a new, thermodynamically consistent, model for the charged-fluid flow and the deformation of the backbone of polymer electrolyte membranes (PEM) in hydrogen fuel cells [3]. The elastomer membrane (e.g. Nafion) is assumed to exhibit small displacement gradients, while the pore is completely filled with water and protons. The model consists of a system of partial differential equations, comprising a linear elasticity equation for displacements within the solid elastomer, a nonlinear Poisson equation for the electric potential within the channel, Stokes flow for the protonated water (liquid) and a modified Young-Laplace equation on the solid-liquid interface.

We solve the coupled non-linear equations numerically and examine the equilibrium pore shape of the channel, see the figures for fluid flow (left) and displacement field and electric field (right) [2,3]. Our numerical algorithms and shape optimization techniques have been verified mathematically [2]. This computationally challenging problem is particularly important in order to better understand the experimentally observed phenomenon of ohmic interface resistance of connecting nanochannels. Parts of this research have been supported by Toyota Motor Corporation.





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Case-specific adaptions of the DIRECTT algorithm to neutron and electron tomography of fuel cell components

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We present improved results of computed tomography (CT) using the DIRECTT (Direct Iterative Reconstruction of Computed Tomography Trajectories) algorithm [1,2]. In the context of fuel cells, we focus on two key issues: (i) water agglomerations in the flow-field channels imaged by neutrons at a resolution of some 100µm and (ii) the estimation of the free surface of metallic catalyst particles imaged by electrons with sub-nanometer resolution [3]. Since both types of experiments differ essentially from ideal CT measuring conditions special tools had to be developed in order to suppress reconstruction artifacts.

Concerning neutron tomography, the main obstacle is the large beam aperture (some cm) which results in blurred projections. The blurring refers to each volume element as a function of its individual detector distance. The position dependent smearing is inserted into the projection part of iteration cycles [4]. Although being rather time-consuming the gain of resolved details justifies the extra effort regarding both model calculations [4] and experimental data (Fig. 1 left).

Electron tomography is affected by a bunch of restrictions. The missing wedge (MW) and the partial opacity turned out to have the widest impact on the reconstruction artifacts. While the latter is a subject of data pre-processing (precise axis alignment and carefully thresholding low intensity), the MW problem does not require any extra measures since DIRECTT accepts even partial trajectories to localize the respective elements within the reconstruction array [5] (Fig.1 right).

Alternatively, we applied a three-stage strategy (two binary stages, one without restrictions) to MW data sets. The advantages of the resulting reconstructions are shown by means of Fourier transforms and are assessed by stochastic (orientational) characteristics of the reconstructed boundaries ("rose of directions" approach) [6].

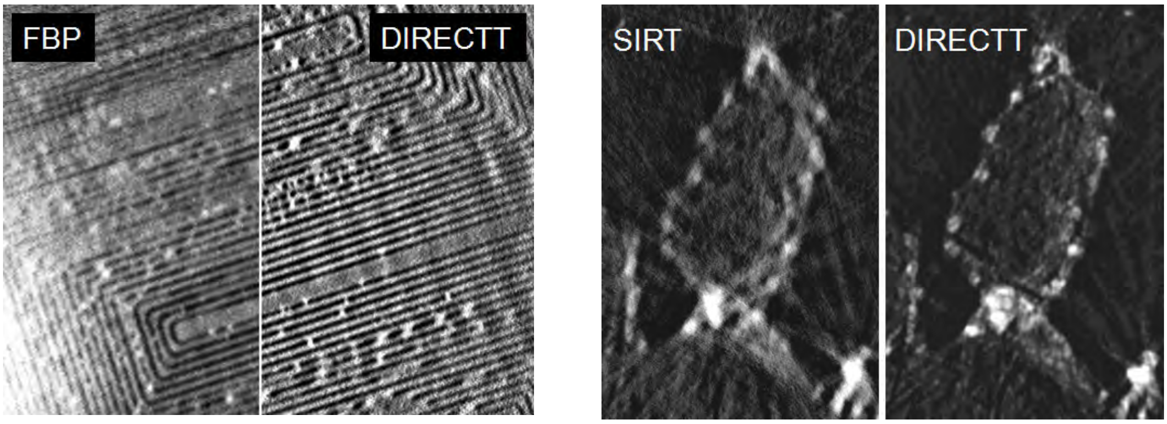

Figure 1. Reconstruction results of conventional algorithms compared to DIRECTT: water agglomerations at a cathode flowfield obtained from neutron tomography (compared to Filtered Back Projection (FBP), left) and nanometer sized catalyst particles on carbon support obtained from electron tomography (compared to Simultaneous Iterative Reconstruction Technique (SIRT), right).

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Microstructure influence on effective transport properties investigated by means of a stochastic simulation model

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The effective transport properties of porous materials used for regenerative energy technologies play an important role for the overall performance. Microstructure degradation may lead to a harmful decrease of the transport properties and associated performance. Thereby it is usually not clear which morphological feature of the microstructure is responsible for the performance loss. The aim of this investigation is to study the fundamental relationship between effective transport properties and morphological characteristics by means of a stochastic simulation model in combination with the finite element technique (FEM). In particular our focus regarding the morphological characteristics is on phase porosity ε, geometric tortuosity τ and a constrictivity parameter β. In previous studies [1,2] using experimental techniques to measure effective transport properties and 3D-microstructure analysis it was shown that there exists a functional coherence between the mentioned parameters and the effective conductivity σ_{eff}, i.e., $\sigma_{eff} = \sigma_0 (\beta\varepsilon / \tau^2)$, where σ_0 is the intrinsic conductivity. This kind of relationship was previously postulated based on theoretical considerations [3]. In principle the parameters in this equation are now accessible with 3D image analysis, and thus the effective transport properties can be predicted. However, there are uncertainties with respect to the validity of the equation mentioned above, which motivates us to test the validity using a 3D microstructure simulation model based on methods from stochastic geometry [4]. More precisely, we develop a stochastic simulation model, which allows generating virtual microstructures covering a wide field of possible parameter constellations for ε, τ and β. The model has proven the potential to describe experimental microstructures gained by 3D FIB-SEM tomography as for example Ni-CGO anodes in SOFC. Thus a set of virtual microstructures with varying parameter constellations is generated. These virtual structures are used as input for transport simulations by FEM. The effective transport properties from FEM are then compared with the ones predicted using the microstructure parameters (β, ε, τ). The elaboration on these relationships is of high relevance, since they open new possibilities to easily access effective transport properties, particularly in cases where the conventional experimental measurements are difficult and/or expensive (e.g. ionic conductivity in Ni-YSZ cermets).

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Mathematical modelling of Direct Ethanol Fuel Cells including free and adsorbed intermediate species

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A 1D+1D model for Direct Ethanol Fuel Cells (DEFCs) is presented. The complex kinetics of the multi-step Ethanol Oxidation Reaction (EOR) is described using as starting point the kinetic model by Meyer et al. [1], which considers free and adsorbed intermediate species on a binary catalytic layer based on Pt. The effect of the adsorbed species is modelled by their corresponding coverage factors on the catalyst surface [2]. Due to the low concentrations of carbon dioxide and methane produced under typical operating conditions, a truncated kinetic model is proposed. The truncated model ignores the influence of these products and their intermediate adsorbed species, which leads to an analytical expression for the coverage factors associated with the most relevant adsorbed species. This simplification speeds up the simulations significantly, thereby reducing computational cost. Following standard practice, the Oxygen Reduction Reaction (ORR) is described by a first-order Tafel-like kinetics [2, 3, 4], while the diffusive (convective) transport of ethanol and product species (acetaldehyde and acetic acid) across (along) the channel is modelled using a simplified 1D approach. Figure 1 shows the computed cell performance at different locations along the channel, exhibiting the characteristic double-hump structure typical of DEFCs. As shown in Fig. 2, the production of acetaldehyde plays an important role on cell performance, leading to concentrations of this species that are comparable to those of ethanol. Since the rate of consumption of acetaldehyde is slower than its rate of production, acetaldehyde accumulates as far as there is enough ethanol to react. However, when mass transport limitation arises due to the shortage of ethanol downstream the channel, the consumption of acetaldehyde becomes the only way to generate current, producing a significant penalty on DEFC performance at high current densities.

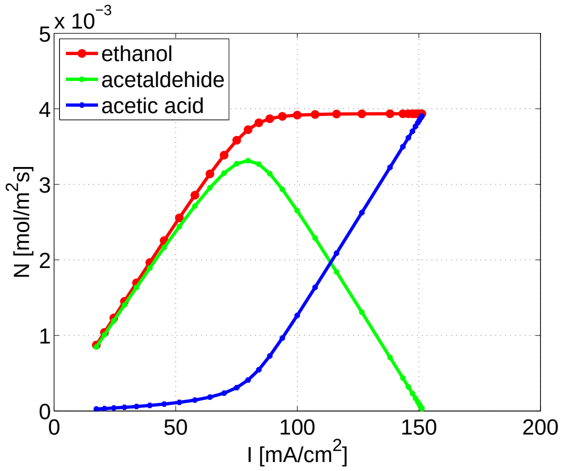

Fig 1: Rate of production/consumption of ethanol, acetaldehyde and acetic acid as function of current density at the mid-point along the channel.

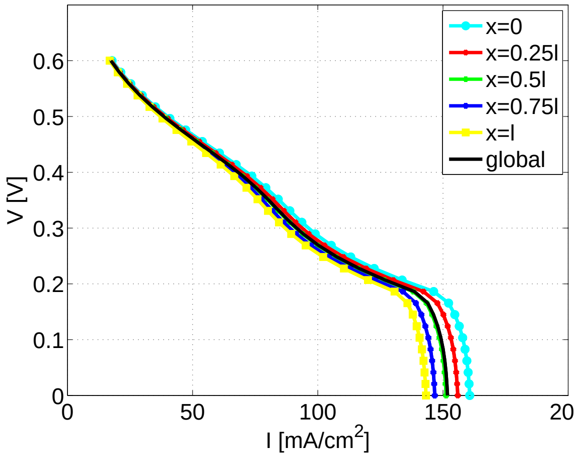

Fig 2: Polarization curves at different position along the channel for a 25 cm^2 with 1M ethanol feed concentration at 5 ml/min. T=70ºC. L=1.15m

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Structural and Dynamical Properties of Li-Ion Batteries Studied by Various NMR Techniques

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In lithium-ion battery research a lot of new electrode materials and electrolytes are developed and investigated aiming for improved capacity and cycling performance. This generates the need for a fundamental unterstanding of the cycling process, i.e. insertion and removal of the lithium ions at the electrodes, changes at the electrode/electrolyte interface and Li diffusion through the electrolyte.

Nuclear Magnetic Resonance (NMR) is a versatile tool to study both structural and dynamical properties of Li-ion batteries. *Ex situ* and *in situ* Solid State NMR Spectroscopy reveals the local environment of the observed nucleus at different states of charge. Lithium diffusion in electrode materials and electrolytes at different time and length scales can be investigated by various NMR techniques such as lineshape analysis, relaxometry and field gradient measurements.

In situ NMR is used to study the formation of Li dendrites on the surface of lithium metal electrodes during cycling [1]. *Ex Situ* Solid State NMR Spectroscopy is applied with a focus on materials related to the anode material SnO_2, namely Zn_2SnO_4 [2] and $Al_ySn_{1-y}O_{2-y/2}$ [3]. Here the idea is to overcome the large volume changes during cycling by embedding the electrochemically active Sn material in a matrix.

NMR relaxation experiments applied to the anode material $Li_4Ti_5O_{12}$ at different states of charge reveal activation energies of 0.45 eV for Li hopping [4]. A combination of NMR techniques allows to study Li ion dynamics over several orders of magnitude in time. This is demonstrated by results from spin-lattice relaxation NMR and lineshape analysis obtained in $LiAlO_2$ [5]. Field Gradient NMR measurements are used to acquire lithium diffusion coefficients and transference numbers in different electrolytes [6].

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A simplified model for O_2 transport and reduction kinetics in porous cathodes of Li-O cells

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Abstract for poster presentation

Oxygen transport and oxygen reduction kinetics are the two most pressing issues of today's Li-O – cells. A large number of cathode structures and materials including catalysers were already investigated, but yet without substantial progress. Few exceptions like nano-porous Au-cathodes show in principle the viability of the Li-O-cells but are cost inefficient. To gain improvement, bottleneck processes of the cells must be identified first. This usually requires a large number of different experiments and analysis.

Therefore a simple, quasi 1 dimensional, mathematical computer model was developed to facilitate the interpretation of data generated by a certain electrochemical method. The model covers the most crucial aspects of Li-O - cells upon discharge, including O_2-absorption from gas phase, diffusive O_2 - transport, O_2-reduction kinetics, passivation of active cathode BET surface and the well known issue of pore clogging. By accepting a certain inaccuracy of the model, the number of unknown and/or difficult to measure parameters is kept rather low, leaving only the effective O_2 diffusion constant, the maximum layer thickness of formed Li_2O_2 and the heterogeneous rate constant as free parameters disregarding the Li-transport completely.

Chronoamperometry is used as the experimental method to generate the data that can be interpreted by means of the model. The computer model simulates a one time discharge at constant potential and calculates a current transient curve which is to be compared to a measured curve. Since the experimental discharge is done at constant potential, the heterogeneous rate coefficient can really be regarded as a constant. Its dependency on potential might be elucidated by performing several discharges at different constant potentials.

The parameters obtained by this simple model might also be considered as starting values for more sophisticated simulation software such as DENIS by Bessler et al.

Simulation and modelling in a SOFC/GT hybrid power plant

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The continuously increasing demand for electrical energy requires the development of power plants with high efficiencies and low emissions. A hybrid power plant consisting of a solid oxide fuel cell (SOFC) system coupled with a gas turbine (GT) promises to fulfill these requirements and also has the advantage of offering a wide range of applications from several 10 kW to multi MW. Indirectly and directly coupled systems are possible, mainly distinguished by the higher operating pressure and reduced heat transfer losses of the directly coupled SOFC system. Since the directly coupled systems with elevated SOFC operating pressure promise to outperform the system efficiency of the indirectly coupled systems [1-2], the DLR has been investigating the corresponding fundamentals and requirements of a directly combined fuel cell and gas turbine power plant for several years.

An elementary kinetic SOFC stack model was developed and experimentally validated [3] in a wide range of operating conditions. This model was integrated into an existing model of a gas turbine [4]. The model is used to carry out stationary hybrid power plant simulations in order to investigate how variations in operating strategy and component characteristics influence the performance of the hybrid power plant as well as the operating conditions of the SOFC. Results show that varying electrical SOFC power while keeping electrical gas turbine power constant strongly influences the overall electrical efficiency of the hybrid power plant.

The experimental and simulation results are to be used to adapt the existing models from stationary to transient regime. This allows for future development of operation and control strategies. A pilot power plant is to be designed and commissioned to validate the transient model accordingly.

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Numerical Simulation and Experimental Validation for Thermal Runaway on Lithium-ion Cells

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Thermal runaway of Li-ion cells is a critical risk for practical operation of large-scale cells [1]. Aiming at the goal of building an early-alert heat management system for Li-ion cells, we present preliminary simulations of exothermic sub-reactions as well as stochastic thermal model. In addition, the cell model is validated with experimental charge and discharge curves. The thermo-electrochemical model is designed for multi-scale mechanisms from nano to macro scale with detailed electrochemical and thermo chemical kinetics [2]. The sub-reactions include three decomposition mechanisms: solid electrolyte interface (SEI) decomposition, electrolyte decomposition (i.e. SEI formation) and evaporation of solvent. Fig.1 shows preliminary simulation results of SEI decomposition/formation under constant heating rate. The results allow us to compare with differential scanning calorimetry experimental data to obtain thermodynamic parameters in the right range. The detailed electrochemical model is coupled to COMSOL via MATLAB and allows thermal simulations in one, two and three dimensions. Adopting a stochastic framework, several models are run simultaneously and represent a probability density function of the current prediction of the battery's temperature state. When measurement data becomes available (e.g. battery surface temperature, voltage), they can be used to update the model prediction during the course of the simulation. The incorporation of real-time data leads to a more accurate temperature prediction. This prediction – update cycle is implemented as a particle filter (e.g. [3]) as a proof of concept. The real-time capability of our method still has to be established, e.g. via model reduction techniques. Finally, the explanatory power of the different measurement quantities on the temperature profile is investigated.

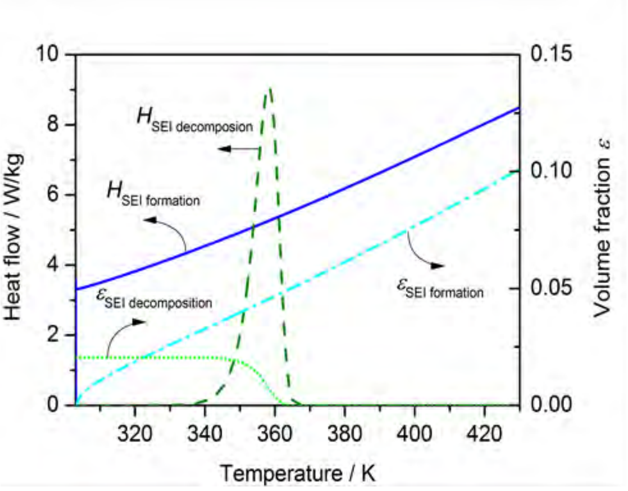

Fig.1 Heat flow and volume fraction profiles for SEI formation and decomposition under constant heating rate of 5K/min.

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Preliminary physical model of DMFC anode impedance

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Electrochemical impedance spectroscopy (EIS) is an in situ measurement technique that permits to monitor the system internal losses during continuous operation. Despite its potentialities the interpretation of EIS data is still object of discussion in the literature and physical modeling becomes crucial to analyze experimental observations. In the literature many works has been carried out on solid oxide fuel cells (SOFC) [1] and polymer electrolyte fuel cells (PEMFC) [2], but there is no reference on the development of physically based model of DMFC anode impedance.

In this work the previously developed 1D+1D DMFC model [3] has been integrated with an electrode of a finite thickness and a detailed description of mass transport phenomena through anode gas diffusion layer (GDL). In particular water is transported through GDL only by liquid convection, while methanol mass transport is governed by liquid convection and gas and liquid diffusion. Moreover the GDL is not assumed to be always flooded with fully liquid pathways, but, as demonstrated in recent studies [4], liquid convection through GDL is intermittent and breakthrough locations change with time,

After obtaining the stationary solution, the transient perturbation solution of the DMFC anode can be obtained linearizing the system about a steady-state value and perturbing each of the variables with a sufficiently low sinusoidal disturbance. Then neglecting the terms with products of the disturbances and subtracting the steady-state equations, it is possible to obtain a system of linear equations for the complex perturbation amplitudes in the frequency domain. Therefore the impedance of the anode can be numerically calculated as the ratio between the oscillating voltage and current.

Fig.1 illustrates preliminary simulation results. The green line represents impedance simulation without the effect of GDL: its contribution has a relevant influence even at low current density. Instead the blue line shows impedance simulation performed with the assumption that GDL is always flooded with fully liquid pathways: the model predictions are inconsistent with the experimental data. This is a further confirmation that liquid convection through the GDL is an intermittent phenomenon. The validation of the developed model on a wide range of operating conditions is in progress.

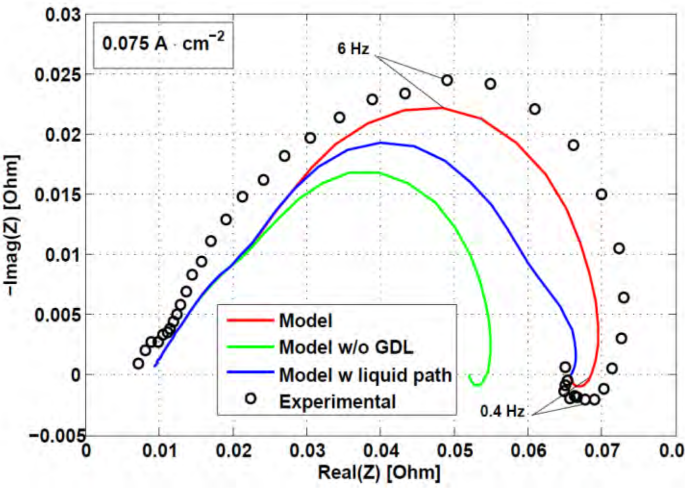

Fig. 1. Simulation results at i=0.075 A/cm^2.

Acknowledgment: work in the frame of the FP7 project Premium Act (EC G.A. 256776).

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Simulation and parametric analysis of a power system equipped with a SOFC stack

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A micro-scale power system based on a micro-tubular Solid Oxide Fuel Cell (SOFC) stack was investigated within the Fuel Cell and Hydrogen Joint Undertaking (FCH JU) funded SUAV project. This system equipped with additional components such as reformer, combustor, heat exchangers will be integrated finally with a battery to power a mini unmanned aerial vehicle (mini-UAV). For a successful integration of the 250 W SOFC sub-system with a battery, parametric optimization and heat management are required.
The commercially available Aspen Plus process simulator was chosen for modelling and parametric analysis of the investigated system. The paper presents the first step of balance of plant simulation. The effect of fuel reforming and operating conditions, i.e. temperature, pressure and air inlet flow were investigated. The unit operation models available in Aspen Plus were used to model the system. The Aspen Plus simulator does not have a model of a SOFC stack, therefore a simplified stoichiometric reactor model was used. Initially, simplified stoichiometry of the electrochemical reaction was based on the reaction of hydrogen with oxygen. The assumed fuel utilization of hydrogen was equal to 0.5. Using that simplification, current–voltage characteristics of the fuel cell stack as well as separate electrochemical reactions at the anode and cathode were not included. However, that simplification allows for an initial assessment of the system design. Actual fuel reforming was simulated in the system by using either steam reforming or catalytic partial oxidation (CPOx) of propane. In both cases a stoichiometric reaction model was used. A sensitivity analysis of the air flow rate at the inlet of the system was performed in order to estimate the gas temperature at the outlet of the fuel cell stack. A minimum air flow rate was computed. Below that value it was impossible to use enthalpy of the exhaust gas to heating the reformer (steam reforming case). From the design point of view dimensions and weight of the mSOFC power system including the fuel tank are very important in a mini unmanned aerial vehicle. Therefore, at that stage the main issue is a determination of the fuel consumption, which was calculated for both reforming types: with steam and CPOx reaction of propane. Lower consumption of propane was found for the steam reforming; however an additional water tank in that system is then required, which increases the weight of the whole power system.

Acknowledgement

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Microstructure of fuel cells and batteries
-
Fuels cell stacks and systems
-
PEM fuel cells

Wednesday, march 20, 2013

Session Chairs: Werner Lehnert, Felix Büchi, and Thomas Jahnke

Model validation for model development in electrochemistry

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Mathematical models can be useful for predicting optimal process controls and designing electrochemical cells. They can also contribute to the understanding of dynamical effects inside electrochemical cells and the interplay of different processes. However, formulating appropriate mathematical models in electrochemistry is a challenging task. The challenge arises from the complexity of electrochemical systems on different length and time scales, in combination with limited available experimental results. As a result of that complexity, models are often formulated with 50 or more model parameters and are often partly or completely disconnected from microscopic phenomena.

We present a rational approach to model validation for model development which addresses the complexity of the system. This approach assesses four criteria: (i) the physical or chemical information content of the mathematical model (e.g. “white”, “gray” and “black” box models), (ii) goodness-of-fit using experimental results, (iii) quality of estimated model parameters (covariance analysis), and (iv) quality of model predictions and cross validation. After assessing these criteria, it is often necessary to extend the model by relaxing physical approximations or including previously neglected effects. The cycle is then repeated until the validation criteria reach acceptable levels. Also, based on these four criteria, different modelling strategies are discussed (e.g. “top-down”, “bottom-up”, combinations there off).

We present two examples of how this approach for model validation for model development is applied in practice. The first example is about a polymer membrane fuel cell, and the second one is on modelling impedance for a lithium-ion battery.

We conclude this presentation by highlighting open questions and problems in the model development that need to be overcome for the successful development of mathematical models for fuel cells and batteries.

Influence of feed gas humidity and current density on the 3D water distribution in PEFC

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The water management in polymer electrolyte fuel cells (PEFC) strongly influences specific power and durability. Efficient water removal and water management is crucial for the performance of polymer electrolyte fuel cells (PEFC), in particular at high current density operation. It's description remains a challenge in PEFC models and requires experimental validation.

X-ray tomographic microscopy (XTM) of polymer electrolyte fuel cells (PEFC) has proven to be a powerful tool to analyse the water distribution in the gas diffusion layer (GDL) [1, 2, 3] at lower operation temperatures of 30 °C to 50 °C. The extension of the low temperature setup [2,3] by custom-made flexible heating tubes allowed fast X-ray tomographic microscopy investigations of the water distribution in the GDL at defined differential conditions at the technically relevant cell temperature of 80 °C [4] at the TOMCAT beamline of the Swiss Light Source.

The water distribution in cells with Toray TGP-H060 GDL with MPL is analysed for different feed gas humidifications around the optimal humidity point at 0.75 A/cm^2, rib widths and current densities. Similarities and differences of the water saturation, cluster size and its distribution, percolation paths, as well as their influence on permeability and effective relative diffusivity are discussed. Saturation dependence of the relative permeability and effective relative diffusivity are compared to common model parameterizations.

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2-phase fuel cell model based on discrete water path network model

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Water management is known to be one mayor issues for stability and performance of Polymer Electrolyte Membrane Fuel Cells. The fragile balance between too dry and too wet conditions has to be ensured to avoid dehydration of the ionomer and flooding of the porous structures in the gas paths.

The water management can be effectively optimized by improving the liquid water transport capabilities of the gas diffusion layers (GDLs) to avoid flooding while operating in high humidity. Due to the high number of degrees of freedom for the optimization, modeling of the liquid water transport in the GDLs is of great interest. Compared to continuum models, discrete models like pore network models have shown to have significant advantages in capturing the liquid water transport phenomena observed in the highly porous and hydrophobic components. However, determination of the influence of GDL characteristics on fuel cell performance is only realistic in combination with the relevant fuel cell processes using continuum fuel cell models. Hence, the influence of the liquid water transport on the fuel cell performance is often determined by extracting the effective transport properties from discrete models for using in continuum fuel cell models. However, this way plenty information like the fingering water transport mechanism and the preferred transport through regions with big pores is lost.

In the presented study, we developed an iterative algorithm to directly couple a discrete liquid water transport model to a continuum fuel cell model. The discrete fuel cell model includes the distribution of temperature, protonic potential, water vapour, dissolved water and oxygen concentration. For the discrete liquid water transport model, we use a water path network model which is an enhanced state of the art pore network model. Since the direct input of the discrete model are the GDL design parameters, the coupled model allows to directly analyse the influence of GDL design parameters on the fuel cell performance.

Distinction of liquid water and ice based on dual spectrum neutron imaging

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For the replacement of combustion engines in automotive applications, polymer electrolyte fuel cells (PEFC) have to resist against various weather conditions, such as subfreezing temperatures. In literature, several studies investigated cold-starts, reporting about the risk of breakdown due to the freezing of product water. Due to the presence of supercooled water [1,2], the freezing of water shows a statistical fluctuation [2], and it is crucial to improve the understanding of the reasons leading to this phase transition. In this talk, a visualisation method will be presented to identify phase transitions in polymer-electrolyte fuel cells (PEFC) based on dual spectrum neutron imaging.

Energy-dependent attenuations of neutrons through liquid water and ice have been published in literature [3,4]. With decreasing neutron-energy, increasing differences between the attenuations of frozen compared to liquid water have been identified. With the energy spectrum of the ICON [5] beamline at PSI (cold neutrons with an average energy at 5 meV), no significant deviations between liquid and solid phase are visible. Introducing a polycrystalline beryllium filter inside the neutron beam, the low energy part of the spectrum is emphasized and phase transitions between liquid water and ice are more distinctive. Since the thickness of water inside a PEFC is not known *a* priori, the analysis compares exposures with the filtered and unfiltered beam. As the water distribution may change over time, consecutive images with and without filter (dual spectrum) have been recorded.

Firstly, the results of this method will be presented on a cylindrical water scale. As expected, liquid water has been distinguished from ice and phase transitions have been identified. Subsequently, the results with a small scale differential PEFC will be analysed. In order to avoid temperature dependencies, a protocol to produce supercooled water has been developed, to compare liquid water and ice at constant temperature. Surprisingly, the result obtained out of this measurement (ratio of attenuation between the filtered and non-filtered beam), is not consistent with the result obtained out of the cylindrical scale measurement, and the reasons for this discrepancy are under investigation. Nevertheless, phase transitions from liquid water to ice have clearly been identified with this method.

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Modified PNP-Stokes equations for electro-kinetic flow in PEM nanopores

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Abstract:

Polymer electrolyte membranes (PEM) play a critical role as the electrolyte of choice in PEM fuels cells. In this application, the PEM is an ion exchange membrane that facilitates proton and water flow through nano-scale pores whose shape changes dynamically, determined by the operating conditions. Understanding the dynamics of this electro-kinetic flow is key to improving the performance of the PEM and, hence, the fuel cell.

In this contribution, we study the flow of protons and water in cylindrical PEM nanopores by use of modified Poisson-Boltzmann equations for the radial proton concentration, incorporating finite ion-size effects [1] and an explicit model for permittivity [2]. Mathematically speaking, we end up with an intricate non-linear eigenvalue problem whose solution poses a more complex task than for planar geometries. Subsequently, Nernst-Planck and Stokes equations yield the flow of charge and water along the pore. The results will be compared to i) experimental data from the literature, especially conductivity and water drag coefficients, and to ii) analytical solutions for a simple PNP-Stokes model [3].

Limits to the use of continuum models will be elucidated along with the usefulness of such approaches, as they can aid in explaining membrane swelling [4], for example. Accordingly, this work is meant to contribute to the renewed interest in classical electro-kinetic flow models [5].

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3D model of a SOFC stack using porous media approach

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For optimal operation of fuel cell stacks, low thermal gradients and high flow uniformity are prerequisites. Due to non-ideal gas supply and thermal integration, these conditions cannot be guaranteed, especially for high current operations. Stack models help to quantify these effects, however, stack models, published in literature, are still very rare due to their enormous computational costs.

For a compact solid oxide fuel cell (SOFC) stack, developed at Fraunhofer IKTS, a 3D thermofluid computational fluid dynamics (CFD) model coupled with a 2D electrochemical model is presented. The stack comprises 40 planar cells in cross-flow design with internal manifolding and has an electric output of 150 W. Due to the large number of gas feeding channels at the cathode side (about 500) and a composite of different Nickel meshes for gas distribution and current collection on the anode side, a porous medium approach is chosen to decrease the computational costs considerably. To obtain the effective properties (anisotropic heat/electric conductivities and permeabilities), detailed models of a representing unit volume were solved. The model represents the stack in a furnace environment. In the 3D CFD model, performed in ANSYS FLUENT® 12.1, conservation equations of mass, momentum and energy are solved. In a separate 2D electrochemical model, based on area specific resistances (ASR) obtained by experimental IV-curves, the electrochemical oxidation of hydrocarbon fuels is implemented in FiPy, an open-source finite volume code. The obtained heat flux distribution is being exported to the 3D CFD model.

The model allows to analyse the temperature distribution inside the stack and the solutions are validated by data measured at a test stack, which are in good agreement. The data show the formation of a hot spot in the centre of the stack. Furthermore the maldistributions of air and fuel gases are quantified.

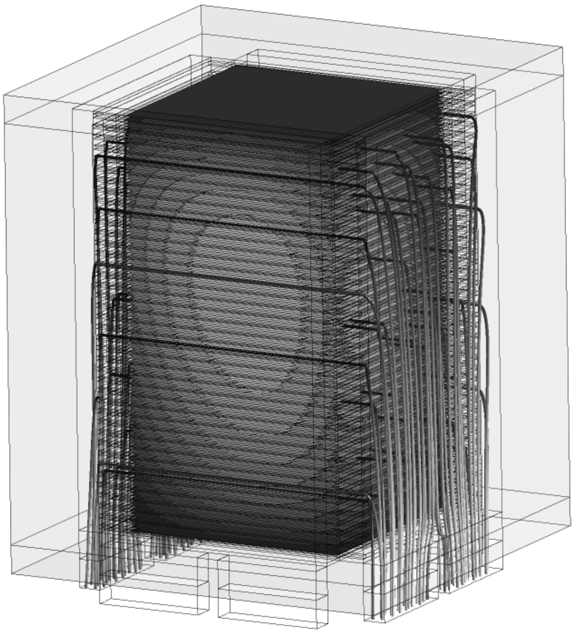

Figure 1: Contour plot of temperature distribution of the active area and streamlines along cathode side of a 40 cell SOFC stack

Cr_2O_3 scale growth rates on metallic interconnectors derived from 40’000 hours solid oxide fuel cell stack operation

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To consider long term power degradation in SOFC stack models we need reliable empirical data either to validate the model prediction or to implement the degradation behaviour into global stack models. The different materials and components in a SOFC stack are exposed to different complex atmospheres such as wet and carbon containing fuels on the anode side or dry ambient air on the cathode side. Stack operation as well as material exposure tests which cover the required life time of 40’000 hours [1] for stationary SOFC applications are commonly not feasible.

One of the major contributions of overall stack degradation is the ohmic loss caused by Cr_2O_3 scale formation on metallic interconnects (MICs) [2]. For this reason oxide scale growth on $Cr5Fe1Y_2O_3$ (CFY) was investigated by scanning electron microscopy (SEM) from post-test samples that were operated in Hexis planar SOFC-stacks under dual atmospheres (i.e. simultaneously exposed to anode and cathode conditions) at temperatures around 900 °C. The study includes unique test results from a stack operated for 40’000 hours, in addition to other degradation experiments. To analyze inhomogeneity in scale thicknesses a dedicated image analysis method was applied on more than 1’000 SEM images. Cr_2O_3 scale growth on the anode side is found to be approximately twice as fast in comparison to the scale growth on the cathode side. Finally, based on our time lapse analyses with extensive sampling it can be concluded that reliable predictions of scale growth requires statistical analyses over a period that covers at least a quarter (i.e. 10’000 hours) of the required SOFC stack life time.

The quantitative description of oxide scale growth by itself does not give the real picture about the effective ohmic losses that occurs in a SOFC stack. Therefore we need to consider as well the microstructure and the adjacent atmospheres which both influence the electric conductivity of the oxide scale [3]. The effects of microstructure can be taken into account by modeling the voltage drop based on the SEM images with FE analysis. For the determination of the intrinsic electric conductivity under the specific atmospheres additional experiments are needed. By the combination of scale size, electrical conductivity and microstructure we should be able to give accurate degradation prediction for the MICs over the required stack life time based on experiments that cover a shorter time span.

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One Dimensional Modeling of an SOFC System With Discretisation in Flow Direction

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Abstract

Combined Heat and Power Production (CHP) based on Solid Oxide Fuel Cells (SOFC) is a very promising technology to achieve high electrical efficiencies. A detailed knowledge of the behavior of all components regarding temperature and concentration distribution is required to achieve optimal electrical efficiency at different operating conditions. The focus of this study is the dynamic modeling and simulation of a SOFC system for CHP application including stack and balance of plant (BOP) like heat exchangers, prereformer, afterburner, pipes and blowers.

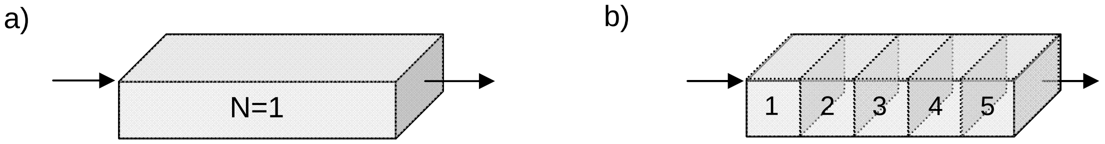

Figure 1: a) 0D model without discretisation, b) 1D model with discretisation of 5 steps

In the model presented here, stack, prereformer, heat exchangers and pipes are discretized in flow direction (figure 1) and modeled based on physical equations using Modelica®. The dynamic behavior of the single components includes heat transfer and chemical reactions in prereformer and stack. Furthermore the current density of the stack in each discretisation volume is calculated implicitly as a function of the voltage. The simulated U-I-characteristic is then validated with experimental data.

The main advantage of the discretisation is a more detailed calculation of the temperatures and concentrations along flow direction compared to a system model in 0D. Therefore the result of the cell voltage is more precise. Furthermore, the accuracy of the model is increased using separate cells at the upper and lower side of the stack to describe the occurring heat losses there. The number of discretisation compartments can be chosen as a compromise between numerical accuracy and calculation time.

1D models allow different geometries to be considered: in particular co- and counter-flow heat exchangers can be distinguished from each other. Thus different system configurations can be tested.

Development of HT-PEFC stacks supported by modelling and simulation

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High temperature polymer electrolyte fuel cells (HT-PEFC), based on phosphoric acid doped polybenzimidazole membranes have a typical operation temperature between 160°C and 180°C [1]. Due to this high temperature HT-PEFCs have a CO tolerance of about 1% [2], which makes them suitable especially for operation in combination with a reformer. Compared to classical polymer electrolyte fuel cells (PEFC), a water management system in order to keep the membrane humidified is not required for HT-PEFCs. Furthermore, the large difference between stack and ambient temperature allows to design a compact cooling system [3]. Possible applications for HT-PEFC systems are auxilliary power units in e.g. commercial vehicles and ships .

A computational fluid dynamics model will be presented, which is suitable to perform full stack simulations of a HT-PEFC with reasonable computational power and time. The model is based on a multi-domain and multi-scale model and is extended by electrochemical equations suitable for operation with reformate gas. A general analysis of possible flow configurations regarding anode, cathode and cooling fluid inside a stack was performed. The most favorite configuration with regard to current density homogenization is anode and cathode in counter-flow with cooling and anode in co-flow when the stack is operated with reformate [4].

Simulation results show very good agreement with the local current density and temperature distributions which were obtained by experiments (Fig. 1). In order to measure the temperature and current density distribution a tailor made measuring board was integrated into the stack assembly [5].

Besides the model, the stack design and a performance analysis of the stack will be presented. The combination of experimental and simulation results allows a profound interpretation of the stack behaviour.

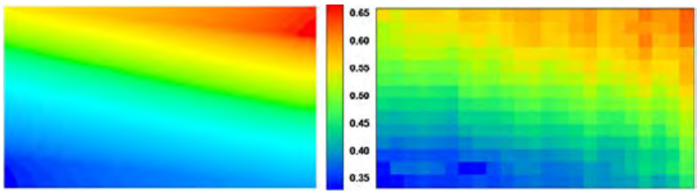

Figure 1: Local current density distribution (i in A cm^{-2}) for an average i = 0.45 A cm^{-2}, left: model; right: experiment [4]

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Water Transport through an Anion Exchange Membrane Used in Alkaline Direct Methanol Fuel Cells

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Using fuel cells of the alkaline type (AFCs) is a promising way of replacing Pt catalyst in low temperature fuel cells by other metal catalysts. Metals like Fe, Co or Ni show better activity and stability in alkaline media compared to acidic media and can be used as catalyst in AFCs. Furthermore, low temperature fuel cells are mainly important for portable and mobile applications. Hence, a fuel with high energy density, e.g. methanol, is desired. This motivates research on Alkaline Direct Methanol Fuel Cells (ADMFCs) in which the following electrochemical reactions take place:

Anode: $CH\ OH + 6\,OH^- \longrightarrow CO_2 + 5\,H_2O + 6\,e^-$
Cathode: $O_2 + 2\,H_2O + 4e^- \longrightarrow 4\,OH^-$

In presence of carbon dioxide, alkaline solutions, e.g. KOH, primarily used as electrolyte in AFCs can cause carbonation and precipitation. Thus, replacing the liquid electrolyte by an electrolyte membrane is beneficial for ADMFCs since CO_2 is produced during the oxidation of methanol. This replacement influences the water management in the fuel cell due to lacking the buffer function of a liquid electrolyte.

Studies about ADMFCs using an electrolyte membrane are scarce in literature especially concerning water management. However, previous studies have shown that water transport through the membrane is essential for water management in ADMFCs.

In the present work, water transport through an anion exchange membrane used as electrolyte in an ADMFC is modelled by an approach taking the model of Neubrand [1] as basis. Since this is a new model approach for anion exchange membranes, some parameters, e.g. the water diffusion coefficient, required for this model are not available in literature yet. Hence, the parameters used for this study are determined experimentally using in-house setups. The experimental results will also be presented in this contribution. Furthermore, the significance of the results for the water management and the performance of ADMFCs will be demonstrated.

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Investigating Bistability in the Polarization Curve of a Segmented PEM Fuel Cell

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The limiting behaviour of PEM fuel cell is investigated in this study with the help of polarization curves of a segmented air/hydrogen PEM fuel cell. The polarization curves are run at various voltage sweep rates (6.6, 2.2, 1.1 and 0.55 V/sec). The temporal and steady state measurements of the polarization curves show a bistability behaviour (see Figure 1), where a drop in the current density followed by a recovery, is measured at every location in the cell (i.e. inlet and outlet of gases). In this work, we hypothesize that this bistability behaviour emerges due to two reasons; first, the coupling of the time dependent oxygen concentration and multi-step reaction mechanisms of the ORR and second, the simultaneous polarization of the anode and cathode catalyst layers. Discussion of this hypothesis will be supported with detailed experimental work with a focus on the effects of oxidant and fuel feed inlet humidity, hydrogen dilution and the use of a helium/oxygen mixture as the oxidant.

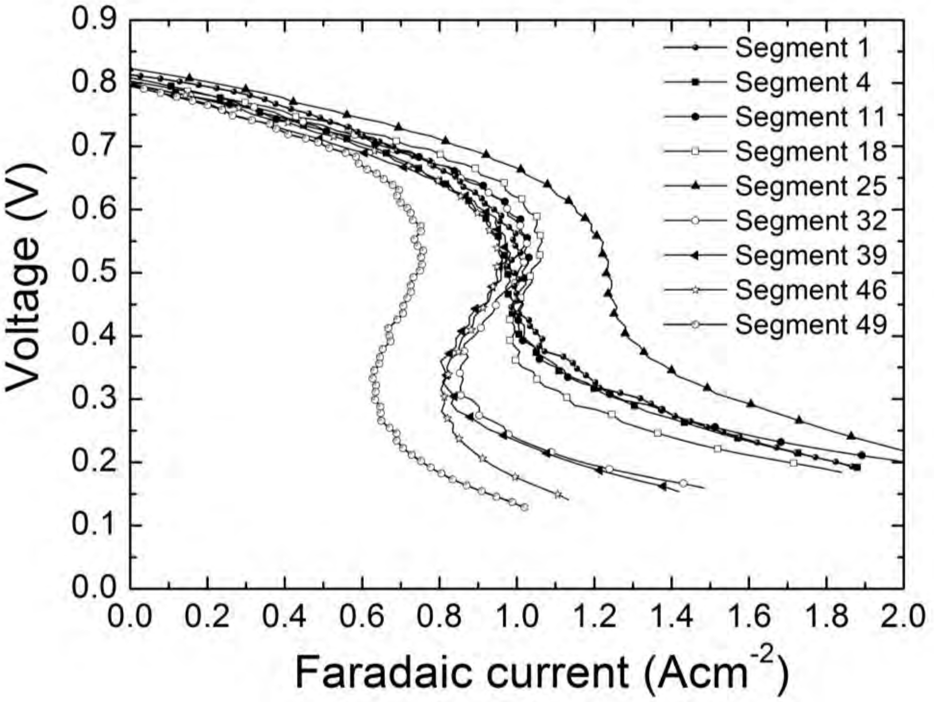

Figure 1: Bistability behavior of transient polarization curve of a segmented Air/Hydrogen PEM fuel cell

Characterization of O_2 diffusive losses in the gas diffusion layer (GDL) of the PEFC by means of simplified flow field patterns

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Improving the performance of the Polymer Electrolyte Fuel Cell (PEFC) is required for reducing the cost of the system in view of its commercialization. The *flow field* is one component that impacts the performance. While its design must be optimized in regards of the integral performance, its effect must also be understood at the local scale. The best set-up suited for this is to use high stoichiometry gas flows in a *differential cell* emulating under controlled condition a chosen local region of the full-size cell. The application of refined diagnostic tools – neutron imaging [1], helox pulse method [2] and electrochemical impedance spectroscopy (EIS) – on such a system allows for a robust characterization of the local loss mechanisms, such as the diffusive losses of oxygen across the gas diffusion layer (GDL) and the effect of liquid water.

Contrary to an optimization study where the best flow field is searched, the present work compares, using the mentioned diagnostic tools and a multi-cell set-up [3], three different patterns of flow fields (Fig.1) whose expected behaviors are to induce “2D”, “1D” or “0D” gradients of O_2 concentration in the GDL. The comparison of the performance indicators, including the estimation of the bulk-diffusion losses by the helox pulse method, for different relative humidity conditions, delivers unique insights and reliable results about the origin of the losses as well as the veritable role of liquid water. In addition, applying EIS on such simplified systems allows for more straightforward interpretations than when full-size cells operated in technical stoichiometries are considered, as it is usually the case in other studies.

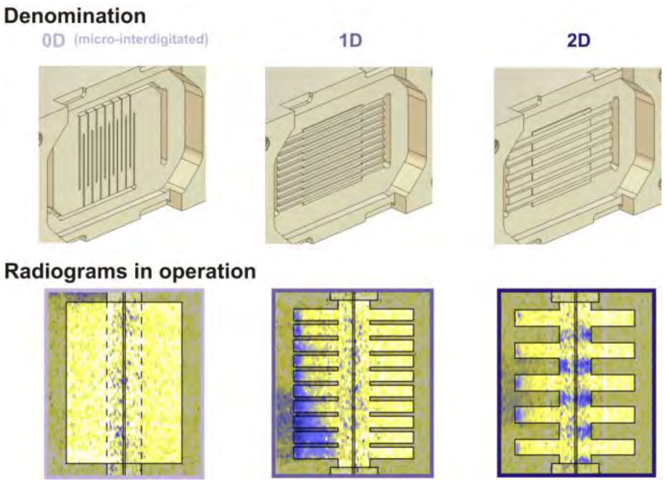

Figure 1. Flow field patterns tested and their radiograms (1 A/cm^2, 70°C, RH = 100%(an.)/0%(ca.)).

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Multiphase Multicomponent Flow through Multilayers of Thin Porous Mediums: Conservation Equations

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Thin porous media flow is encountered in a variety of environmental and engineering applications such as filters, groundwater flow, fuel cells, and batteries. Some layers are only several pores thick. Nevertheless, thin porous mediums are usually modelled as three-dimensional (3D) domains. Often, this is in contradiction with the concept of Representative Elementary Volume (REV) and other averaging concepts. Also, we are usually not interested in the details of distribution of phases and species in the direction of the layer thickness. But, for modelling purposes, one is forced to discretize across the thickness of the layer. This has led to prohibitive (and in fact unnecessary) computational efforts in most cases.

Polymer electrolyte fuel cells (PEFCs) contain several thin porous medium layers, like gas diffusion layer (GDL), catalyst layer (CL), and micro porous layer (MPL). In the development of PEFCs, tremendous efforts have been invested in the numerical modelling of water movement and distribution of reactants in these layers[1]. Usually, many hours of computations are needed for the modelling of even one PEFC unit. Given the fact that a PEFC stack consists of hundreds of units, as an automotive engine, it becomes evident that, for the time being, fully domain-resolved modelling is impossible for the stack level application. Another major shortcoming of current numerical models is that they cannot match experimental measurements well, particularly in terms of liquid water distribution.

In this work, we develop a novel approach to the modelling of thin multilayer porous media. We model the layers as 2D interacting continua. Following a mathematically rigorous approach, we derive governing equations for thermodynamic properties averaged over the layer thickness. We start with the pore-scale conservation equations in each layer and average them over the layer thickness and in-plane direction at the same time, for a proposed REV shown in Fig. 1. As a result, we obtain a full set of conservation equations for all the layers. There is exchange of mass, momentum, energy, and entropy between neighbouring layers. Then, we develop constitutive relationships for those exchange terms following a methodology based on the exploitation of the second law of thermodynamics[2]. Our research objectives are as follows:

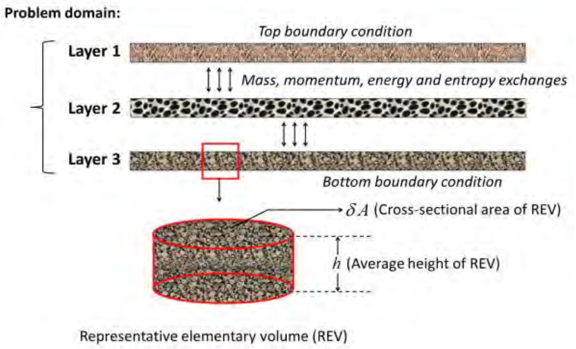

Fig.1: *Schematic graph of flow through triple layers of thin porous mediums (note that layer thickness can have a spatial distribution, and an average height is used in the definition of REV).*

1. Re-examine models of multiphase multicomponent flow through multilayers of thin porous media based on a rigorous thermodynamic approach.
2. Considerably reduce computational efforts by modelling each layer as a 2D, instead of 3D, continuum.
3. Apply the new approach to PEFC stack-level modelling.

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Local EIS studies in PEM fuel cells - Distinguishing between through-plane mass tansport limitations and convective in-plane oxygen effects

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Electrochemical impedance spectroscopy (EIS) is a powerful tool for characterizing fuel cells. With the use of a broad frequency range, processes responsible for the cell voltage loss can be distinguished and the rate-determining step identified if the processes occurring on different time scales. This technique is widely accepted for analyzing small fuel cells at high gas flow rates (called differential cells). However, this is not true for single cells and stacks with large active area as a low frequency loop in the impedance spectra originating from undesired intrinsic oxygen concentration oscillations (OCO) downstream the gas channel. Depending on the amplitude and phase of the OCO, the spectra can even flip to the 2nd quadrant of the complex plane. By means of a segmented (7x7) PEM fuel cell and the capability of local voltage perturbation with our 50-channel impedance spectrometer, we analyze the effect of the OCO on local spectra in detail. The limits of the EIS technique on technical cells regarding operating conditions such as load current and stoichiometry are investigated. The presented analysis is supported by a numerical 2+1D EIS model taking into account kinetics, cross current, the OCO in the flow field as well as diffusion in the GDL.

Lithium-ion and post-Li-ion batteries
-
Lithium-ion battery thermal behavior

Wednesday, March 20, 2013

Session Chairs: Jonathan Mueller, Nigel Brandon, and N.N.

From conventional Vanadium Redox Flow Batteries to Vanadium Oxygen Fuel Cells – Modeling and Simulation

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Vanadium redox flow batteries (VRBs, figure 1 left) are electrochemical storage devices for stationary applications. In these batteries the electrical energy is stored in different oxidation states of the element vanadium, which is dissolved in sulphuric acid. In a battery stack the electrical energy is converted to chemical energy and vice-versa. This converter is built up very similar to a fuel cell stack.

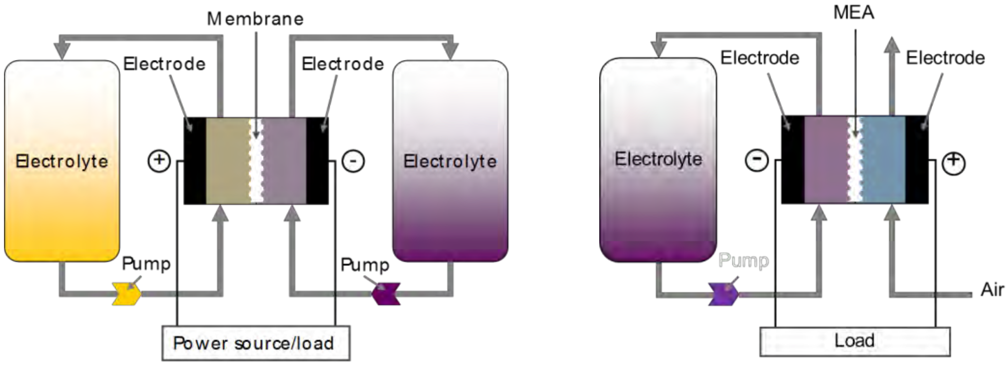

Figure 1: Schematic drawings of a Vanadium Redox Flow Battery (left) and a Vanadium Oxygen Fuel Cell (right)

Regular flow batteries do not provide the energy density needed for mobile or portable applications. However, the energy density can be nearly doubled by the usage of an air cathode. The resulting system, a vanadium oxygen fuel cell (figure 1 right), can be regarded as a hybrid between a flow battery and a fuel cell.

In this work we first modelled and simulated a VRB with COMSOL Multiphysics. Basis for the simulation is the 40 cm^2 VRB test cell used at our institute. Several physical properties e.g. the viscosity at different state of charge were measured for the model. The flow inside the cell is modelled using the Brinkman equation. Thus, both the free flow in the inlet and outlet structures and the porous media flow within the battery cell can be simulated at the same time. The electrochemistry is modelled with a first principle approach. The simulation results are validated with experimental data.

For the vanadium oxygen fuel cell, the model of the existing VRB model is extended. The cathode side is replaced by an air cathode with a catalyst layer. A compartment with sulphuric acid is added to the model; this compartment is intended to avoid crossover of vanadium ions. With these additions, a vanadium oxygen fuel cell is simulated.

Modeling Crystallization in Lithium-Oxygen Batteries

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Lithium-oxygen (Li-O_2) batteries are a potential alternative to conventional combustion technologies in the mobility sector. However, the development of Li-O_2 cells is still at an early stage and a list of challenges needs to be addressed [1]. While the theoretical energy densities of Li-O_2 batteries are large compared to state-of-the-art lithium intercalation batteries, cyclability and power densities need to be improved. In this talk we make use of continuum models to enlighten the role of crystallization during discharge of Li-O_2 batteries.
Li-O_2 batteries rely on conversion reactions with solid and insulating reaction products. On the one hand, these compact and lightweight reaction products enable large energy densities, on the other hand, they limit electron transport and can passivate active electrode surfaces. Therefore, it is crucial to understand the complex nucleation and growth process of the crystalline reaction products in Li-O_2 batteries.
Applying a multi-scale continuum Ansatz, we model two design concepts of Li-O_2 batteries with aqueous and organic electrolyte [2]. In the latter case, electronically insulating lithium peroxide is produced on the active surfaces of the cathode in complex morphologies [3]. While some experiments observe small films of Li_2O_2, other experiments report the growth of toroid-like particles. In the case of the aqueous electrolyte, lithium hydroxide dissolves before precipitating as lithium hydroxide monohydrate. Due to a concentration gradient in the cell, precipitation tends to occur close to the anode [4]. We apply the classical theory of nucleation and growth to study this inhomogeneous precipitation and its impact on cell performance.

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3D CFD simulation of lithium-air batteries based on electrochemical models

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One of the major obstacles standing in the way of a complete electrification of the powertrain is the restricted range of electric vehicles due to limited battery capacity. The lithium-air (Li/air) battery cell technology exhibits an approach for the extension of the electric vehicle range up to one order of magnitude [1]. The European research project 'LABOHR' investigates materials and methods of a Li/air battery system including the required ancillaries for operation in the automotive field. The studies of novel electrodes and electrolytes for a Li/air cell prototype are supported by 1D and 3D simulations of the cell chemistry. By means of these simulations the impact of system parameter variations (e.g. temperature, porosity, current density) on cell operation can be investigated which will assist material scientists in improving the development of Li/air cell components.

The electrochemical model, based on the works by Doyle et al. [2] and Andrei et al. [3], has been implemented in the multiphysics software package AVL FIRE®. Nine non-linear coupled differential equations are solved in order to calculate the spatial and temporal distributions of the electric/ionic potentials, Li/O_2 concentrations and Li_2O_2 volume fraction in the electrolyte, gas velocity, pressure and O_2 mass fraction in the flow channel, as well as the temperature in all domains. Additionally, electrochemical reaction equations of the Butler-Volmer type are solved resulting in the reaction rates at the negative (Li foil) and the positive (carbon/Li_2O_2) electrode, respectively. Figure 1 left shows a comparison of discharge curves for various current densities calculated with FIRE (1D model) to the results by Andrei et al. [3]. Figure 1 right shows an exemplary result (3D model) of the current density vectors in the positive collector and the oxygen concentration in the liquid electrolyte for a certain time step.

The research leading to these results has received funding from the European Union's Seventh Framework Programme under EC-GA No. 265971 'LABOHR'.

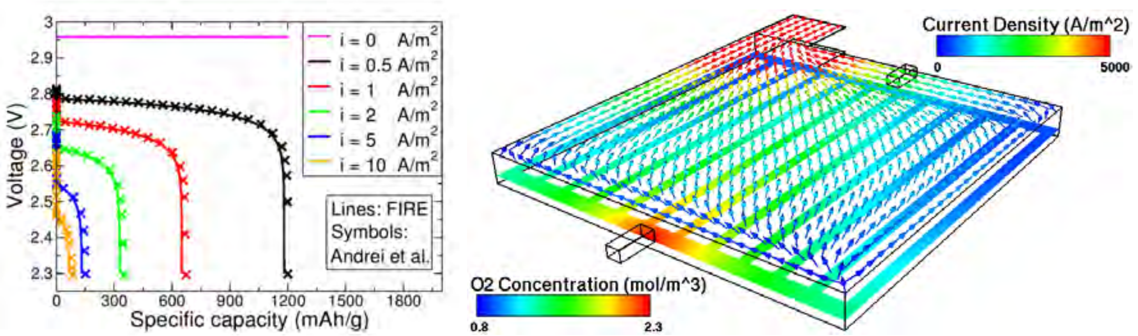

Figure 1: Comparison of discharge curves in FIRE and [3] (left); 3D distribution of current density and O_2 concentration (right)

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Low-Temperature Charging of Lithium-Ion Cells Part I: Electrochemical Modeling and Experimental Investigation on Degradation Behavior

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Fast charging is one of the main challenges in automotive battery management and one of the key factors for electrification of the drive train. As a particularly problem at low temperatures and high charging rates, metallic lithium deposits on the anode surface (so-called lithium plating) instead of intercalation into the particles of the electrode active material due to kinetic limitations. This results in capacity loss, which affects expected lifetime and performance of the battery dramatically. Electrochemical models help to understand internal processes and predict aging effects, which finally lead to optimized charging strategies.

In this work, a 1D+1D (pseudo-2D) model is set up over a wide temperature (T = –25°C - 40°C) and current range (I = 0.1C - 3C) and coupled with a lumped thermal model. For parameterization, the complete model is fitted against electrical measurement data sets of the full cell in both time and frequency domain. EIS (Electrical Impedance Spectroscopy) data in a frequency range from 5 kHz to 10 mHz and discharge/charge curves for different rates are measured. The different material parameters as well as temperature and concentration dependencies needed for the model are obtained by piecewise investigation of the data. All fitted parameters are transformed into consistent analytical functions and the model is validated against dynamic pulse profiles.

In the experiments, cells are charged under different operating conditions, e.g. current-rate, temperature, cut-off-voltage, pulsed operation and pausing times. Capacity fade is measured after a significant number of cycles and compared to simulated anode potential. Quantitative correlation is found between degradation in experiment and the anode potential dropping below 0 V vs. Li/Li^+ at the separator-anode boundary in the simulation. For qualitative predictions a side reaction for the lithium deposition is implemented in the model and evaluated for multiple cycles. The accuracy of the model is suitable to derive optimized charging strategies without Li deposition. The transfer of the model into an on-board applicable form is presented in the companion contribution (Part II).

Low-Temperature Charging of Lithium-ion Cells
Part II: Model Reduction and Application

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Lithium-ion batteries are a key component in current and prospective electric vehicles. For an appropriate operation of these batteries ensuring high performance and long lifetime, monitoring of the cells is essential. On the one hand, the available power and the resulting possible driving range in the present operation point have to be determined. On the other hand, the state-of-health (SOH) of the cells has to be identified since aging (i.e. degradation of the battery) can occur due to different reasons. To recognize degradation, usually the effects of aging, i.e. a loss of capacity or a rise of the internal resistance, are monitored [1].

By a more accurate understanding of the degradation mechanisms, an operation strategy preventing degradation can be developed. One method of gaining this knowledge is strict electrochemical modeling, which allows a deeper insight in non-measurable cell characteristics, e.g. anode potential as indicator for metallic lithium deposition (lithium plating) during charging. Such an electrochemical model describing the charging process at low temperatures is worked out in the companion contribution (Part I) and analyzed for the ability to predict harming cell states.

For the application of such a model within a model-based on-board control avoiding adverse system states, a reduction of the model is necessary to fulfill the challenging computational and real-time requirements of the battery management system. This can be performed e.g. through approximations and mathematical simplifications [2]. Additionally, the model needs to be evaluated with a constant sample time period and low computational effort. Discrete-time linear parameter-varying (LPV) electrical models of batteries are known to fulfill these requirements [3].

In this contribution, model-reduction based on system identification methods is introduced, resulting in an LPV model for terminal voltage and anode potential prediction. This model is identified from input-output signals applied to the original electrochemical model. Thereby, the input signals show a high excitation and cover the whole SOC and temperature range of the validated electrochemical model. The model-reduction process is explained and the reduced-order model is validated against the primal electrochemical model. Based on the reduced-order LPV model, a model-based charging strategy and its possible advantages are discussed.

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From Micro to Macro – Modeling and Simulation of Lithium Ion Batteries on Multiple Scales

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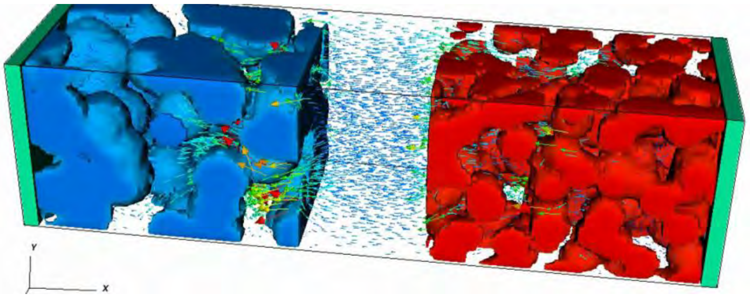
Lithium ion batteries are currently one of the most important electrochemical energy storage systems. Electromobile applications, in particular, strongly add to this trend for the near future. At the same time the demands on power and energy density as well as on safety, life time and reliability increase. Thus, finding ways to optimize battery performance and understanding and assessing degradation phenomena is essential. To this end, computer simulation of the relevant electrochemical processes can provide valuable insight.

Based on our thermodynamically consistent theory for ion, charge and heat transport in electrolytes and electrode material [1] we have developed the simulation tool BEST (Battery and Electrochemistry Simulation Tool) that can compute many global and local quantities (e.g. potentials, lithium concentrations, ion fluxes, current densities, overpotentials) with full three-dimensional resolution on different scales: The original equations from [1] describe the processes above the scale of the electrical double layer, i.e. above a few hundred nanometers. With BEST, which is based on the finite volume method, it is possible to solve these coupled, highly nonlinear equations on the explicit three-dimensional electrode microstructure and to gain valuable information on local quantities, which is important for example for assessing battery performance or for estimating the degradation risk. For instance, a potential drop below 0V can trigger plating.



In order to upscale the simulation to the cell level, the microscopic transport equations have to be homogenized. Inspired by the porous electrode theory of Newman and coworkers [2] we show how this can be done without restricting oneself to 1+1 dimensions. Thus without resorting to the microscopic electrode structure we can still perform simulations on a three-dimensional battery cell in order to study for example the influence of current collector placement or the structuring of the electrode as in microbattery applications. Besides the simple volume averaging techniques of [2] we also follow mathematically rigorous homogenization methods based on [3] for deriving equations on the cell level.

In this presentation we describe our simulation approach on the micro level, show how we arrive at macro-homogeneous models suitable for three-dimensional cell scale simulations and discuss how both approaches compare to each other.

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Critical review of parameterisation methods for equivalent circuit based, spatially resolved models of lithium-ion cells

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Lithium-ion cells used in electric vehicles are in general much larger than lithium-ion cells for consumer electronics. Consequently inhomogeneities in transport mechanisms are intensified, which leads to a limited applicability of performance predicting lumped cell models and to a reduction of their accuracy. Recent publications from an industrial background show a growing interest in modelling spatial inhomogeneities for the design of cells and cooling systems [1,2].

One group of suited modelling approaches is based on electrochemical transport laws [3,4]. Due to the high computing costs simulation models are restricted to small volumes, which are a fraction of a full cell. Furthermore they are not suited for control algorithms, where a short computing time is required. The parameterisation effort for such models is known to be expensive and time consuming. The delivered information of internal processes however is very detailed and the obtained parameters have a high degree of generality.
Another group of phenomenological models employs networks of equivalent circuits [1,2,5–7]. The available information is reduced to those operation states, which are necessary for control purposes. The parameterisation is done using measurement data from e.g. pulse profiles or impedance spectroscopy as well as information on material properties. The duration of the necessary measurements is comparatively short.

This work investigates the parameterisation of an equivalent circuit based, spatially resolved, electrical cell model, which employs measurements of cell current, cell voltage, and the temperature distribution of the cell. A sensitivity analysis of the parameters of the equivalent circuit model is carried out in time and frequency domain. The results of the analysis revealed that single parameters cannot be uniquely identified using the cell voltage response. To overcome that problem a modification of the parameter identification is presented and discussed. Furthermore the impact of that result on similar model and parameterisation methods is outlined.

Acknowledgement: This work is funded by the project KF2613901WD0 of AiF ZIM.

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Electrochemical Impedance Spectroscopy on Complete Li-Ion-Battery Cells: Internal Interfaces and Influence of State-of-Charge and Cycle Number

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Electrochemical impedance spectroscopy (EIS) is a versatile, non-destructive tool to study the internal interfaces in Li-ion batteries and how these are affected by operation of the battery [1-3]. These interfaces include those between the electrolyte and the electrodes but also those between the electrodes and the current collectors. We investigated half cells with $LiCoO_2$ or $Li_4Ti_5O_{12}$ electrodes against Li metal as well as full cells with $LiCoO_2$ and $Li_4Ti_5O_{12}$ as positive and negative electrode. EIS was used to study the changes at the internal interfaces during storage of the batteries and during galvanostatic cycling. A simple equivalent-circuit model was developed to describe the changes in the EIS spectra as a function of both state-of-charge and cycle number. Systematic variation of the battery components allows the assignment of the different features in the EIS spectra to these components [1]. Different parameters deduced from fitting the equivalent-circuit model to the EIS data can be used to obtain information about the state-of-charge and state-of-health of these batteries [2].

These measurements are used to investigate the formation of the solid-electrolyte interface between the electrodes and the electrolyte during storage of the batteries and the formation of dendrites on the surface of the Li metal electrodes during charging of the batteries. We also studied the influence of different electrolytes on these processes and showed that Li dendrite formation can be suppressed by the use of ionic liquids [3]. The results were compared with observations from scanning electron microscopy and *in situ* ^{7}Li nuclear magnetic resonance spectroscopy.

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Towards a computational method for advanced battery systems supported by experimentally determined parameters

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Advanced numerical simulation tools are important for the improvement of existing battery systems such as Li-ion batteries, or for the development of superior battery systems such as the Li-air battery. Computational methods can provide insight into physical and chemical aspects of battery systems which is not or hardly achievable by experiments. In this project, a numerical method for investigations on cell level is developed, incorporating porous media, dilute and concentrated electrolyte solutions, and complex electrode reactions such as intercalation of Lithium ions or growth of solid-electrolyte-interface (SEI)-layers. The development of the computational model is strongly linked to the design of experiments for determining physical parameters such as diffusion coefficients.

The molar concentration of each ionic species is governed by a nonlinear partial differential equation including diffusion and migration as potential transport mechanisms. The ion-transport equations are based either on the dilute or the concentrated solution theory, as described in [3]. Both solution theories are formulated in the context of porous media as shown, e.g., in [2]. Since the electrical potential is an additional unknown, the system of equations is closed either by the conservation of charge or by the electroneutrality condition originating from the assumption that the electrolyte is locally electrically neutral. In [1], a computational method based on the dilute solution theory for electrochemical systems was already developed.

In this presentation, we will first outline the mathematical problem for dilute and concentrated electrolyte solutions in porous media. We will then present the development of a finite element formulation for this problem, including an efficient procedure for monolithically solving the resulting system of equations. We consider the exemplary setup of two parallel Lithium electrodes separated by a porous medium and filled with a binary electrolyte. Results from applying our proposed numerical approach to this experimental setup will be presented. Among other things, the influence of experimentally determined model parameters on those numerical results will be discussed. Finally, we will show the upcoming steps towards an entire cell model including porous electrodes and associated surface reactions.

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Measuring Entropy Profiles of Commercial Li-Ion Batteries – Separating Influences of Time and Temperature

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We report on the thermodynamic properties of commercial 18650 Li-ion batteries as measured via the temperature dependence of the open circuit voltage (OCV). Such thermodynamic measurements gained increasing attention in the recent past. They provide deeper insights into the electrochemical processes [1,2] and are also useful for improved modeling of the thermal behavior of cells.[3] The response of the OCV E_0 on temperature changes is proportional to the cell reaction entropy $\ {}_{r}S(x)$ according to

$$\left(\frac{\partial E_0(x)}{\partial T}\right)_{p,x} = \frac{1}{F}\left[\frac{\partial}{\partial x}\ S(x)\right]_{p,x} = \frac{1}{F}\ \ {}_{r}S(x)$$

x = state of charge (SOC)
p = pressure
F = Faraday constant

Plotting $\Delta_r S(x)$ vs. x yields to characteristic “entropy profiles” (See Fig. 2) that serve as “fingerprint” spectra, reflecting structure and chemistry of anode and cathode. The method has been frequently used in fundamental research for the characterization of small coin or pouch cells.[1,2] Despite the vision of an application for battery monitoring under operation conditions, however, there are no reports on entropy profiles of commercial cells with higher capacities so far. We will show that entropy profiles can be reproducibly measured for various types of new and aged 18650 cells. A main challenge arises from the fact that for larger cells, in particular for aged ones, the OCV does not reach steady-state values within reasonable waiting times (2 hours or more). Measurements of the temperature dependent OCV are thus superimposed by time-dependent drift (see Fig. 1). Ignoring this drift can lead to substantial misinterpretation of thermodynamic measurement data (Fig. 2a), whereas an appropriate background subtraction protocol gives rise to reproducible entropy profiles (Fig. 2b). We will also demonstrate that mathematical nature and characteristic time constants of OCV relaxation curves provide useful information about battery chemistry and ageing status. We will discuss in how far these OCV relaxation curves can be attributed to specific transport processes in Li ion batteries and how they could be combined with the entropy profiles, yielding a comprehensive picture of a battery’s state of health.

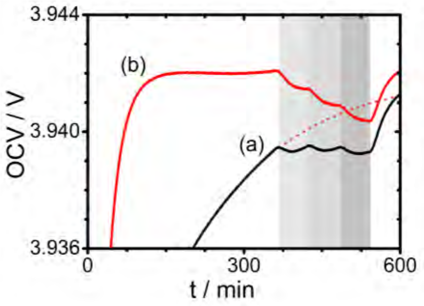

Fig.1. Temperature dependent OCV (a) without and (b) with background subtraction (dashed line). The different grey shades indicate the change of Temperature from 26 - 22 - 18 - 14 - 26℃

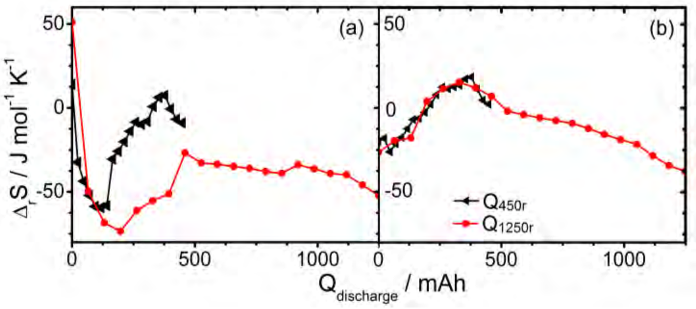

Fig. 2. Entropy profiles of two aged 18650 cells (NCM chemistry) with remaining capacities of 450 mA·h and 1250 mA·h. $\Delta_r S(x)$ calculated (a) without and (b) with background subtraction.

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Modelling and measurement of uneven heat generation in lithium-ion battery packs

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Lithium-ion battery packs for automotive applications typically consist of hundreds of cells connected in series and parallel to achieve practical voltages and capacities. Depending on the pack architecture, interconnect resistances can cause uneven current loadings in cells of the same parallel cell strip due to different resistance pathways, with cells nearer the pack current collector experiencing higher currents than those further away. This leads to localised heating of cells and a change in the pack performance due to the temperature dependency. Pack assembly faults can result in still higher interconnect resistances which, depending on the magnitude of the resistance, can effectively isolate certain cells in a pack [1].

It has been shown experimentally and via simulations that a current interrupt technique can be used as a low cost and fast method of detecting the location of faults in a large battery pack [1]. Combined with simulation results using a Newman based coupled 1D thermal-electrochemical battery model integrated into a pack model, we show that the rebalancing of currents can take on the order of 100s of seconds with constant current loads, and may never reach steady state under the dynamic loads typically seen in automotive applications. Results show localised heating in the cells nearest the current collectors of a large pack and a continued heat generation after load removal due to rebalancing caused by differences in the open circuit potentials of parallel cells. If not accounted for, this could lead to operation outside of the manufacturers prescribed limits and possible thermal runaway (ref Fig. 1).

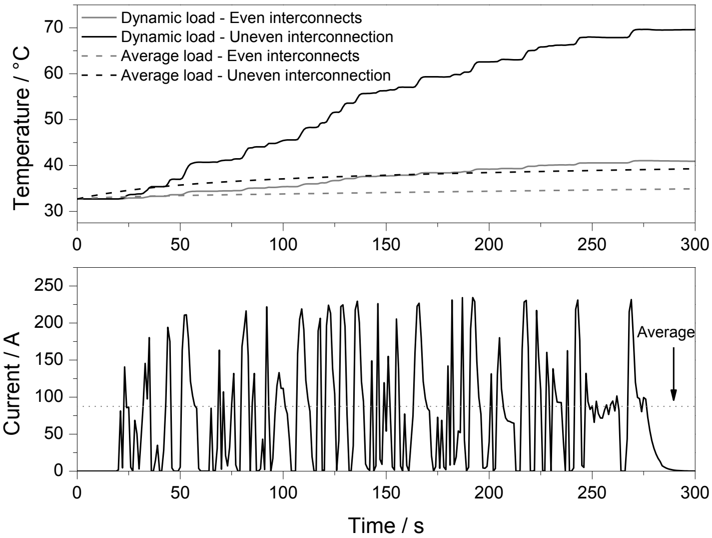

Fig. 1: Simulated temperature of the hottest cell in a 12P7S battery pack under static and dynamic loads with equal and unequal interconnect resistances

This uneven heat generation and current redistribution is well documented on the cell level but has not been well explored on the pack level. This effect therefore becomes an important consideration to pack designers and battery management system developers.

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3D Thermal-Electric Li-Ion Battery Model

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Thermal management of Li-Ion Batteries is crucial for their safe and efficient operation especially in high performance applications. Simulation has proven as a valuable tool to assist the design process for cells and packages, cooling system and operation strategy. One important aspect is the monitoring and prevention of localised thermal overheating (hot spots) which eventually may act as starting points for sudden cell failure. The model analysis of hot spots in battery cells does involve the simultaneous consideration of both global geometry and structural details (contacting structure, cell winding) of the cells and a sufficiently deep description of the complex electrochemical and thermal processes (such as electro-thermal coupling). This is an ambitious task especially when being restricted to conventional PC based computing power. It has been succeeded by applying homogenisation concepts for reducing the structural complexity (winding structure), by use of an empirical model for description of the local electr(o-chem)ical characteristics of the cell laminate and by taking advantage of the flexible possibilities of modern modelling software tools (COMSOL).

Thermal electric 3D finite element models for two different geometrical design variants (continuous and separated contacting tabs) of cylindrical cells has been created and analysed. The description of the electrochemically active winding structure was based on a 3-phase continuum model (anode + cathode + electrolyte composite phases) with 3 DOF (cathode + anode side electric potential, temperature). An simple analytical approach (adapted form of Shephard' model [1]) was used as constitutive equation for the electro-chemical characteristics which accounts for the local variation of intrinsic cell voltage and polarisation resistance with current density, state of charge and temperature. It is defined by a number of temperature dependent parameters which had been estimated from an elaborate process of experimental characterisation with state of the art testing equipment. The geometry description of the cell was completed by the cell housing and contacting structures and the model is capable to analyse static and transient behaviour of the cells. The results of the model analysis confirmed the field concentration effects at the current collectors as a source of thermal hot spots and highlighted the importance of the consideration of dynamic effects in the modelling for the analysis of critical thermal behaviour of the cells.

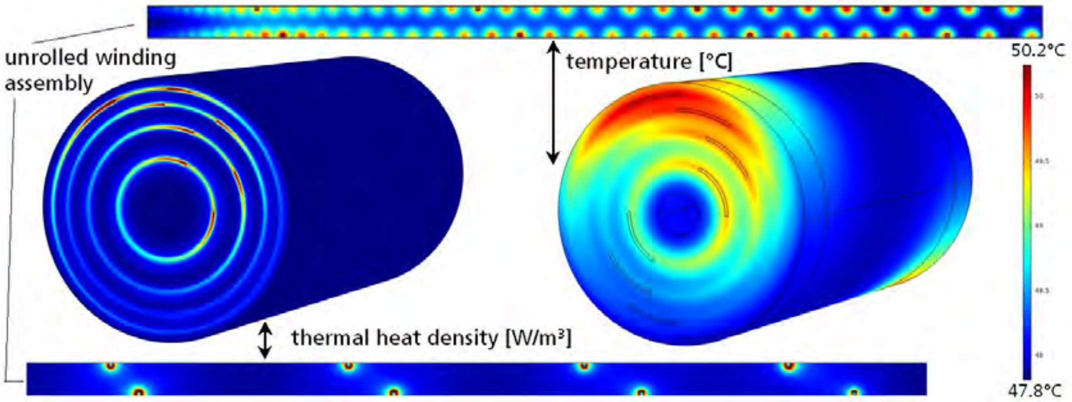

Fig. 1: Model results: heat density (left) and temperature (right) for pulse load (I=90A, Δt=5s)

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Effect of temperature spatial non-uniformity on electrochemical impedance in lithium-ion cells

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We investigate the relationship between cell internal temperature distribution and electrochemical impedance, focusing on the variation in impedance phase shift at a single frequency in the 40-100 Hz range. This can be rapidly measured in on-board monitoring systems. Combined with a measurement of cell surface temperature and a simple thermal model, accurate estimation of maximum internal cell temperature is possible.

Studies have shown that: (1) the impedance of various types of li-ion cells at high frequencies (>30 Hz) is dominated by the anode [1], therefore impedance measurements in this range are unaffected by changes to the cathode structure; (2) the degradation of li-ion cells under normal conditions is primarily at the cathode [2], and so the anode structure may remain stable even after several thousand cycles [3]; and (3) the impedance due to the SEI layer is approximately independent of SoC, but highly dependent on temperature [1]. Therefore, impedance phase shift at a frequency in the 40-100 Hz range is directly indicative of *average* cell internal temperature [4], and with calibration it is possible to use this as a type of cell temperature measurement for the range -20 to 66°C [5]. However, previous work assumes the cells are at uniform temperature, whereas under typical operating conditions they may exhibit large internal temperature non-uniformities [6]. Therefore the temperature estimated using this technique may differ from the true maximum internal temperature.

To investigate this, we test three cylindrical cells connected in parallel in order to represent the inner, middle and outer volume elements of a single cell (Fig. 1), after Fleckenstein [7]. The radial temperature distribution which occurs in a single cell is then modelled by maintaining each of these three cells at a different temperature.

Using this approach, it is shown that a phase shift measurement at a certain uniform temperature may be equivalent to that measured for a range of different temperature distributions. By using an additional surface temperature measurement in combination with the phase shift measurement, the internal temperature distribution, and consequently the maximum internal temperature, may be estimated.

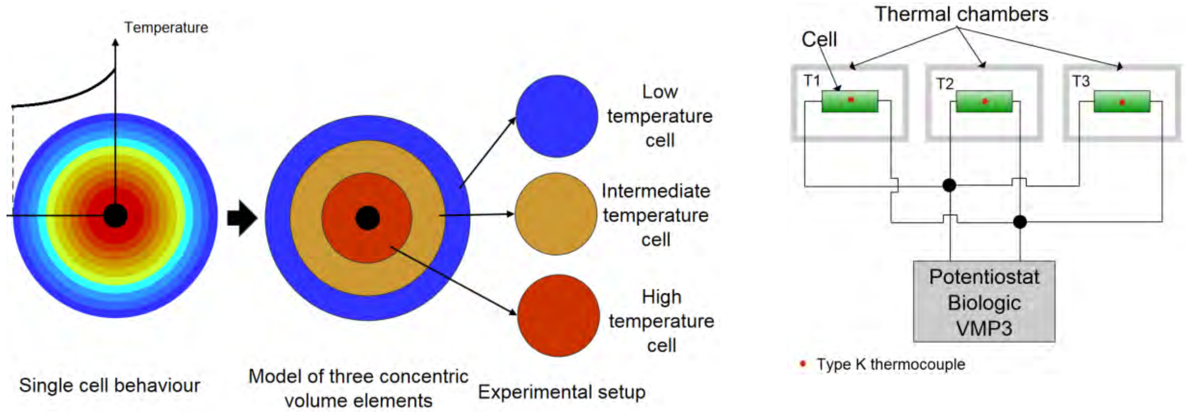

Figure 1 Experimental approach using three cells in parallel to represent the inner, middle and outer elements of a single cell; left: approximation of continuous temperature distribution as three concentric volume elements; right: experimental setup with three cells each maintained at different temperatures in seperate thermal chambers.

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The effect of temperature gradients on the performance of Li-ion batteries

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Lithium-ion batteries are emerging as the technology of choice for automotive applications due to their relatively high energy and power density. Safety, performance, and extended life are the major challenges with which battery manufacturers are faced today. Moreover they are strongly affected by the temperature and therefore the thermal control and management of lithium cells within the pack is crucial: heat generated within single cells in a pack may lead to an onset of thermal runaway and premature failure of the entire battery pack.

This work combines electrochemical and thermal modelling with experimental tests to investigate the effect of temperature gradients on the performance of a 4.8 Ah Kokam lithium-ion polymer cell. Such gradients are likely to be present inside the battery pack due to the thermal boundary conditions imposed by the pack architecture. An experimental rig was built for the testing of prismatic cells, in which the surface temperatures of opposite sides of a cell can be independently and accurately controlled by Peltier elements, in the absence of a climate chamber.

Cells subjected to thermal gradients perform as if under an uniform temperature that is higher than the average of the imposed temperatures, with the charge transfer resistance showing the strongest dependency on the value of the applied thermal gradient (as shown in Fig. 1). The steeper the temperature gradient applied, the stronger the effect. This behaviour can be rationalised from the perspective of the cell's inner structure, together with information from measurements of electrochemical impedance spectroscopy at uniformly imposed temperature boundary conditions, and from high fidelity cell modelling.

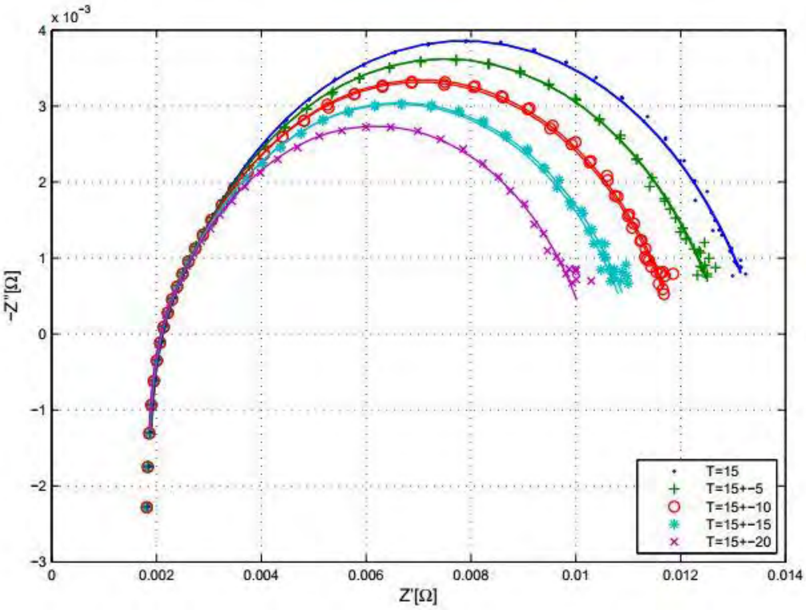

Figure 1: EIS measurements on a 4.8 Ah Kokam cell greatly depend on the magnitude of the thermal gradient across it, with the cell performing as one warmer than the average temperature. SOC = 80%, T_{avg} = 15°C.