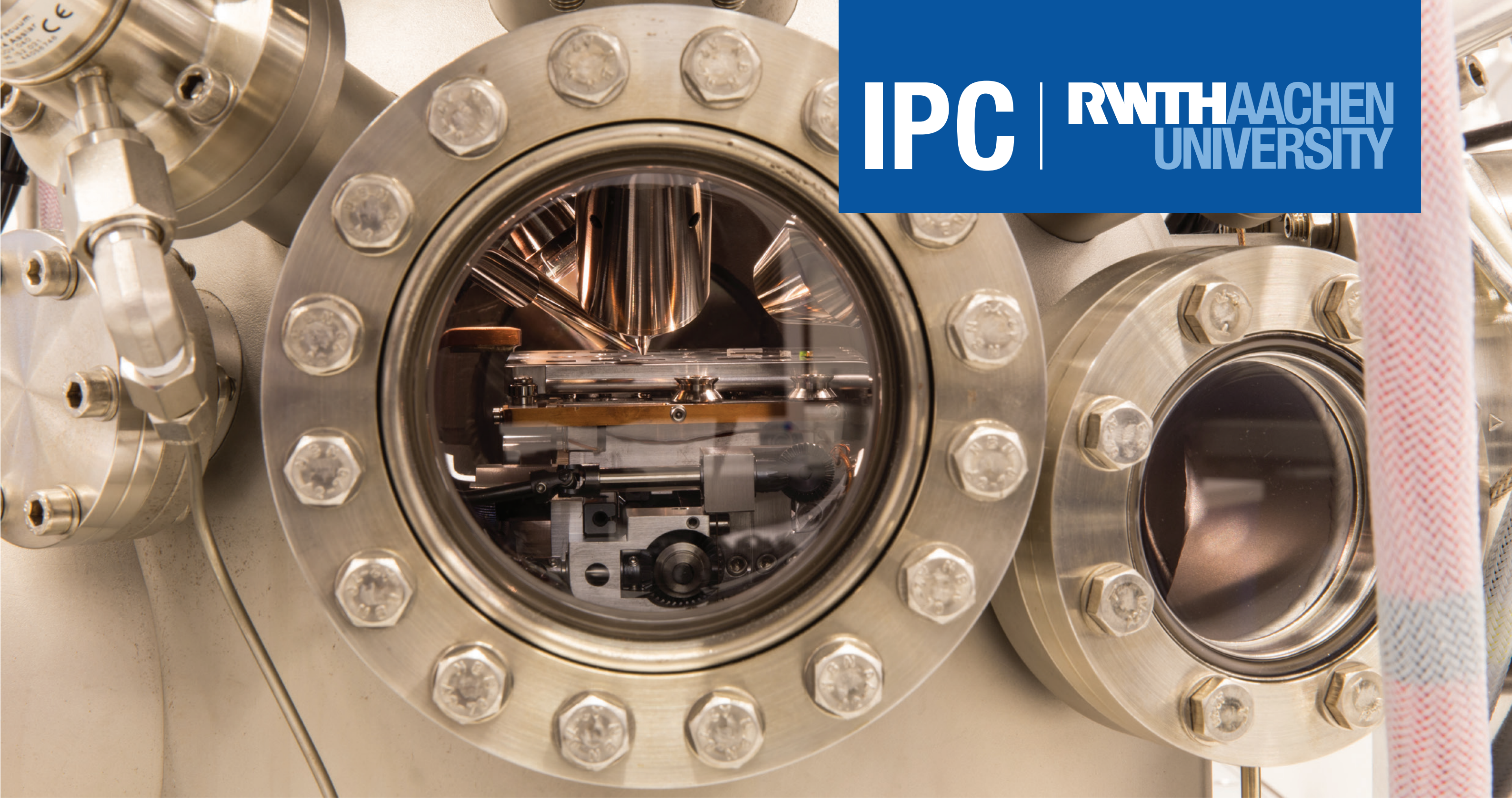

Bunsen Colloquium

New Horizons in Solid State Ionics

July 28 - 29, 2022
Institute of Physical Chemistry, RWTH Aachen University

Bunsen Colloquium on the occasion of the
68th birthday of Manfred Martin

Welcome to RWTH Aachen University

Solid State Ionics is the field devoted to the study of ion transport and reactivity, as well as structure–property relationships, in the solid state. It has a long and illustrious history, which started with the studies of Michael Faraday and which was set on a firm foundation by the fundamental work of Nernst, Frenkel, Schottky and Wagner. Since those beginnings, interest in the subject has increased continuously, with a focus on materials for solid oxide fuel cells, lithium batteries and sensors. In the last twenty years or so, there have been several surprising developments in the field, not only in terms of the materials systems that are attracting attention, and in terms of possible applications, but also in terms of new and improved methods of investigation, both experimental and computational. This Bunsen colloquium will provide a forum to discuss the latest developments in the field of Solid State Ionics and to examine the prospects for the future. In addition, the convergence of solid state ionics and solid state electronics will be discussed.

This Bunsen Colloquium is being held on the occasion of Prof. Manfred Martin's 68th birthday. For the three of us, hosting this Colloquium is a special honour, since Prof. Martin has been our mentor and colleague for a cumulative 60 years (30 + 20 + 10). It has been a pleasure to work with him, and we hope that our discussions and collaborations will continue in the years to come.

We hope you enjoy this Bunsen Colloquium, and we are looking forward to many interesting discussions on New Horizons in Solid State Ionics.

Roger A. De Souza

Michael Schroeder

Andreas Falkenstein

Program

Thursday, 28th July 2022

8:00	Registration & Mounting of Posters
9:00 – 9:25	**Opening Ceremony** **Ulrich Rüdiger (Rector of RWTH Aachen University)** **Roger A. De Souza (RWTH Aachen University)**
9:25 – 10:00	**Plenary Speaker:** Joachim Maier (Max-Planck-Institut für Festkörperforschung) » Solid State Ionics: Mission Uncompleted?
10:00 – 10:20	*Coffee Break*
10:20 – 12:05	Session I (Chair: Susanne Hoffmann-Eifert)
10:20	**Invited:** Neil Allan (University of Bristol) » Local Structure and Ion Migration – Insights and Surprises from Simulation
10:45	**Oral:** Andreas Klein (TU Darmstadt) » The Fermi energy as a common descriptor for charge compensation in ionic solids and its relation to the conductivity limits of donor doped In_2O_3 thin films
11:05	**Invited:** David Müller (Forschungszentrum Jülich) » What can X-Rays tell us about point defects (and what not)?
11:30	**Plenary Speaker:** Truls Norby (University of Oslo) » The *p*-*n*-junction has nothing to do with ionics. Does it?
12:05 – 13:35	*Lunch*
13:35 – 15:05	Session II (Chair: Steffen Neitzel-Grieshammer and Annalena Genreith-Schriever)
13:35	**Invited:** Klaus-Dieter Becker (TU Braunschweig) » Spectroscopic Studies of Defects and Diffusion in Oxides
14:00	**Invited:** Paul Heitjans (Leibniz University Hannover) » About the Role of NMR in Solid State Ionics
14:25	**Oral:** Juliusz Dąbrowa (AGH University of Science and Technology) » Defects and transport in high-entropy oxides
14:45	**Oral:** George F. Harrington (RWTH Aachen University) » Modifying transport in rare-earth substituted ceria films: the impact of strain, interfaces, and above-bandgap radiation
15:05 – 15:25	*Coffee Break*
15:25 – 17:05	
15:25	**Oral:** Rotraut Merkle (Max-Planck-Institut für Festkörperforschung) » The fascinating complexity of oxides with three mobile carriers
15:45	**Oral:** Matthew J. Wolf (RWTH Aachen University) » 3D-to-2D Transition of Anion Vacancy Mobility in $CsPbBr_3$ under Hydrostatic Pressure
16:05	**Invited:** Peter C. Schmidt (TU Darmstadt) » Thermomigration of oxygen vacancies in $SrTiO_3$
16:30	**Plenary Speaker:** Han-Ill Yoo (Seoul National University) » Complete documentation of all the mass/charge transport properties of $La_2NiO_{4+\delta}$ and puzzling thermomigration behavior
17:05 – 18:30	**Poster Session** *with Beer & Pretzels*

We gratefully acknowledge financial support by:

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Program

Friday, 29th July 2022

9:00 – 10:15	Session III (Chair: Paul Heitjans and Yoshitaka Aoki)
9:00	**Plenary Speaker:** Rainer Waser (RWTH Aachen University)
	» Redox-Based Memristive Switching in Metal Oxides - Variants and Prospects in Neuromorphic Computing
9:35	**Oral:** Ho Won Jang (Seoul National University)
	» Halide Perovskites for Memristive Data Storage and Artificial Synapses
9:55	**Oral:** Susanne Hoffmann-Eifert (Forschungszentrum Jülich)
	» Analysis of short-range order in amorphous HfO_2 thin layers grown by atomic layer deposition
10:15 – 10:35	*Coffee Break*
10:35 – 12:40	
10:35	**Invited:** Steffen Neitzel-Grieshammer (RWTH Aachen University)
	» Kinetic Monte Carlo simulations for solid state electrolytes
11:00	**Invited:** Masanobu Nakayama (Nagoya Institute of Technology)
	» Computational and informatics studies on NASICON-type Li ion conductor
11:25	**Oral:** Julian Eigen (RWTH Aachen University)
	» Rechargeable Oxide Batteries: Storage Capacities and Kinetics
11:45	**Oral:** Annalena R. Genreith-Schriever (University of Cambridge)
	» Ni–O-redox, oxygen loss and singlet oxygen formation in $LiNiO_2$ cathodes for Li-ion batteries
12:05	**Plenary Speaker:** Jürgen Janek (Justus Liebig University Gießen)
	» Solid State Batteries – A Showcase for Solid State Ionics
12:40 – 14:10	*Lunch*
14:10 – 15:20	Session IV (Chair: Rotraut Merkle and Michael Schroeder)
14:10	**Invited:** Jong-Ho Lee (Korea Institute of Science and Technology)
	» A Mechanistic Study on the Multi-step Phase Dismantling Process of Single-phase $Ce_{0.75}Zr_{0.25}O_2$: Complete Separation into Ceria and Zirconia
14:35	**Invited:** Yoshitaka Aoki (Hokkaido University)
	» Topotactic transformation of barium indate zirconate perovskite in H_2 atmosphere
15:00	**Oral:** Adrian L. Usler (RWTH Aachen University)
	» Why we should not trust (but still might use) the Mott–Schottky model for grain-boundary impedance
15:20 – 15:40	*Coffee Break*
15:40 – 17:20	
15:40	**Oral:** Tomáš Duchoň (Forschungszentrum Jülich)
	» Beyond stoichiometry in photoemission spectroscopy: *c*–*f* hybridization in cerium compounds
16:00	**Oral:** John P. Arnold (RWTH Aachen University)
	» Theoretical and Computational Description of the Polaron Migration in Ceria
16:20	**Invited:** Steve P. Harvey (National Renewable Energy Laboratory)
	» Renewable Energy from a Big Picture Perspective to Nanoscale Insights via TOF-SIMS
16:45	**Plenary Speaker:** Manfred Martin (RWTH Aachen University)
	» Defects and transport — still plenty to be done
17:20 – 17:30	Poster Award Ceremony

Program

Poster Presentations

P01: P. Odenwald (Forschungszentrum Jülich)
» Enhanced Sintering and Ionic Conductivity in Zr-Deficient NaSICON Solid Electrolytes

P02: A. Yang (Forschungszentrum Jülich)
» Enhanced ionic conductivity in $Na_{4.92}\square_{0.08}Y_{0.92}Zr_{0.08}Si_4O_{12}$

P03: C. Ader (RWTH Aachen University)
» Numerical Simulation of the Kinetic Unmixing and Decomposition in Barium Titanate

P04: N. Ahr (RWTH Aachen University)
» Numerical simulations of the Hebb-Wagner polarization method of perovskite-type oxides

P05: S. Ambaum (RWTH Aachen University)
» Anti-Frenkel defect formation and oxygen diffusion in brownmillerite $Sr_2Fe_2O_5$

P06: A. Bielefeld (Justus-Liebig-University Gießen)
» The Link between Solid-State Ionics and Microstructure Effects in Solid-State Batteries

P07: A. Bonkowski (RWTH Aachen University)
» A molecular-dynamics study of oxygen diffusion in polycrystalline $(La,Sr)FeO_3$

P08: J. Eigen (Forschungszentrum Jülich)
» Rechargeable Oxide Batteries: Concepts and Materials

P09: J. Eigen (Forschungszentrum Jülich)
» Rechargeable Oxide Batteries: Storage Capacities and Kinetics

P10: M.T. Elm (Justus-Liebig-University Gießen)
» Charge transport in mesoporous oxides with high surface area

P11: H. Fukuda (Nagoya Institute of Technology)
» Optimization of NASICON-type solid electrolyte composition using both experiments and Bayesian optimization

P12: S. He (Forschungszentrum Jülich)
» Evolution of structural, magnetic and electrical properties of oxygen-deficient $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ thin films under deoxygenation

P13: L. Heymann (Forschungszentrum Jülich)
» Separating the effects of band bending and covalency in hybrid perovskite oxide electrocatalyst bilayers for water electrolysis

P14: A. Kaus (Forschungszentrum Jülich)
» Hybrid oxide superlattices as electrocatalysts for the oxygen evolution reaction in alkaline electrolyte

P15: D. Kemp (RWTH Aachen University)
» Recipes for superior ionic conductivities in thin-film ceria-based electrolytes

Program

Poster Presentations

P16: S. J. Kim (Seoul National University)

» Vertically aligned two-dimensional halide perovskites for reliably operable artificial synapses

P17: C. Korte (Forschungszentrum Jülich)

» Reaction kinetics in the system Y_2O_3/Al_2O_3 – Control of the product phase formation in a system forming multiple product phases by applying an external electric field

P18: S. Lansab (TU Dortmund)

» Dynamics study of nitrile-based electrolytes for lithium-ion batteries

P19: D. Mroz (RWTH Aachen University)

» Interaction between the surfaces of $LiCoO_2$ and NMC811 and electrolytes

P20: T. Ohlerth (RWTH Aachen University)

» Arresting the cubic metastable phase in HfO_2 nanoparticles as a model compound for 3-dimensionally confined resistive switching

P21: C. Rodenbücher (Forschungszentrum Jülich)

» Investigation of Localized Reduction Phenomena in Yttria Stabilized Zirconia Electrolytes

P22: D. Röhrens (RWTH Aachen University)

» A- and B-site doping of perovskite oxides enables microwave-assisted catalysis: A case study on CO oxidation

P23: A. Roßbach (Forschungszentrum Jülich)

» Preparation, characterization and conductivity of NASICON-type $Li_{1+x}M^{(III)}_xTi_{2-x}(PO_4)_3$ ($M^{(III)}$ = Al, Cr, Fe; $0.5 \leq x \leq 2.0$) materials via modern, scalable synthesis routes

P24: J. Schütt (Forschungszentrum Jülich)

» Multi-Scale Investigation of Na^+ Migration in doped $NaZr_2(PO_4)_3$ NASICONs

P25: G. Winterhoff (RWTH Aachen University)

» Proton migration and interactions in doped barium zirconate: review of DFT data and simulating of conductivity

P26: C. Xiao (Max-Planck-Institut für Festkörperforschung)

» Unification of Bulk Storage and Supercapacitive Storage

P27: Y. Yamaguchi (Nagoya Institute of Technology)

» Drawing a materials map with an autoencoder for all-solid-state Li-ion batteries

P28: J. W. Yang (Seoul National University)

» Tailored Indium Oxide Nanostructures for Efficient Charge Separation in Water Splitting Photoanodes

P29: C. Perkampus (RWTH Aachen University)

» Computational study of oxygen diffusion in the perovskites $CaTi_{1-x}Fe_xO_{3-\delta}$

Solid State Ionics: Mission Uncompleted?

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Roughly one hundred years ago the thermodynamic and kinetic foundation of Solid State Ionics have been laid and thus the solid state opened for a proper treatment of charge carrier chemistry. The application to functional materials especially in the field of high-temperature chemistry has been enormously successful and high-temperature sensors (λ-probe) or high-temperature fuel cells (SOFC) have emerged from such considerations.

It was clear right from the beginning that the significance of Solid State Ionics is much more general. It appeared to be just a matter of time until its importance would have recognized in solid state chemistry or solid state physics. However, by now, one has to state that the "mission is far from completed".

In that spirit the contribution is not only concerned with novel developments in the proper field of Solid State Ionics, but describes the potential for solid state science in general. As far as more recent solid stats ionic developments are concerned, the size and complexity coordinates are highlighted. As far as the more general significance is concerned, examples from solid state physics, photovoltaics, battery research and catalysis are referred too in which the combination of ionic and electronic effects is crucial but not adequately appreciated.

🕒Thu 9:25 am

Local Structure and Ion Migration – Insights and Surprises from Simulation

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Ab initio simulation techniques are increasingly able to provide often general new insights into diffusion processes in condensed phases. In this presentation:

(i) Links between *local structure* and ionic migration are explored by examining the energy landscapes, calculated ab initio, of fast-ion conductors. Examples include: (a) fast-ion oxygen-deficient perovskites where oxygen transport involves transitions between basins in the energy landscape corresponding to different local minima; (b) the high-temperature disordered phase of δ-Bi_2O_3 where a very different picture from the conventional emerges. Only the *mean* structure is cubic - transitions between energetically accessible minima, with structures similar to low symmetry motifs in the low temperature ordered phases are responsible for the high oxide mobility. We compare δ-Bi_2O_3 and BIMEVOX [1].

(ii) We discuss recent ab initio molecular dynamics simulations for fluoride ion transport in PbF_2 [2] and hydride ion conduction in Ba_2ScHO_3, a recently synthesized oxyhydride with an unusual anion ordering [3].

(iii) We discuss the interstitial diffusion of noble gases in MgO, which as periclase is an important component of the Earth's mantle, at both ambient and high pressures [4].

[1] H.J. Stroud, C.E. Mohn, N.L. Allan, Phil. Trans. Roy. Soc. A, 2021, 20200430
[2] C.E. Mohn, M. Krynski; W. Kob, N.L. Allan, Phil. Trans. Roy. Soc. A, 2021, 20190455
[3] H.W.T. Morgan, H.J. Stroud, N.L. Allan, Chem. Mater. 2021, 133, 177-185
[4] C.E. Mohn and N.L. Allan (to be published)

Thu 10:20 am

The Fermi energy as a common descriptor for charge compensation in ionic solids and its relation to the conductivity limits of donor doped In_2O_3 thin films

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The determination of defect concentrations requires the assumption of charge neutrality, which means that any positive or negative charge in the system must be compensated by an opposite charge. Which charges are present, depends on the active compensation mechanism. Addition of dopants, which are charged defects, may result in the generation of electronic charge carriers, lead to the formation of ionic defects such as vacancies or interstitials, or change the valence of a lattice atom (trapped electronic charges, e.g. Ce^{3+} in CeO_2). Moreover, dopants added to a material may also trap charges and thereby change their valence and eventually become neutral (e.g. Fe^{4+} in $SrTiO_3$). While these compensation mechanisms are described by their respective defect reactions, a relation between the different reaction constants is not evident from this description. This is different, if the defect concentrations are derived in a different way. In ab-initio calculations of defect formation enthalpies by means of density functional theory, defect concentrations are typically calculated for a reference state of chemical potentials and given by their dependence on chemical potentials and the Fermi energy. In this description, the formation enthalpy of a defect with charge state q is given by [1]:

$$\Delta H_D = H^q_{defect} - H_{ideal} + q(E_F - E_{VB}) + \sum\nolimits_i \Delta n_i \mu_i \tag{1}$$

Equilibrium defect concentrations are then determined by finding the Fermi energy, at which the sum of all defect concentrations vanishes. While this seems to invert the common understanding that defect concentrations determine the Fermi energy, the two approaches are fully equivalent as the equilibrium Fermi energy is the same in both descriptions. As all potential charge compensation mechanisms can be described by the characteristic dependence of the formation enthalpy of the involved defects on the Fermi energy, it becomes possible to gain insights into the origin of the prevailing compensation mechanism. Interestingly, this may even include the solubility of dopants, as their formation enthalpies are also a function of the Fermi energy as that of any charged defect.

As example for the analysis of the charge compensation mechanisms, results for undoped and donor-doped In_2O_3 thin films will be presented. X-ray photoelectron spectroscopy, also in combination with in-situ analysis of electrochemical cells, will be combined with conductivity and Hall effect relaxation measurements. Conductivity limits will be shown to be determined by valence changes of oxygen vacancies or Sn donors. Moreover, dopant segregation and the effect of combined oxygen and dopant diffusion will be addressed.

[1] S. B. Zhang, J. E. Northrup, Phys. Rev. Lett.1991, 67, 2339.

Thu 10:45 am

What can X-Rays tell us about point defects (and what not)?

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Charged point defects are responsible for many of a material's properties that are harnessed in electrochemical applications. Naturally, the observation and quantification of ionic charge and its evolution during (electro)chemical reactions is desired in order to identify reaction mechanisms, driving forces and form a predictive understanding of such materials. Electrochemical methods from two centuries ago provide the tools to unambiguously identify and quantify ionic and electronic charge carriers and their movement through the solid and its interfaces, albeit in an indirect way[1]. With the advent of X-ray spectroscopic methods made possible in atmospheres approaching ambient pressure and at elevated temperatures in the recent past, supposedly there is now a more direct way of observing the evolution of charged species during reactions by probing the electrons of the material's constituents *in operando*. In a nutshell, these experiments are carried out to determine the oxidation state of a specific ion.

To the experimenter's (and even more so the theoretician's!) dismay, the results obtained from X-ray photoelectron and absorption spectroscopy (XPS and XAS, respectively) can show severe discrepancies to those obtained from electrochemical methods and calculations [2], which can be understood quickly when taking a step back and reassessing what XPS and XAS actually probe. One of the most important aspects is that, even though element specific, those techniques cannot probe an isolated atom or ion in a material but rather how it is present in its immediate surrounding. This leads to the realization that those spectroscopic tools can be used to identify properties and processes that are far beyond the simplistic concept of an oxidation state.

In this contribution I will first show how the seemingly straightforward use of XPS and XAS to determine ionic charge or oxidation states can lead to dangerous misconceptions, but then expand on how the origin of these misconceptions provides insights into peculiar properties of perovskite materials used in electrochemical devices. Showcasing prototypical materials, and (Pr,Ba)$CoO_{3-\delta}$, we will explore how X-Ray spectroscopic techniques could identify the active species in the cathode material (La,Sr)(Fe,Co)$O_{3-\delta}$, elucidate a percolation conduction mechanism in the oxygen separation membrane compound Sr(Ti,Co)$O_{3-\delta}$, and how the (alleged) electronic performance descriptor of the water splitting catalyst (Pr,Ba)$CoO_{3-\delta}$ is influence by ordering and decomposition phenomena.

[1] R. A. De Souza, D. N. Mueller, Nat. Mater. 2020, 20, 443-446.
[2] A. Walsh, A. A. Sokol., J. Buckeridge, D. O. Scanlon, C. R. Catlow, Nat. Mater. 2018, 17, 958-964.

🕒Thu 11:05 am

The p-n-junction has nothing to do with ionics. Does it?

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The semiconductor p-n-junctions of computer processors and storage, photovoltaic cells, and LEDs are generally doped *homojunctions* and hence kinetically stable only as long as temperatures are low enough to prevent dopant interdiffusion. As an alternative, *heterojunctions* can be thermodynamically stable (coexistent) across solid solubility gaps. This allows infinite thermal stability as well as bottom-up fabrication routes and novel geometries. This has not been explored for p-block elemental or compound semiconductors, but there are known cases among oxides, such as p-type NiO and n-type ZnO.

During fabrication and use of stable oxide heterojunctions, the establishment of solid solubility equilibria, mutual doping, and distribution of foreign dopants take place by (inter)diffusion of cations. To achieve the desired properties – whether ohmic behaviour for thermoelectric junctions or rectification for electronics or optoelectronics – therefore requires interactive understanding of semiconductor physics, thermodynamic driving forces, diffusion kinetics, and fabrication processes.

Once the principles of thermodynamically stable p-n-heterojunctions junctions are established, they open up not only infinite stability and bottom-up fabrication and, in turn, novel nano- and microscale geometries, but also novel applications. The p-n-junction can self-assemble in a percolating network in a volume and transform 2D devices like photovoltaic cells or LEDs to 3D. Moreover, if the 3D LED has percolating porosity as a 3rd phase, we may use the embedded light for photocatalytic reactions including purification of air and water. Finally, water may adsorb and provide surface protonic conduction over the p-n-junction, forming a "zero-thickness" or "electrolyte-free" electrochemical cell, like a single chamber fuel cell provided that the right electrocatalysts can be applied.

The talk will take us from the thermochemical principles that allow design and fabrication of novel coexistent semiconductor p-n heterojunctions, to how they may function in novel photochemical and electrochemical applications.

Acknowledgement: The work is in part financed by the Research Council of Norway (ENERGIX, 320805, "RADICON").

Thu 11:30 am

Spectroscopic Studies of Defects and Diffusion in Oxides

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Local probe spectroscopies like optical spectroscopy, EPR, and Mössbauer spectroscopy can provide insight not only into the crystallographic structure of materials but also into their defect structure as well as into diffusion-related kinetic processes. In the present contribution, examples will be reported for the latter spectroscopies applied to important functional materials at thermodynamically defined high-temperature conditions.

Mixed ionic-electronic conducting oxides of the perovskite structure are of interest, e.g., for ceramic membranes for energy-efficient separation of oxygen from air as well as for electrode materials in solid oxide fuel cells. $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ (BSCF5582) is a mixed conducting material which is characterized by highest oxygen permeation and by an extremely large oxygen deficit. We report on an ^{57}Fe Mössbauer in-situ study of BSCF5582 conducted between room temperature and 1000 °C. The study provides insight into oxygen vacancy disorder and into the distribution of oxygen vacancies on different sites in the structure. In the paramagnetic high-temperature phase ($T \gtrsim 315$ °C), a_{O2}-dependent changes in spectra reveal stoichiometry-related changes in the valence and the local coordination of the nuclear iron probes [1,2].

Oxidation and reduction of oxides represents an important class of solid state reactions associated with changes in crystal stoichiometry and many crucial materials properties. In the case of $LiNbO_3$, optical spectroscopy can be used to monitor such redox processes at high temperatures [3,4]. Absorption induced by small electron polarons provides information on the a_{O2}-dependence of polaron concentration. The kinetics of redox processes has been studied by means of a_{O2}-jump experiments.

[1,2] P. Gaczynski, A. Harpf, J. Böer, R. Kircheisen, R. Kriegel, K.-D. Becker, Solid State Ionics, 316 (2018) 59 / 369 (2021) 115659.
[3] J. Shi, H. Fritze, G. Borchardt, K.-D. Becker, Phys.Chem.Chem.Phys, 13 (2011) 6925.
[4] D. Sugak, O. Buryy, Yu. Suhak, Ya. Zhydachevskii, K.-D. Becker, N.V. Martynyuk, U. Yakhnevych, S. Ubizskii, Optical Materials 99 (2020) 109543.

🕒Thu 1:35 pm

About the Role of NMR in Solid State Ionics

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Corresponding to the key topics of Solid State Ionics which are also reflected by the subtitle 'Diffusion and Reactions' of the homonymous interdisciplinary journal, the specific role of Nuclear Magnetic Resonance (NMR) in Solid State Ionics is associated with the study of ion dynamics rather than with structure elucidation.

Fortunately, small ions being mobile in solids, *e.g.* H^+, Li^+, Na^+, F^-, often bear nuclei which are well suited for NMR motional studies. There are numerous examples in the literature since the early days of Solid State Ionics in the late 1970s. One of the first corresponding NMR reviews was given in [1]. In the following decades, the number of studies in particular on Li^+ as mobile ions steadily increased due to the growing interest in solid Li ion conductors as potential electrolytes or electrodes in Li ion batteries.

This has been favoured by the fact that besides the excellent probe nucleus ^7Li, as a second stable isotope ^6Li with complementary properties is available. Furthermore, it was early shown on several examples [2] and recently independently confirmed [3] that spin-lattice relaxation of the short-lived beta-emitter ^8Li is another useful tool to study diffusional processes.

Nowadays extensive material on the role of NMR in Solid State Ionics is available [4,5].

Several own examples will be presented illustrating the large dynamic range of the different NMR techniques and the detailed information on ion dynamics which can be gained.

[1] D. Brinkmann, Solid State Ionics 1981, 5, 53–58.
[2] P. Heitjans, Solid State Ionics 1986, 18-19, 50–64.
[3] W. A. MacFarlane, Z. Phys. Chem. 2022; 236, 757–798.
[4] C. V. Chandran, P. Heitjans, Ann. Rep. NMR Spectrosc. 2016, 89, 1–102.
[5] C. V. Chandran, P. Heitjans, Ann. Rep. NMR Spectrosc. 2022, 106, 1–51.

Thu 2:00 pm

Defects and transport in high-entropy oxides

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Over the last decade, high-entropy materials have become one of the most prominent topics in materials science. Among them, the high-entropy oxides (HEOx), are gaining special attention, proving themselves a viable replacement for the state-of-the-art materials in numerous energy-conversion technologies, including Solid Oxide Fuel Cells (SOFCs), Li-ion, and Na-ion batteries. Similarly, as in the case of their conventional counterparts, it can be postulated that their often exceptional performance is to a large degree a direct consequence of their transport properties, which can be further correlated with the defect chemistry of these materials. In the presented study, these interrelations are discussed based on the experimental examples, covering a wide range of HEOx structures (Rock salt-structured oxides, fluorites, perovskites, double perovskites, Ruddlesden-Popper phases), transport mechanisms (solid electrolytes, mixed oxygen-electronic conductors, mixed lithium ion-electronic conductors), and potential applications (Li-ion, SOFC, oxygen separation membranes). The results indicate that in multiple cases the high-entropy approach leads to obtaining otherwise inaccessible features in terms of both properties and defect chemistry, proving that it may potentially provide a unique design tool for obtaining new functional materials. On the other hand, it is also shown that the effects emerging as a consequence of the high-entropy approach utilization might not always be considered beneficial, in some cases compromising the materials' properties. Lastly, it is presented that in some cases despite the high-entropy configuration of the composing ions, the systems might directly follow the rule-of-mixtures predictions. The results indicate that similar to the case of most design strategies, the high-entropy approach comes with both advantages and disadvantages, requiring an in-depth understanding of the studied systems in order to fully exploit its potential benefits.

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Thu 2:25 pm

Modifying transport in rare-earth substituted ceria films: the impact of strain, interfaces, and above-bandgap radiation

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In recent decades there has been a de-emphasis in compositionally tuning oxides for enhanced functional properties, as focus has shifted to alternative methods to tailor desirable properties such as lattice strain, electric-field modified mobility, interfacial effects, and above-bandgap radiation. Thin film structures provide an experimental platform where strain, microstructure, interfacial density, and geometry down to the nanoscale can be engineered.

Rare-earth substituted ceria (RE:CeO_2) is, as well as one of the best commercially available O-ion electrolytes, an excellent model material to study transport phenomena in ionic and mixed ionic-electronic conducting systems. In this contribution, we discuss three approaches to engineer the transport in RE:CeO_2: (1) the effect of strain on the mobility of oxygen vacancies, (2) how the concentration of charge carriers can be modified at interfaces in Pr:CeO_2, (3) the impact of above-bandgap radiation on the transport across grain boundaries in Gd:CeO_2.

First, we discuss the modification of the migration energies for O-vacancy hoping in RE:CeO_2 (RE=La, Gd, La). Through a combination of experiments and computational simulations, we have been able to deconvolute the effects of strain on the migration barriers, defect-association, and migration direction.

Second, in mixed conducting Pr:CeO_2 we discuss the changes in the defect concentration in the vicinity of interfaces and grain boundaries. Using a combination of impedance spectroscopy in conjunction with in-situ optical transmission measurements we explore the deviations from bulk behaviour in materials dominated by a high density of interfaces or grain boundaries.

Third, we explore how an enhancement in the specific grain-boundary conductivity of Gd:CeO_2 induced by above-bandgap radiation can be attributed to a decrease in the blocking space-charge effect. By fabricating films with a variety of well-defined grain boundary types and by employing impedance spectroscopy and ^{18}O tracer diffusion under UV radiation in a custom-built exchange rig the effect of above-bandgap radiation on the diffusion of oxygen across grain boundaries of different character can be unambiguously assessed.

Thu 2:45 pm

The fascinating complexity of oxides with three mobile carriers

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Oxides with three mobile carriers exhibit interesting properties regarding defect concentrations as well as transport properties. This will be discussed on the example of perovskites which contain mobile oxygen vacancies, protons, and electron holes. This materials class ranges from materials that are mainly of fundamental interest (Fe-doped $SrTiO_3$) to triple-conducting $Ba(Fe,Co,Zr,Y,Zn)O_{3-\delta}$ perovskites that may serve as positrode in protonic ceramic fuel and electrolysis cells.

The proton uptake for triple-conducting perovskites may occur either by the dissociative hydration

$$H_2O + V_O^{\cdot\cdot} + O_O^{x} \rightleftharpoons 2\,OH_O^{\cdot} \tag{1}$$

or by a redox reaction at expense of holes

$$H_2O + 2\,h^{\cdot} \rightleftharpoons 2\,OH_O^{\cdot} + 0.5\,O_2 \tag{2}$$

depending on and concentrations. Further complexity arises from strong deviations from ideally dilute behavior. Already a small hole concentration strongly decreases the proton uptake, even if the sample is still in the regime dominated by the hydration reaction (1).[1,2] This is attributed to a partial transfer of holes from Fe to O, decreasing the negative charge density and thus basicity of the oxide ions. DFT calculations support this picture.[3]

Triple-conducting perovskites with a high concentration of redox-active B-site cations typically show much lower degrees of hydration than $Ba(Ce,Zr,Y)O_{3-z}$ electrolyte materials. Interestingly, oversized redox-inactive B-site dopants such as Zn^{2+}, Y^{3+} strongly increase the proton uptake.[1] X-ray absorption measurements (EXAFS, XANES, O-XRS) elucidate how these dopants introduce local lattice distortions which decrease the Fe-O covalency and thus help to preserve a high oxide ion basicity.[4]

A complex behavior may be encountered in the kinetics of stoichiometry changes (2-fold relaxation with strongly differing time constants, nonmonotonic changes).[5] This is rooted in the fact that the electroneutrality condition holds only for all three carriers together, i.e. the simple coupling of carrier fluxes valid in systems with only two carriers does not apply any more. As a consequence, non-monotonic changes of optical absorption, conductivity, or electromotive force may occur after a pH_2O change applied to a proton/oxygen vacancy conductor with minor electronic defect concentration because the net water uptake is decoupled into hydrogen and oxygen incorporation. Vice versa, a pO_2 step may lead to complex stoichiometry relaxation kinetics changing the sample‘s proton conductivity as the oxygen uptake is split into dehydrogenation and hydration steps.[6]

These examples demonstrate that a detailed defect-chemical understanding of triple-conducting oxides is indispensable for further optimizing such oxides for electrochemical or catalytic applications, as the desired properties are often in conflict with each other.

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🕒 Thu 3:25 pm

3D-to-2D Transition of Anion Vacancy Mobility in $CsPbBr_3$ under Hydrostatic Pressure

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Unlike typical inorganic semiconductors, lead–halide perovskites (LHPs) exhibit significant ionic conductivity, which is believed to affect their performance and stability. Motivated by a recent experimental study that suggested pressure as a means to control ionic conductivity in $CsPbBr_3$ [1], we present a detailed theoretical study of the atomic scale effects of pressure on anion migration in the low temperature orthorhombic *Pnma* phase of $CsPbBr_3$ [2]. Using nudged elastic band calculations based on density functional theory, we compute all symmetrically inequivalent activation barriers for anion migration to their closest neighbours, as a function of hydrostatic pressure in the range 0.0–2.0 GPa. We then use those values as parameters in a kinetic model which allows us to connect the atomic scale calculations to the macroscopic anion mobility tensor as a function of applied pressure.

We find that the mobility is enhanced by pressure in the plane spanned by the [100] and [001] lattice directions, while along the [010] direction it is diminished, leading to an effective 3D-to-2D transition of the mobility at elevated pressures. This can be explained by the fact that a network of only a few symmetrically inequivalent paths dominates the mobility at elevated pressures. Our results demonstrate the significant influence of pressure on both the rate and direction of anion migration in $CsPbBr_3$, which we consider likely to hold for other LHPs.

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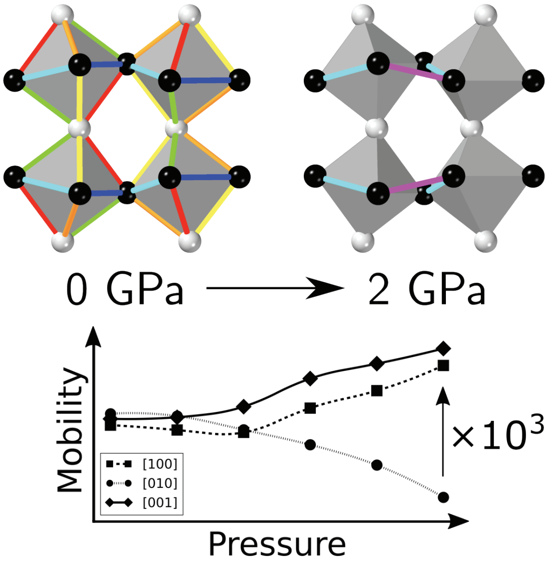

Thu 3:45 pm

Thermomigration of oxygen vacancies in $SrTiO_3$

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We studied the migration of oxygen vacancies in a temperature gradient theoretically by molecular dynamic simulations using both a semi-empirical and a quantum mechanical approach with periodic boundary conditions. The temperature gradient is generated by non-equilibrium molecular dynamics (NEMD [1]). For the semi-empirical studies we used LAMMPS [2], whereas VASP [3] is used for the density functional calculations. The LAMMPS investigations have been performed using unit cells with up to 1600 atoms, while distinctly smaller cells were used for VASP because of computer time limitations. Both methods show the same trend in the thermomigration of oxygen vacancies.

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Thu 4:05 pm

Complete documentation of all the mass/charge transport properties of $La_2NiO_{4+\delta}$ and its puzzling thermomigration behavior

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Layered-structured $La_2NiO_{4+\delta}$ persist hyperstoichiometric ($\delta>0$) across in its entire stability range with the majority disorder type $\{O_i'', h^{\bullet}\}$ which unusually exhibit a strong positive deviation from the ideal behavior. Its isothermal mass/charge transport properties (L_{ii}; $L_{ih}=L_{hi}$; L_{hh}) have earlier been well documented across the entire stability range at elevated temperatures. [1] However, its non-isothermal transport properties (L_{iT}; L_{hT}) are yet to be measured and understood.

In this work, we have measured the mass/charge transport properties (L_{iT}, L_{hT}) under temperature gradients (∇T) on the system of $La_2NiO_{4+\delta}$ against oxygen activity, or composition δ, across its entire stability range at 800, 900, and 1000 °C, respectively.

We will review the non-isothermal measurement principle based on the ionic/electronic thermopower, [2] and complete the documentation of all the mass/charge transport properties of $La_2NiO_{4+\delta}$ once and for all in the form of the coupling coefficient matrix L such that

$$\begin{pmatrix} J_i \\ J_h \end{pmatrix} = \begin{pmatrix} L_{ii} & L_{ih} & L_{iT} \\ L_{hi} & L_{hh} & L_{hT} \end{pmatrix} \begin{pmatrix} -\nabla \eta_i \\ -\nabla \eta_h \\ -\nabla T \end{pmatrix}$$

where J_k and η_k denote the flux and electrochemical potential of the k-type charged component ($i=O^{2-}$; $h=h^+$), respectively. We will then evaluate the thermomigration flux of chemical component O and chemical equivalent of ∇T, and discuss the puzzling thermomigration behavior (L_{kT}), the mobile component O being rendered from thermophilic ($J_O \propto \nabla T$) to thermophobic ($J_O \propto -\nabla T$) with increasing T and δ.

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[2] J. Janek, C. Korte, Solid State Ionics, 1996, 92, 193-204

Thu 4:30 pm

Redox-Based Memristive Switching in Metal Oxides - Variants and Prospects in Neuromorphic Computing

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Redox-Based Resistive Switching Memories (ReRAM), also called nanoionic memories or *memristive* elements, are widely considered to provide a potential improvement beyond the limits of current memory technology with respect to write speed, write energies, and scalability as well as an energy-efficient approach to neuromorphic computing concepts.

In this talk, fundamental aspects of the physics and chemistry (lattice disorder, ionic and electronic transport processes, and phase formation) of these elements will be presented[1]. In particular, the polarity of the switching (eightwise or counter-eightwise) and the geometry (conducting filament vs. area dependent switching) will be discussed. Furthermore, the ultra-high non-linearity of the switching kinetics of redox-based resistive switching devices will be outlined with an emphasis on the so-called valence change mechanism (VCM) typically encountered as a bipolar switching in metal oxides, but also mentioning the electrochemical metallization (ECM) cells. The involved electrochemical and physical processes can be either electric field/voltage enhanced or accelerated by a local increase in temperature due to Joule heating.

The major strands of neuromorphic computing, namely the computational neuroscience for decoding the human brain, the computing-in-memory and the artificial neural networks for pattern recognition, will be worked out. And the different requirements on memristive elements to be applied in these strands will be discussed.

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🕘Fri 9:00 am

Halide Perovskites for Memristive Data Storage and Artificial Synapses

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Halide perovskites have been noted for their exotic properties such as fast ion migration, tunable composition, facile synthetic routes, and flexibility in addition to large light absorption coefficients, long carrier diffusion lengths, and high defect tolerance. These properties have made halide perovskites promising materials for memristors. Applications in the field of resistive switching memory devices and artificial synapses for neuromorphic computing are especially noteworthy. This perspective covers state-of-the-art perovskite-based memristive devices. Moreover, the fundamental mechanisms and characteristics of perovskite-based memristors are elucidated. Interesting opportunities to improve the performance of perovskite-based memristors for commercialization are provided, including improving film uniformity and air stability, controlling the stoichiometry, finding new all-inorganic and lead-free halide perovskites, and making perovskites into single crystals or quantum dots. We expect our perspective to be the foundation of realizing next-generation halide perovskite-based memristors.

Fri 9:35 am

Analysis of short-range order in amorphous HfO_2 thin layers grown by atomic layer deposition

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Thin layers of HfO_2 with thickness of about three to five nanometer are intensively investigated for up-to-date electronic devices. This success is due to various key properties: (1) monoclinic HfO_2 is a wide band gap insulator which forms a stable interface in contact with silicon paving the way to high-k gate oxide/metal gate field effect transistors (FET), (2) the recently discovered orthorhombic phase is ferroelectric enabling FeFETs, (3) amorphous HfO_2 thin films grown reproducibly by atomic layer deposition at temperatures below 400 °C enable filamentary-type resistive switching suitable for high-density back-end-of-line (BEOL) integrated redox-based resistive random access memory (ReRAM) devices. Understanding special features of amorphous HfO_2 thin layers is of utmost importance for the understanding of the resistive switching performance, its stability and reliability.

This contribution addresses the analysis of short range order in amorphous HfO_2 thin films studied by means of grazing incidence total X-ray scattering and pair distribution function (PDF) analysis. The thin films were grown by plasma-enhanced atomic layer deposition at temperatures between 200 °C and 300 °C from tetramethylethylamino-hafnium and oxygen plasma.[1] The X-ray total scattering measurements were carried out in EH2 of beamline P07 at the storage ring PETRA III, DESY, Germany. Additionally to the structural studies of the short-range order in the amorphous films, the influence of additional layers [2] and the evolution of long range ordering during in-situ annealing experiments will be discussed. The measurement results will be compared with recent simulation results of the migration of ions in amorphous HfO_x obtained from large-scale, classical molecular-dynamics simulations.[3] The results provide a deeper understanding of the local structure in amorphous HfO_2, and with this, of the migration of oxygen ions in amorphous HfO_2, which might help optimization and downscaling of HfO_2-based ReRAM devices.

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🕘Fri 9:55 am

Kinetic Monte Carlo simulations for solid state electrolytes

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Solid electrolytes, as found in solid state batteries or fuel cells, represent complex solid solutions with high concentrations of defects. In these materials, the interactions between the charge carriers and interactions with other defects can no longer be neglected when estimating the ionic mobility and conductivity. In fact, the transport properties result from the ionic trajectories through various local environments with individual migration barriers. Hence, an analytical solution is generally not available and atomistic simulations are required.

An efficient approach is the Kinetic Monte Carlo method where the individual vibrations of the ions are neglected and the transport of charge carriers is represented by a chain of state-to-state transitions with varying probabilities. This approach is especially powerful for the simulation of ionic transport in strongly doped materials with interacting defects allowing fast simulation of ionic conductivity for varying temperatures and compositions.

We designed the software MOCASSIN to provide easily accessible Monte Carlo simulations in crystalline electrolytes and simulate a wide range of systems.[1] Parameterized with energies from density functional theory calculations, a better understanding of transport behavior as well as prediction of ionic conductivity is possible.

In this talk, I present our recent applications of Kinetic Monte Carlo simulations to solid electrolytes including cationic and anionic conductors for batteries and fuel cells.[2] Combining first principles calculations with the KMC simulations, the link between the microscopic energy landscape and the macroscopic transport is established. Here, I demonstrate the strength of this method and discuss possible limitations.

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Fri 10:35 am

Computational and informatics studies on a NASICON-type Li ion conductor

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All-solid-state Li-ion batteries are of considerable interest as safer alternatives to Li-ion batteries that contain flammable organic electrolytes. However, at room temperature, achieving sufficient charging and discharging rates and capacity using all-solid-state batteries has been challenging. To overcome these issues, material simulations and informatics investigations of a relatively new Na superionic conductor (NASICON)-type $LiZr_2(PO_4)_3$ (LZP) electrolyte were conducted to elucidate its characteristics and material functions. The thermodynamic and kinetic properties of NASICON-type Li-ion conductive oxides were investigated in terms of the crystal structure using mainly materials simulation and informatics approaches, such as 1) the electrochemical stabilities of LZP materials with respect to Li metal [1] and 2) Li-ion conductivities in the bulk and at the grain boundaries [1,2]. In addition, an efficient materials informatics search was employed to optimize the material functions of the LZP electrolyte via Bayesian optimization (Figure 1) [3]. This study should promote the application of LZP in all-solid-state batteries for use in technologies like mobile devices and electric vehicles and enable more complex composition and process control.

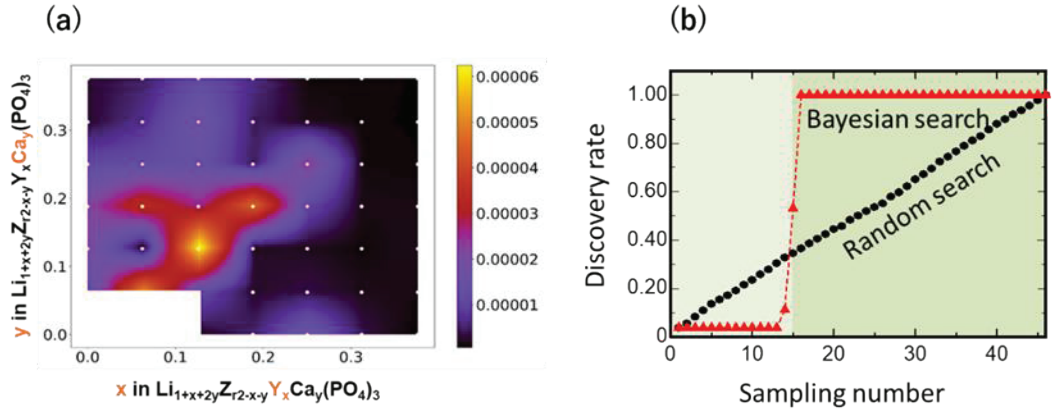

Figure 1 (a) Ionic conductivity of Li as a function of composition. (b) Discovery rate of the best composition as a function of sampling number for the Bayesian and random search methods. [3] (reproduced with permission from the publisher: ©The Royal Society of Chemistry)

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Fri 11:00 am

Rechargeable Oxide Batteries: Storage Capacities and Kinetics

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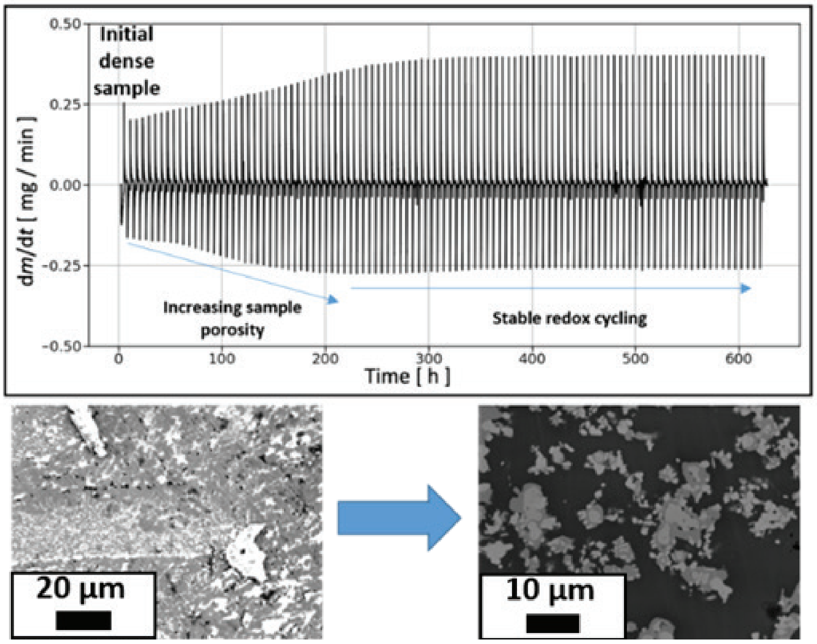
For rechargeable oxide batteries (ROB) to be viable, stable long term cycling needs to be achieved. Additionally, a high energy density is desired for the storage material.[1] The conversion between the chemical energy, in which the energy is stored, to electrical energy available to the consumer needs to be fast enough to keep up with demand. For this purpose, the kinetics of redox reaction of the storage material during charge and discharge is of interest. To characterize the kinetics, the rate of mass change in thermogravimetric measurements were analyzed and fitted for reduction and oxidations by means of Johnson-Mehl-Avrami-Kolmogorow (JMAK) equations. Reaction parameters were chosen to simulate the working conditions expected in a ROB.

The iron in the Fe_2NiO_4/YSZ composites undergo two reaction steps (subsequent iron oxidation from Fe to FeO and FeO to Fe_3O_4) during the discharge process under ROB operating conditions, requires two JMAK equations for the characterization. The resulting parameters received from these JMAK equations are consistent with microstructural developments seen in SEM images, enabling an accurate description of the reaction process throughout the redox cycling process.[2]

The reaction kinetics for the $(Fe_{1-x}Mn_x)_yO_z/Ce_{0.8}Gd_{0.2}O_{2-\delta}$-composites on the other hand can be described by combining the JMAK equation with the Prout-Tompkins or Jander model. As was the case before, further complementary microstructural investigations by means of SEM and XRD were completed. This provides a combined picture of the redox processes taking place during the charge and discharge processes during redox cycling.



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Fri 11:25 am

Ni–O-redox, oxygen loss and singlet oxygen formation in $LiNiO_2$ cathodes for Li-ion batteries

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Ni-rich cathode materials such as $LiNiO_2$ achieve high voltages in Li-ion batteries but are prone to structural instabilities and oxygen loss. Mitigating this degradation requires a comprehensive understanding of the cause and mechanism of oxygen loss, also accounting for the formation of singlet oxygen. Using *ab initio* molecular dynamics simulations, we observe spontaneous O_2 loss from the (100) surface of delithiated $LiNiO_2$, singlet oxygen forming in the process. We find that the origin of the instability lies in the pronounced oxidation of O during delithiation, *i.e.*, a central role of O in Ni-O redox in $LiNiO_2$. For $LiNiO_2$, NiO_2, and the prototype rock salt NiO, a range of computational tools including density-functional theory and dynamical mean-field theory calculations based on maximally localised Wannier functions yield a Ni charge state of *ca.* +2, with O varying between -2 (NiO), -1.5 ($LiNiO_2$) and -1 (NiO_2). The O_2 loss route observed here consists of 2 surface $O^{•-}$ radicals combining to form a peroxide ion, which is then oxidised to O_2. In leaving the surface, O_2 leaves behind 2 O vacancies and 2 electrons, reducing the 2 nearest surface $O^{•-}$ radicals to O^{2-} ions: effectively 4 $O^{•-}$ radicals disproportionate to O_2 and 2 O^{2-} ions, forming 2 O vacancies. The reaction liberates *ca.* 3 eV. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion, with spin conservation dictating the preferential release of $^1O_2$. The strongly exergonic reaction easily provides the free energy required for the formation of $^1O_2$ in its excited state.

[1] A. R. Genreith-Schriever, H. Banerjee, A. J. Morris, C. P. Grey, in press.

Fri 11:45 am

Solid State Batteries – A Showcase for Solid State Ionics

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From the very beginning of Solid State Ionics as an internationally visible interdisciplinary research field in the 1980s, solid state battery (SSB) cells played an important role in the field, and early cell concepts date back even to the 1960s. The rise of the lithium ion battery with a liquid electrolyte from the 1990s was a major "game changer", and research into solid state batteries with inorganic solid electrolytes (SE) was more or less stopped, while the development of polymer-based batteries continued.

Within the recent period of electrification of transportation and the related ever-growing demand for resource-efficient and low-cost batteries with superior storage properties, solid-state batteries gain again great interest. In fact, expectations are high, and world-wide investments and research activities mark a very fast development.

While this technological trend suggests that all fundamental issues are solved and mainly engineering of cells and battery packs remains to be tackled, there are still a number of critical issues that relate to "classical" thermodynamic and kinetic problems in solid state ionics – and which will be highlighted in this presentation:

a) *Defects*: The reversible, high-rate and long-time stable parent metal anode of the type Me/SE is considered as a key ingredient to future high-energy SSBs. Interestingly, the inherent problems of vacancy injection, pore formation and dendrite growth (essentially morphological instabilities) are still not solved.

b) *Nonstoichiometry*: The volume change of active storage materials upon charging/discharging poses a challenge for the stability of electrodes and full cells, thus, the "chemo-mechanics" of non-stoichiometric storage phases and resulting strain in electrode composites remains to be solved.

c) *Mixed conduction and partial conductivities*: On the way to high-capacity solid state electrode composites, the ion- and electron-conducting percolation networks have to be optimized, and the analysis of impedance data in terms of individual transport processes is important to support this task.

d) *Solid state reactions at interfaces*: Strong driving forces cause degradation of solid electrolytes and electrode materials at interfaces, and the control of reactivity plays a major in the stabilization of SSBs.

Ultimately, solid state batteries provide exciting scientific challenges but also are an excellent example for the role of solid state ionics at the crossing of solid state chemistry, physics and electrochemistry.

🕒Fri 12:05 pm

A Mechanistic Study on the Multi-step Phase Dismantling Process of Single-phase $Ce_{0.75}Zr_{0.25}O_2$: Complete Separation into Ceria and Zirconia

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CeO_2-ZrO_2 solid solution has been widely used as a catalysts or catalysts support in various catalytic devices such as three-way catalyst, membrane reactor and fuel cells, because of its superior oxygen releasing/storing capability and relevant electrocatalytic properties. However, the phase stability of CeO_2-ZrO_2 solid solution has been controversial for a long time. There have been many conflicting reports on structural or compositional changes due to the instability of CeO_2-ZrO_2 solid solutions. Hence, in order to properly utilize the CeO_2-ZrO_2 as a promising electrocatalyst, thorough understanding and exact clarification of the cause, mechanism and effect of phase separation are essential. Here, we performed well-defined model experiment by using the epitaxial $Ce_{0.75}Zr_{0.25}O_2$ (CZO) thin films of which crystal orientation and the initial stress level are systematically controlled. The origin and a sequence of phase separation in CZO thin film was analyzed by means of surface morphology characterization by scanning electron microscopy, crystallographic data by X-ray diffraction, and element distribution mapping by crystal transmission electron microscopy equipped with energy dispersive spectroscopy.

Fri 2:10 pm

Topotactic transformation of barium indate zirconate perovskite in H_2 atmosphere

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Metal oxyhydrides, including the hydride anion (H^-), are rare but have recently become appealing hydrogenation catalysts for ammonia synthesis[1-3] and CO_2 conversion[4, 5]. H^- is simply the counter form of H^+, but the electrochemical activity of the former could clearly be distinguished from that of the latter because the high redox potential of H_2/H^-, at −2.3 V versus a normal hydrogen electrode, may facilitate electron donation to adsorbed molecules.[2, 6] The oxyhydrides must be important H^- ion conductors because the large polarizability and extraordinary ion-size flexibility of H^- anion is advantageous for the long-range diffusion. On account of the transferability and redox activity of the H^- anion, therefore, materials with significant H^- ion conductivity are promising options not only for catalytic substances but also for ceramic electrochemical devices,[7, 8] such as co-electrolysis cells[9-11] and membrane reactors,[12] Cubic perovskite type barium zirconate, $BaZr_{1-x}In_xO_{3-\delta}$ ($0<x<0.7$), have been intensively studied for their excellent proton conductivity and tolerance to high p_{H2O} atmosphere. Despite the fact that In(III) oxides are readily reduced at elevated temperature under reduced atmosphere, the thermochemical behavior of $BaZr_{1-x}In_xO_{3-\delta}$ under reduced conditions is still unclear. Herein, we demonstrated that $BaZr_{0.5}In_{0.5}O_{2.75}$ (BZI55) is converted to highly-oxygen-deficient perovskite phase with metallic conductivity by reduction in H2 gas at elevated temperature. BZI55 was synthesized by solid state reaction method. Pale white BZI55 was changed to black-colored phase by heating at 800 C for 24h in dry H_2. Hereafter, the black phase after the H_2 reduction was denoted as H-BZI55. The XRD measurements confirmed that H-BZI55 still retained cubic perovskite structure and the change of lattice constants by the H_2 reduction was only -0.07%. TG measurements revealed that BZI55 loose the weight by about 2% by H_2 reduction at 800 °C, and thus the stoichiometry of H-BZI55 was estimated to $BaZr_{0.5}In_{0.5}O_{2.27}$ by assuming that mass loss was caused only by the loss of lattice oxygen. The neutron powder diffraction structure refinement precisely determined the nominal composition of H-BZI equaling $BaZr_{0.5}In(II)_{0.5}O_{2.25}H_{0.5}$, in which H atoms occupy O anion sites and fcc interstitial sites. Combined with XAFS measurements confirmed that $BaZr_{0.5}In(III)_{0.5}O_{2.75}$, as the parent phase, was topotactically hydrogenated via simple H_2 gas annealing at 800 °C under ambient pressure with the reduction of In atoms and insertion of vacancies and H^- ions into O sites bridging two In atoms (O_{In}^{In}). Membrane devices comprising dense $BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5}$ films on porous Ni-cermet supports were fabricated by conventional sintering and post-reduction, because low lattice contraction (-0.07%) following hydrogenation allowed for the bulk hydrogenation of $BaZr_{0.5}In_{0.5}O_{2.75}$ sinters without structural collapse. The resultant devices exhibited higher hydrogen permeability than protonic ceramic ones at 500 °C because H^--ion hopping through the percolation of O_{In}^{In}-type site vacancies gave rise to H^- ion conductivity of 10^{-3} S cm^{-1}. Given their superior H^- ion conductivity and ease of manufacturing, the synthesized materials have great potential for applications in mixed conducting electrodes and hydrogen permeable membrane supports of ceramic electrochemical cells.

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Fri 2:35 pm

Why we should not trust (but still might use) the Mott–Schottky model for grain-boundary impedance

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Identifying the excess resistivity of grain boundaries with the presence of space-charge layers has become widely accepted in the context of high-purity oxide-ion conducting polycrystals: the considered space-charge models usually involve a positively charged grain-boundary core, surrounded and compensated for by negatively charged space-charge layers. A mathematical description with closed-form expressions can be provided if it is assumed that the acceptor cations take a uniform concentration profile throughout the sample (*Mott–Schottky case*). This approximation may be justified with the typical range of measurement temperatures, in which the cation mobility is negligible, such that non-equilibrium configurations may be retained.

Nevertheless, the analysis of impedance data with the Mott–Schottky model is problematic in two aspects: first, this dilute-solution model is often applied to heavily substituted electrolyte materials, the electrical conductivities of which are known to be largely determined by point-defect interactions. Second, ion-conducting ceramics prepared by conventional sintering have necessarily been subject to temperatures that were high enough to render the cations mobile, so the acceptor-cation concentration profile should approach the electrochemical equilibrium before the cation transport is frozen-in upon cooling.

In this work, we have calculated impedance spectra from continuum-level simulations of a bicrystal geometry, with space-charge layers at the grain boundary. Different space-charge models for dilute and concentrated solid solutions are considered. Specifically, space-charge layers are simulated in the scope of the restricted-equilibrium model [1, 2] and the Poisson–Cahn model [3, 4] to account for the thermal history and for point-defect interactions, respectively. Based on the simulation results, the common practice of analysing grain-boundary impedance with the standard closed-form expressions is assessed. Special attention is paid to the electrical grain-boundary width as a measure of the extent of a space-charge layer in the dilute and the concentrated cases.

Our results indicate that, given a restricted-equilibrium scenario, the Mott–Schottky expressions may substantially underestimate the true space-charge potential, even though the results display a general qualitative agreement with the Mott–Schottky case. Furthermore, it is demonstrated that, in concentrated solutions, grain-boundary impedance must be considered as being virtually decoupled from the space-charge potential, owing to variations of ion mobility within the space-charge layer. Different consistency checks [5, 6] are discussed that require only the impedance-spectroscopic experimental setup and that can reveal cases not adequately described by the Mott–Schottky model.

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Fri 3:00 pm

Beyond stoichiometry in photoemission spectroscopy: *c–f* hybridization in cerium compounds

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Photoemission spectroscopy offers insights that go beyond the routine inquiries into composition and stoichiometry. While accessing many of these asks for intricate geometries and experimental considerations, even the simplest spectrum hints at electronic configurations that break the assumptions the oversimplifying picture of the nominal oxidation state brings in [1]. In this contribution, I will showcase how *c–f* hybridization manifests itself in the core level and valence band spectra of cerium compounds [2,3]. In doing so, I will expose the difficulties faced by the community in establishing univocal guidelines for stoichiometry determination from the Ce *3d* core level spectra and the 4d→4f resonant enhancement ratio, concepts which extend beyond the special case of the cerium compounds.
While the added complexity emerging from the step outside of the picture of the nominal oxidation state makes analysis challenging, it also offers new opportunities. Here, the ability to gauge the *c–f* hybridization represents both a window into elementary phenomena, such as closed shell screening, and a new aspect of rational design in chemical conversion, providing a guide for bond-length modification in valence band engineering towards charge transfer-limited reactions.

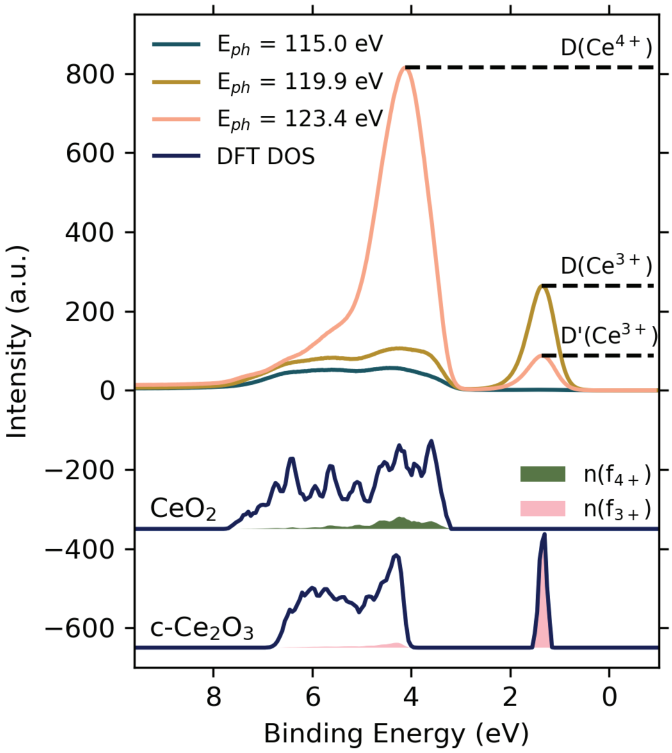

Figure 1: *c–f* hybridization in the valence band of cerium compounds revealed by resonant photoemission spectroscopy and density functional theory.

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Fri 3:40 pm

Theoretical and Computational Description of the Polaron Migration in Ceria

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Polarons have been the subject of increasing interest due to their presence in a great variety of materials. [1] Within ceramics, polarons up to the size of unit cells (called small polarons) may form and become the predominant charge carriers of electronic conduction. Prominent examples are reduced ceria, yttrium-doped barium zirconate or BCFN. [2,3,4] A small polaron is created by an excess electron or hole that is strongly localized by a self-created potential well due to the displacement of surrounding atoms. In addition, it can migrate via a thermically activated jump mechanism, for which a theoretical description is given by Markus-Emin-Holstein-Austin-Mott (MEHAM) theory. [5] Here the energy of a system containing a polaron is expressed by harmonic oscillators describing the local structure distortion, and a charge stabilization contribution proportional to the distortion. Fitting MEHAM theory to the polaron migration energy profiles obtained from density functional theory (DFT) simulations may yield additional information such as the characteristic frequency associated with and the adiabaticity of the migration.

To our knowledge, no study has tried to fit MEHAM theory to the whole migration energy profile. Instead, only the part around the ground states is considered. [6] However, with this approach it is up to the author to select the data points which are included or excluded from the fit. In addition, linearly interpolated structures of the initial and final state of transition are often used to describe the migration path. This enables a simple definition of the reaction coordinate based on the proportion used of both states. However, nudged elastic band (NEB) calculations have shown that the migration path from this linearized approach may be unfavorable. [3] If instead the path produced by NEB is used, the previous definition of the reaction coordinate is no longer valid, as the images produced by NEB may not be simple interpolations.

Here we present a way to solve both issues. We show how the migration coordinate can be defined for the polaron transition when structures produced from NEB are used and how MEHAM theory can be quantitively fitted to the whole migration path. As an example, we use the polaron migration in ceria.

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Fri 4:00 pm

Renewable Energy from a Big Picture Perspective to Nanoscale Insights via TOF-SIMS

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The world is rapidly changing the way that gets energy due to rapid price declines in renewable energy sources and storage within the last ten years making wind and solar the cheapest energy source for new power plant installations in many parts of the world. We will briefly discuss solar energy trends as a whole, before diving into our recent contributions to the field using time-of-flight secondary-ion mass spectrometry (TOF-SIMS) at the National Renewable Energy Laboratory to improve the performance and reliability of solar cell and battery materials, and we will present some recent work that highlights the versatility of TOF-SIMS. This work includes: 1) Multi-scale, multi-technique investigations of photovoltaic module failure including TOF-SIMS to enable insights into the root-cause mechanisms of module degradation at the nanoscale that are observed at the length scale of meters [1]; 2) Investigations into the performance and stability of hybrid perovskite solar cell devices and our work to understand measurement artifacts in this materials class when profiling [2]; 3) Using TOF-SIMS to investigate the fundamentals of solid electrolyte interface in 100% silicone lithium battery anodes to enable next generation lithium ion batteries [3].

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Fri 4:20 pm

Defects and transport – still plenty to be done

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The field of Solid State Ionics is concerned with the understanding and tailoring of defects, diffusion and reactions in solids. It has nowadays wide technological applications in energy conversion and storage, data storage, sensors etc. Thus, Solid State Ionics and its technological implications are inevitable for a future sustainable development of our world.

In this contribution I will, however, focus on some fundamental questions and still unresolved problems in the science of Solid State Ionics. I will discuss two major topics: The first is concerned with the role of defect interactions. This topic is of particular importance in materials with high defect concentrations where defect interactions are unavoidable. Interestingly, nearly all materials with technological importance belong to this class of materials. In contrast, the theoretical treatment of interactions is mostly limited to diluted systems. I will show a possible route to solve this problem by combining ab initio calculations with Monte Carlo simulations. In this way, not only the problem of defect interactions can be solved, but also the link between the microscopic energetics and dynamics and the macroscopic thermodynamics and kinetics can be made. As examples, I will discuss our results for oxygen ion conductors and proton conductors.

The second topic is concerned with the number of components in a material. Nowadays, most materials in Solid State Ionics are multicomponent materials containing, e.g., three or more chemical elements. Thermodynamically, this is a challenge as the phase diagrams become rather complicated and are mostly unknown. On the other hand, there is another subtle problem which is concerned with the number of mobile species. Historically, most often only two mobile species were considered, e.g., two mobile cations during interdiffusion or one mobile anion and electrons in mixed conductors. The situation becomes, however, more complicated if there are three mobile species, e.g., two ionic defects and one electronic defect. I will discuss corresponding examples and the thermodynamic and kinetic implications.

Fri 4:45 pm

Enhanced Sintering and Ionic Conductivity in Zr-Deficient NaSICON Solid Electrolytes

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Sodium All-Solid State Batteries (ASSBs) have the potential to achieve high capacities, with increased safety and long term durability, while also maintaining low material cost due to abundant sodium resources. ASSBs rely on solid-state electrolytes with high ionic conductivity, which can be achieved in polycrystalline materials with Sodium (**Na**) **S**uper-**I**onic **CON**ductors (NaSICON) with kosnarite structure [1,2].

Several parameters need to be considered for NaSICON materials with high ionic conductivity, namely: a. relative density (fully sintered samples with optimized sintering conditions), b. sodium concentration (3 – 3.5 mol Na per formula unit), and c. crystallographic structure (monoclinic polymorph).

In our group, ionic conductivities in the range of 1 – 5 mS/cm at room temperature have been obtained for NaSICON materials [3,4], which is among the highest values reported in literature. To gain a deeper understanding of phase formation and associated properties, the effects of glassy phases are investigated in two series of NaSICONs with Zr deficiency and hypothetical O^{2-} vacancies.

The series with the formulas $Na_{3.4}Zr_{2-3x/4}Si_{2.4-x/4}P_{0.6+x/4}O_{12-11x/8}$ and $Na_{3.4}Zr_{2-3x/4}Si_{2.4+x/4}P_{0.6+1.5x/4}O_{12-x/16}$ (both with $0 < x < 0.8$) were prepared and used for sintering experiments. The series have constant Si+P content and additional Si+P atoms, respectively, and O^{2-} vacancies to compensate for Zr deficiency. To better understand the phase formation of this NaSICON system, the samples are characterized using X-ray diffraction (XRD) with by Rietveld refinement and scanning electron microscopy (SEM). XRD can identify predominantly monoclinic or rhombohedral NaSICON phase. The ionic conductivity improves with the formation of the monoclinic lattice. NaSICON grains and glassy components were identified in the microstructure. The latter lead to a significant decrease in sintering temperatures. The composition of the NaSICON grains suggested by the stoichiometry of the material differs from the XRD and SEM results. The crystalline phase is close to compositions without Zr deficiency and O^{2-} vacancies, and the additional amounts of Na, Si and P form glass phases. The stoichiometric composition of the grains and the glassy components was specified by energy dispersive X-ray spectroscopy (EDX) and, together with the refined lattice parameters, provides information about the Na concentration in the NaSICON phase. The ionic conductivities were measured as a function of and composition and can also give insight into the phase formation of the NaSICON structure [5] and the influence of the glassy phases.

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P01

Enhanced ionic conductivity in $Na_{4.92}\square_{0.08}Y_{0.92}Zr_{0.08}Si_4O_{12}$

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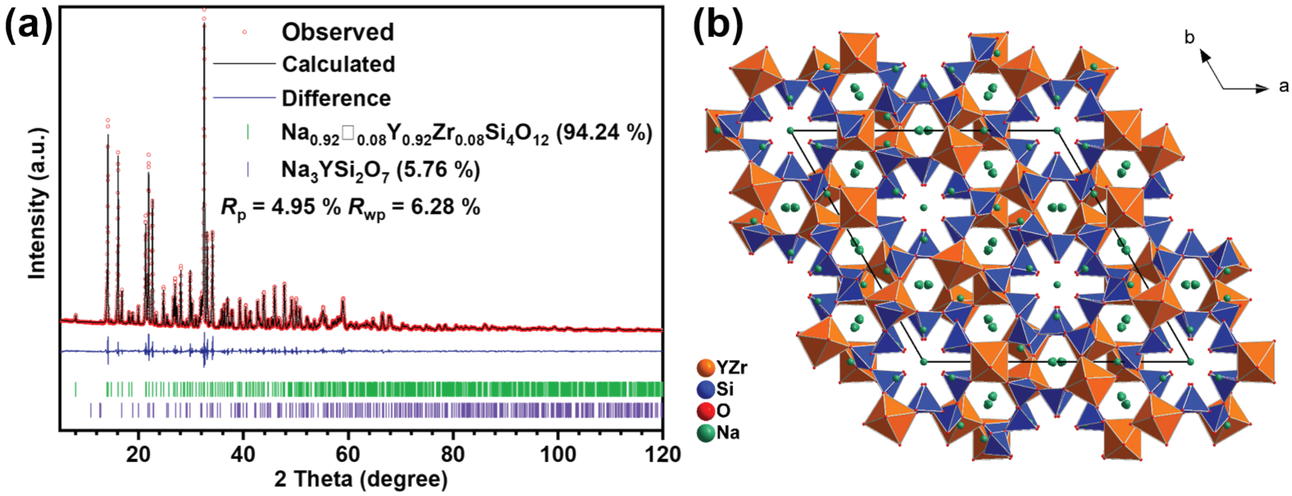
The development of cost-effective and reliable solid-state sodium metal batteries (SS-NMBs) with good performance is of great significance for stationary energy storage. Herein, the solid-state electrolyte with high conductivity and stability is a vital constituent to facilitate the application. In this work, the strategy of heterovalent cation substitution has been used to enhance the ionic conductivity while preserving the crystal structure (see figure below). Partial substitution of Y^{3+} in $Na_5YSi_4O_{12}$ (NYS) with Zr^{4+} introduces Na^+ ion vacancies and shortens the distances between neighboring Na^+ ions, giving rise to the high bulk and total conductivity up to 6.5 and 3.3 mS cm^{-1} at room temperature with the composition of $Na_{4.92}Y_{0.92}Zr_{0.08}Si_4O_{12}$ (NYZS). NYZS shows excellent electrochemical stability (up to 10 V vs. Na^+/Na) and good critical current density of 2.4 mA cm^{-2} against Na metal. Due to the inherently good chemical stability of silicates, composition of NYZS remained unchanged and still offered a high conductivity of 2.1 mS cm^{-1} after two months of exposure in air. The transport pathway of Na^+ ions in NYZS is further elucidated by combining solid-state nuclear-magnetic-resonance techniques and theoretical simulations. NYZS extends the list of applicable solid-state electrolytes [1,2] and paves the way for facile synthesis of stable, low-cost Na^+ ion silicate electrolyte materials.



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P02

Numerical Simulation of the Kinetic Unmixing and Decomposition in Barium Titanate

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Perovskite oxides are important materials for solid oxide fuel cells, light emitting diodes or lithium bat-teries.[1] Accordingly their behaviour under the influence of an electric field is of great importance. Since normally the mobilities of the two cations in the perovskite oxide are different, they move in an electric field with different velocities and thus unmix. The faster cations accumulate at the cathode while the slower ones remain behind at the anode. As long as the material stays in its stability range, this behaviour is called *kinetic unmixing*, else the material decomposed and the behaviour it is then referred to as *kinetic decomposition*.[2]

While there are already experimental studies of the kinetic unmixing in barium titanate and perovskites in general,[3-4] this work focuses on a theoretical approach. We developed a model that does not only take the three main ions (Ba^{2+}, Ti^{4+}, O^{2-}) and their vacancies into account, but also considers acceptor doping on the B-site and electrons and electron holes as minority defects. Since the model uses several variables, we focused on the material properties of barium titanate, but of cause the model is easily adaptable to other perovskites.

By solving the partial differential equations from this model numerically, we are able to simulate the kinetic unmixing. With this model we investigated not only the profiles along the gradient of the electric field, but also various relations between input parameters, such as applied voltage or thickness of the sample, and output values such as the degree of unmixing or the time it takes to reach a steady state. When the stability range is taken into account, the decomposition voltage at which the material decom-poses or the time it takes to reach the decomposition can be studied. Moving away from the material properties of barium titanate, we also investigated theoretical materials where the ratios of the mobilities show extreme cases like the A and B cations being equally fast or one much faster than the other.

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P03

Numerical simulations of the Hebb-Wagner polarization method of perovskite-type oxides

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Ternary oxides ABO_3 are known for their mixed ionic and electronic conductivity, which is well investigated depending on temperature, oxygen partial pressure, and composition. A famous technique that enables the determination of the partial conductivities is the Hebb-Wagner polarization method introduced by Hebb and Wagner in the 1950s [1,2]. Depending on the type of electrodes used for the polarization, it is possible to measure the ionic or electronic conductivity of the material depending on the oxygen partial pressure. The kinetics of the polarization process and the corresponding relaxation time were not studied in detail in literature, although both are of utmost importance for a better understanding of electrochemical polarization processes. A prominent example is resistive switching of oxides, where the prevailing conductivity is modulated by slow ionic motion caused by an applied AC voltage. The observed hysteresis in the *I-V* curve depends critically on the ratio of the relaxation time and the switching rate [3,4]. In this contribution, the kinetics of the relaxation process during the Hebb-Wagner polarization of a nominally undoped perovskite-type oxide ABO_3, is simulated by means of numerical methods and using $SrTiO_3$ as a model system. The advantages of the theoretical approach are the prediction of the expected relaxation time for experiments and the exact reproduction of the fluxes of all involved mobile species simultaneously. Thus, it is possible to investigate the dependence of the relaxation time on different experimental variables, such as the applied voltage, acceptor concentration, temperature, and external oxygen partial pressure. In addition, the influence of parameters such as sample length *L*, equilibrium constants for defect equilibria and diffusion coefficients of the mobile species can be studied to identify the relaxation times of different parameter sets for practical experimental application of the Hebb-Wagner polarization method.

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P04

Anti-Frenkel defect formation and Oxygen diffusion in brownmillerite $Sr_2Fe_2O_5$

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The brownmillerite oxides have the general composition $A_2B_2O_5$. At sufficiently high temperatures they undergo a phase transition to an oxygen-deficient perovskite $ABO_{3-\delta}$ phase. Oxygen diffusion in the high-temperature perovskite phases have attracted attention, due to their high degree of oxygen deficiency and the general high mobility of oxygen vacancies in the perovskite structure. Very recently, oxygen diffusion in the brownmillerite phase has attracted attention because of the possibility of using the phase transition in a resistive switching memory device.

In this study, we investigated oxygen diffusion in the system $Sr_2Fe_2O_{5\pm x}$ using molecular dynamics (MD) simulations with empirical pair potentials (EPP). Specifically, we obtained oxygen tracer diffusion coefficients as a function of temperature for both brownmillerite and perovskite phases, and subsequently, the activation enthalpies of oxygen tracer diffusion. We also examined the simulations to extract information on the two possible mechanisms of oxygen diffusion in the brownmillerite phase (by interstitials or by vacancies). Furthermore, with the aid of MD simulations we quantified the formation of oxygen vacancies and oxygen interstitials (anti-Frenkel disorder) in stoichiometric $Sr_2Fe_2O_5$ and determined the enthalpy and entropy of defect formation. Moreover, simulations on $Sr_2Fe_2O_5$ with oxygen deficiency or oxygen excess revealed preferential oxygen diffusion by means of oxygen vacancies instead of diffusion by means of oxygen interstitials in the stoichiometric compound. But in both cases, the diffusion showed a highly anisotropic behaviour and took place almost exclusively two-dimensional in the respective planes ($Sr_2Fe_2O_{5-x}$: FeO_6-plane; $Sr_2Fe_2O_{5+x}$: FeO_4-plane) of the layered structure of $Sr_2Fe_2O_5$.

P05

The Link between Solid-State Ionics and Microstructure Effects in Solid-State Batteries

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Composite electrodes in solid-state batteries can be regarded as interwoven electronic and ionic conduction networks. In contrast to liquid electrolytes, the solid electrolyte (except for polymer-based solid electrolytes) does not infiltrate (micro-)porosities and possesses its proper morphology. This implies that even ductile solid electrolytes go along with residual voids in the composite. Thus, the electrode microstructure can be decisive for the performance, even though it may not be straightforward to be accessed experimentally. Especially the role of voids in the composite is barely understood.

We approach the electrode microstructure from the perspective of modeling and simulation and study the conduction networks [1], the efficacy of ion conduction [2] and the charge behavior [3] in synthetic microstructures that are reconstructed based on scanning electron microscopy images. These feature cathode active material, solid electrolyte, void space and partly also binder.

To develop a broad understanding of microstructural influences we study a variety of electrode design parameters such as particle sizes and their distributions, the electrode composition or the binder content and identify trade-offs, both between energy and power electrode layouts and electronic and ionic conduction. An example thereof is the active material particle size: Small active material particles favor highly interconnected electronic conduction clusters that may redundantize conductive carbons in the composite [1]. They also offer short ion diffusion paths inside the particles [3]. On the other side, high surface area goes along with enhanced degradation and may impede ionic conduction leading to more tortuous ion pathways [2, 4].

In order to assess the impact that the microstructure has on the cell performance we estimate achievable current densities through ASSB cathodes and find that the microstructure issues that go along with solid electrolytes are a strong argument for highly conductive solid electrolyte materials [2].

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P06

A molecular-dynamics study of oxygen diffusion in polycrystalline (La,Sr)FeO_3

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(La,Sr)FeO_3 is a well-known mixed ionic and electronic conducting perovskite oxide [1-5], with application in Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs).

In this study we employed molecular-dynamics (MD) simulations based on empirical force fields [6,7] to investigate oxygen transport in the solid solution $La_{1-x}Sr_xFeO_{3-x/2}$ (x = 0.1, 0.25 and 0.4). Simulations were performed at temperatures $1000 \leq T / K \leq 3000$. Oxygen tracer diffusion coefficients obtained for both orthorhombic and cubic structures are compared with experimental data [1-5], and are found to give a satisfactory description of the oxygen transport behaviour as a function of T and x. Subsequently, we examined oxygen tracer diffusion in polycrystalline cells of $La_{1-x}Sr_xFeO_{3-x/2}$ with differing numbers of grain boundaries. In all cases, we find that oxygen tracer diffusion in the polycrystalline systems is lower than in the single-crystal systems. Our results thus indicate that in perovskite-oxide ceramics with homogeneous cation distributions there is no faster diffusion of oxygen along grain boundaries. A detailed analysis of diffusion data for polycrystalline simulation cells is demonstrated with a new in-house analysis tool [8].

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P07

Rechargeable Oxide Batteries: Concepts and Materials

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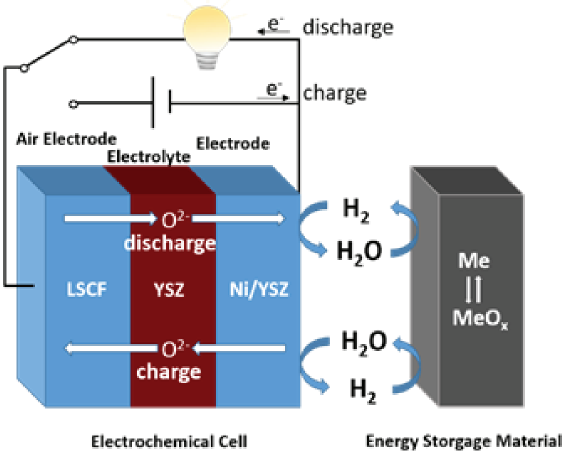
The increasing demand for sustainable and renewable carbon free energies sources requires the development of energy storage systems to balance supply and demand throughout the day. The rechargeable oxide battery (ROB) provides the means to store electrical energy as chemical energy and functions along the principles of a solid state metal-air battery.[1] The ROB can be viewed as the combination of an electrochemical cell with an external storage system which is coupled through a gaseous H_2/H_2O redox shuttle (Fig. 1). The operation temperature hereby depends electrolyte material in the electrochemical cell (650-800 °C depending on the electrolyte material) to ensure sufficient oxygen-ion transport through the solid electrolyte.

One major advantage of the ROBs is that it allows for a decoupling of power and capacity of the ROB. Furthermore, a wide range of potential storage materials can be considered, however, the most common approach found in literature is focused on iron-based materials. A major issue with these iron based storage materials has been a capacity fading throughout the cycling lifetime due to densification of iron at the sample surfaces. The addition of scaffolding materials has shown to help limit these densification effects, but not fully prevent them.[2]

Work done in our group has mainly focused on two different systems, an iron-manganese compound ($(Fe_{1-x}Mn_x)_yO_z$ with $0.2 < x < 0.8$) utilizing a ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) scaffold, and Fe_2NiO_4 combined with an 8YSZ scaffold. The advantage of adding manganese to the iron is a lower oxygen pressure required for oxidation leading to higher open cell voltages (OCVs).[3] Addition of nickel on the other hand leads to slightly lower OCVs, however, also inhibits the iron mobility during redox cycling. This prevents the agglomeration of iron at the storage material surfaces leading to sustainable long term cycling. These properties were investigated by means of DC-conductivity and thermogravimetric measurements followed by an analysis by XRD, SEM and EDX.[4]



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P08

Rechargeable Oxide Batteries: Storage Capacities and Kinetics

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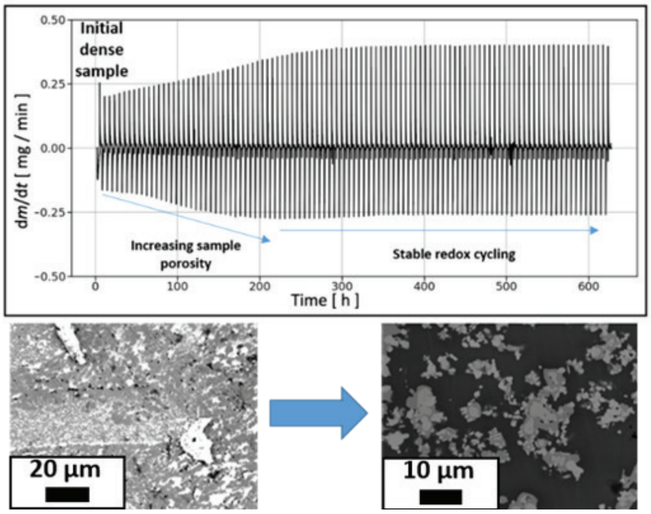
For rechargeable oxide batteries (ROB) to be viable, stable long term cycling needs to be achieved. Additionally, a high energy density is desired for the storage material.[1] The conversion between the chemical energy, in which the energy is stored, to electrical energy available to the consumer needs to be fast enough to keep up with demand. For this purpose, the kinetics of redox reaction of the storage material during charge and discharge is of interest. To characterize the kinetics, the rate of mass change in thermogravimetric measurements were analyzed and fitted for reduction and oxidations by means of Johnson-Mehl-Avrami-Kolmogorow (JMAK) equations. Reaction parameters were chosen to simulate the working conditions expected in a ROB.

The iron in the Fe_2NiO_4/YSZ composites undergo two reaction steps (subsequent iron oxidation from Fe to FeO and FeO to Fe_3O_4) during the discharge process under ROB operating conditions, requires two JMAK equations for the characterization. The resulting parameters received from these JMAK equations are consistent with microstructural developments seen in SEM images, enabling an accurate description of the reaction process throughout the redox cycling process.[2]

The reaction kinetics for the $(Fe_{1-x}Mn_x)_yO_z/Ce_{0.8}Gd_{0.2}O_{2-\delta}$-composites on the other hand can be described by combining the JMAK equation with the Prout-Tompkins or Jander model. As was the case before, further complementary microstructural investigations by means of SEM and XRD were completed. This provides a combined picture of the redox processes taking place during the charge and discharge processes during redox cycling.



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P09

Charge transport in mesoporous oxides with high surface area

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Ion-conducting ceramic oxides are widely used for various applications in the field of electrochemical energy storage. While ceria and zirconia-based materials are used as electrolyte or electrode material for oxygen storage devices or solid oxide fuel cells, $LiCoO_2$-based ceramics are still the state-of-the art electrode material for lithium-ion batteries. In both cases, the electrode material exhibits a complex, porous architecture with a high surface area to ensure on the one hand the transport of the electronic and ionic charge carriers within the porous framework and on the other hand the exchange of oxygen with the surrounding atmosphere or the exchange of lithium ions with the electrolyte, respectively. However, due to the high grain boundary density and surface area, the material may exhibit different electronic an ionic transport properties compared to the bulk. In particular, surface effects can dominate the overall behavior and, thus, significantly alter the electrochemical properties of nanostructured porous oxides. As the working principle of all electrochemical devices is based on the transport of charged carriers, a fundamental understanding of the defect-chemistry at surfaces is needed to further optimize the device performance.

In order to elucidate the impact of surface effects on charge transport in ceramic oxides suitable model systems are needed. Usually, surface effects are often investigated by studying thin films, where the surface contribution to the overall properties increases with decreasing thickness. However, if the thin films thickness decreases below a critical value, the substrate may offer a second current path if its resistance is too low resulting in defective conductivity measurements. To prevent such problems, the transport properties of yttria-stabilized zirconia (YSZ) thin films (of thickness > 100 nm) with a mesoporous structure and highly crystalline walls are investigated in this work. The mesoporous thin films exhibiting a high surface-to-volume ratio and are either prepared using a sol-gel approach or were deposited by pulsed laser deposition resulting in a highly regular or random pore arrangement, respectively. Electrochemical impedance measurements show deviations in the electrical conductivity of the mesoporous YSZ thin films compared to their bulk counterparts revealing the impact of the high surface area on the transport properties. In addition, we will present recent results on the electrical properties of mixed conducting composites, which were prepared from mesoporous oxides by conformal surface coating using atomic layer deposition.

P10

Optimization of NASICON-type solid electrolyte composition using both experiments and Bayesian optimization

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Replacing the liquid electrolyte in conventional Li-ion batteries with solid electrolytes has the advantages of reducing flammability and increasing energy density. Recently, the NASICON-type solid electrolyte, $LiZr_2(PO_4)_3$ (LZP), has attracted attention as an oxide-based solid electrolyte with high Li ionic conductivity.[1] Reportedly, Li ionic conductivity can be improved by doping stoichiometric LZP with other elements. [2] In this study, we focused on Ca-and Si-doped Li-rich NASICON-type LZP solid electrolytes. We evaluated the Li-ionic conductivity for 49 compositions of $Li_{1+x+2y}Ca_yZr_{2-y}Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 0.3$, $0 \leq y \leq 0.3$) and demonstrated a Bayesian optimization (BO) approach to efficiently search for an optimal composition with high Li ionic conductivity.

Fig. 1 (a) displays a heatmap of the measured Li ionic conductivities at 30 °C, where $Li_{1.2}Ca_{0.05}Zr_{1.95}Si_{0.1}P_{2.9}O_{12}$ shows the highest ionic conductivity (2.56×10^{-5} S cm^{-1}). This suggests that the double doping strategy is effective for improving the ionic conductivity in comparison with single doping of Ca or Si. Fig. 1(b) compares the random vs. the Bates search performance to determine the highest ionic conductivity among 47 compounds. Bayes optimization improved the search performance, where 23 experiments lead to >99% prediction. This was approximately 60% of the number of experiments required compared with the random search method.

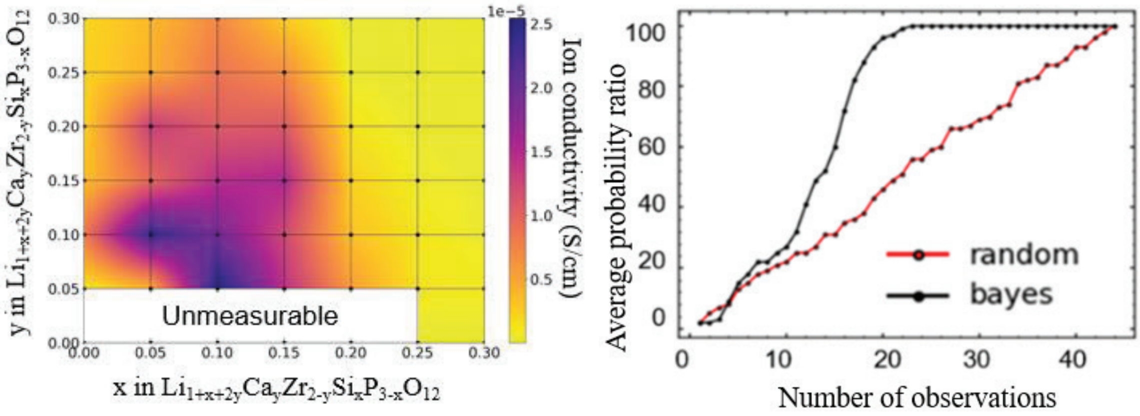

Fig. 1(a) Heatmap of measured ionic conductivities at 30 °C. (b) Comparison of Bayesian optimization and random search performance using the conductivity data of 47 Li-ion compounds.

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P11

Evolution of structural, magnetic and electrical properties of oxygen-deficient $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ thin films under deoxygenation

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Oxygen defects play a crucial role in the understanding the physical properties of complex oxides. [1] [2] In the limit of large oxygen vacancy concentration, a layered vacancy-ordered brownmillerite (BM) structure can be realized from an initial perovskite (PV) framework by removing significant amount of oxygen from the lattice. The special feature of oxygen vacancy distributions and dynamics are intrinsically coupled with magnetic, electronic and transport properties. However, the specific influence of the vacancy ordering on the structural, magnetic and electronic properties is still under debate.

In the present study, we employ $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSCO) thin films fabricated by pulsed laser deposition (PLD) as model systems for a systematic study of the phase transition from perovskite to brownmillerite. In situ x-ray diffraction under reducing conditions reveals the structural evolution of the LSCO thin film, which can be attributed to the release of oxygen during the annealing at elevated temperatures, and ultimately the structural transition into a coherently ordered brownmillerite phase. By comparing the magnetic and electronic properties of the sample in different oxygen deficient states, however, we demonstrate that the structural transition is not taking place at the same time scale as a magnetic and electronic transition.

Using in situ polarized neutron reflectometry (PNR), we explore the nuclear scattering density (nSLD) and quantify the change in oxygen stoichiometry of the LSCO film during annealing. The PNR fit shows a significant decrease of nSLD for the annealed film indicating a reduction in oxygen concentration. The oxygen stoichiometry is found to vary from $La_{0.6}Sr_{0.4}CoO_3$ before annealing to about $La_{0.6}Sr_{0.4}CoO_{2.5}$ for annealed films. The magnetic depth profile extracted from PNR describes in greater detail the influence of oxygen on magnetic transitions in the film during annealing. It demonstrates that disordered oxygen vacancies forming in the initial phase reduction phase govern the magnetic properties of LSCO film and immediately lift the ferromagnetic ordering of the as-grown perovskite thin films. Our work provides crucial information regarding the dynamics and coincidence of structural, magnetic and electronic phase transitions in complex oxide thin films.

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P12

Separating the effects of band bending and covalency in hybrid perovskite oxide electrocatalyst bilayers for water electrolysis

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The Co-O covalency in perovskite oxide cobaltites like $La_{1-x}Sr_xCoO_3$ is believed to impact the electrocatalytic activity during electrochemical water splitting at the anode where the oxygen evolution reaction (OER) takes place. Additionally, space charge layers through band bending at the interface to the electrolyte may affect the electron transfer into the electrode, complicating the analysis and identification of true OER activity descriptors.

Here we separate the influence of covalency and band bending in hybrid epitaxial bilayer structures of highly OER active $La_{0.6}Sr_{0.4}CoO_3$ and undoped and less active $LaCoO_3$. Ultra-thin $LaCoO_3$ capping layers of 2-8 unit cells on $La_{0.6}Sr_{0.4}CoO_3$ show intermediate OER activity between $La_{0.6}Sr_{0.4}CoO_3$ and $LaCoO_3$ that is evidently caused by the increased surface Co-O covalency compared to single $LaCoO_3$ as detected by x-ray photoelectron spectroscopy. A Mott Schottky analysis revealed low flat band potentials for the different $LaCoO_3$ thicknesses, indicating that no limiting extended space charge layer exists under OER conditions as all catalyst bilayer films exhibited hole accumulation at the surface. The combined x-ray photoelectron spectroscopy and Mott Schottky analysis thus enables to differentiate between the influence of the covalency and intrinsic space charge layers, which are indistinguishable in a single physical or electrochemical characterization. Our results emphasize the prominent role of transition metal oxygen covalency in perovskite electrocatalysts and introduces a bilayer approach to fine-tune the surface electronic structure [1].

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P13

Hybrid oxide superlattices as electrocatalysts for the oxygen evolution reaction in alkaline electrolyte

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Due to their tunability concerning the individual A- and B-site cations perovskites are an interesting material for the oxygen evolution reaction. Stable materials are mostly less active and active materials are not stable. This inverse relationship between activity and stability was tried to overcome in this study by unit cell precise superlattices.

The active but considerably unstable perovskite $La_{0.6}Sr_{0.4}CoO_3$ was used as a benchmark thin film catalyst and tried to be optimized using an artificially designed superlattice structure. Therefore, $SrTiO_3$ as a stable but inactive perovskite was introduced and combined with $La_{0.6}Sr_{0.4}CoO_3$ via superlattice structure. Two types of superlattices were synthesized, which can be distinguished by their top layer: (1) $SrTiO_3$-terminated, and (2) $La_{0.6}Sr_{0.4}CoO_3$ -terminated surface.

The measured lifetime of the $SrTiO_3$-terminated superlattices exceeded the reference lifetime of bare $La_{0.6}Sr_{0.4}CoO_3$ by multiple hours. It was found that 17 internal interfaces gave the highest recorded lifetime of 27 h under static load of 5 mA/cm^2, which is an improvement by 17 h (170% increase) compared to the single layer $La_{0.6}Sr_{0.4}CoO_3$ catalyst (10 h). The higher stability led to a decreased activity, which is observed by the increased overpotential of 100 mV.

The post-mortem superlattices showed degradation on the surface but maintained the superlattice like features in the bulk, visible through x-ray diffraction analysis. These results suggest that the introduction of superlattice structure in catalysts can lead to an improved structural and electrochemical stability and is an exciting approach to make water electrolysis more efficient and therefore economically feasible in the future.

P14

Recipes for superior ionic conductivities in thin-film ceria-based electrolytes

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Improving the overall performance of a solid oxide fuel cell (SOFC) involves, in many cases, increases in the rates of oxide-ion transport displayed by the electrolyte and electrode materials. This aim becomes particularly critical in the case of the Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC): improved performance at ever lower operating temperatures is required, but lower temperatures mean lower rates of (thermally activated) oxide-ion transport. This can be offset partly by reducing its thickness, since its resistance is the important factor. New possibilities to offset the lower operating temperatures would, therefore, be extremely welcome.

In this study [1], we utilised a powerful combination of two well-established simulation methods — molecular dynamics (MD) and Metropolis Monte Carlo (MMC) — and applied them to one of the best electrolyte materials for IT-SOFC — $Ce_{1-y}Gd_yO_{2-y/2}$. The MMC simulations were used to generate equilibrium distributions of the substituted Gd cations that were compared with random distributions of Gd. The former are similar to those found in sintered ceramics (a point often neglected in many computational studies). MD simulations allowed us to extract the ion mobilities as a function of electric field and temperature directly, a task that is non-trivial for highly concentrated solid solutions.

Two important findings emerged from our results: In all cases studied, the random distribution displayed a higher conductivity than the equilibrium distribution, with the difference being up to an order of magnitude. Second, the reduction of the film thickness to a few nanometres and the use of an operating voltage of only 1 V can lead to an additional increase in the conductivity by an order of magnitude due to nonlinear field effects. Additionally, we established an analytical model that describes all the conductivity data. On this basis, we can predict the conductivity at different concentrations, field strengths and temperatures.

Thus, with our study, we provide two new recipes for the development of superior ceria-based thin-film electrolytes for use in IT-SOFC. We showed that field-enhanced ion transport is possible in these electrolytes at physically realistic voltages and film thicknesses, and, in combination with maintaining a random Gd substituent distribution, can lead to tremendous increases in ionic conductivity.

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P15

Vertically aligned two-dimensional halide perovskites for reliably operable artificial synapses

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Halide perovskites, fascinating memristive materials owing to mixed ionic-electronic conductivity, have been attracting great attention as artificial synapses recently.[1,2] However, polycrystalline nature in thin film form and instability under ambient air hamper them to be implemented in demonstrating reliable neuromorphic devices.[3] Here, we successfully fabricated vertically aligned 2D halide perovskite films (V-HPs) for active layers of artificial synapses, showing moisture stability for several months. Unlike random-oriented HPs, which exhibit negligible current hysteresis, the V-HPs possess multilevel analog memristive characteristics, programmable potentiation and depression with distinguished multi-states, long-short-term plasticity, paired-pulse facilitation, and even spike-timing-dependent plasticity. Furthermore, high classification accuracy is obtained with implementation in deep neural networks. These remarkable improvements are attributed to the vertically well-aligned lead iodide octahedra acting as the ion transport channel, confirmed by first-principles calculations. This study paves the way for understanding HPs nanophysics and demonstrating their potential utility in neuromorphic computing systems.[4]

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P16

Reaction kinetics in the system Y_2O_3/Al_2O_3 – Control of the product phase formation in a system forming multiple product phases by applying an external electric field

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Ceramic material are used in many technologically important applications in the fields of electronics, sensors technology, energy conversion and storage. Solid state reactions as degradation process play an important role at elevated temperatures, especially in the case of short distances for diffusion or if an extended lifetime is required. This includes redox reactions and reactions only due to the transport of ions, resulting in the (heterogeneous) formation of product phases. Under working conditions, devices are not only subjected to elevated temperatures but also to electric fields, acting as a second driving force on the mobile charge carriers in addition to the chemical potential gradients. Beyond, the importance for degradation processes, the influence of external electric fields on solid state reactions gains also more importance for the preparation of ceramics. In the last years the field-assisted (flash) sintering (FAST) and the spark plasma sintering (SPS) technique were developed to a mature state and are used for ceramic synthesis.

Linear transport theory predicts a time independent growth rate (linear law) for the product layer(s), depending on magnitude and direction of the electric field induced ionic current. The rate constant depends on difference of the cationic transference numbers in the product phase instead on the Nernst-Planck coupled conductivities. This is different to an only thermally activated reaction, i.e. decreasing growth rate with increasing product layer thickness (parabolic law). In a preceding study, it is demonstrated for the model system MgO/In_2O_3 that forms $MgIn_2O_4$ as single product phase [1] When analysing the kinetics of a solid state reaction forming multiple product phases, it can be concluded, that the different dependencies on the cation conductivities should allow a control of the product phase formation to kinetically enhance or to suppress the growth of a distinct phase by the electric field.

In this experimental study the influence of an electric field on the kinetics of the solid state reaction between Al_2O_3 and Y_2O_3 is investigated. [2] Three product phases are formed, $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP) and $Y_4Al_2O_9$ (YAM). The reaction couples were prepared by means of pulsed laser deposition (PLD) by growing Y_2O_3 films on single crystalline alumina substrates with an (0001) orientation. The solid state reaction was performed at a temperature of 1400 °C (up to 72 h reaction time). An electric field of 350 V/mm was applied by using attached platinum electrodes. An ionic current is drawn due to the decomposition/formation of the starting oxides at the (porous) electrodes. The cross-sections of the reacted samples were characterised by means of SEM and XRD. The electric field driven ionic current through the reacting sample modifies partially the growth kinetics of the three product phases/layers. Depending on the direction of the ionic current, the kinetics of the YAP phase formation in particular was strongly influenced. [3] The effect on the YAG and YAM phase is less significant.

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P17

Dynamics study of nitrile-based electrolytes for lithium-ion batteries

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Nitrile-based plastic crystals N≡C-$(CH_2)_n$-C≡N such as succinonitrile (n = 2) or adiponitrile (n = 4), doped for example with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium hexafluorophosphate ($LiPF_6$) have proven to be suitable electrolytes for Li-ion batteries [1-4]. This is due to their high ionic conductivity ($\sigma \approx 10^{-3}$ S/cm at room temperature) [5], their large electrochemical stability window (up to 6 V vs. Li^+/Li) [3], as well as their low inflammability. Succinonitrile, in particular, makes a perfect candidate for pliable or stretchable cells due to its plastic phase [6], where its molecular constituents exhibit partial alignment arising from the orientational degree of freedom that are located on well-defined lattice sites. Furthermore, the temperature window in which this plastic phase exists, happens to be easily extendable by the addition of sufficient quantities of glutaronitrile (n = 3) [7]. In this work, mixtures of 60% SN (succinonitrile) and 40% GN (glutaronitrile) [8] doped with LiTFSI or $LiPF_6$ at different concentrations have been investigated with dielectric spectroscopy. Additionally, the dynamics of the methylene (CD_2) groups of SN and that of the Li^+ ions within the mixture, were both studied in a large temperature range, with the use of ^2H NMR and ^7Li NMR, respectively. Static-field-gradient proton NMR was used to probe the molecular diffusion within the matrix. Our findings are relevant for the understanding of the ionic transport mechanism involved in dinitriles.

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P18

Interaction between the surfaces of $LiCoO_2$ and NMC811 and electrolytes

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The interactions between organic electrolyte molecules and the surfaces of cathode materials are of great interest for the current state of the lithium-ion battery research and the commercial utilization in various fields. More in-depth insides about the interactions between electrolytes and the surfaces of cathode materials, as well as studies of decomposition products are very helpful to improve stability and lifetime of these materials. A theoretical approach can provide new insides by utilizing DFT methods to investigate these systems.

Here, two systems have been investigated, namely $LiCoO_2$ and NMC811. For $LiCoO_2$, three different commonly used electrolytes have been chosen (VC, EC and FEC). By utilizing two different starting configurations and various distances between electrolyte and the surface for all test systems, the effect of initial structure on the final relaxation result could be studied. Overall, smaller distances between molecule and surface resulted in the increase of stabilizing interaction effects, which could be expected due to interplays between the partial charges of the atoms in the molecules and the ions on the LiCoO2 surface. Furthermore, the starting configuration did not show a significant effect on the final result and the various initial distances also resulted in very similar final distances, except for the cases in which molecule and surface were far apart.

Additionally, the surface of the NMC811 material was investigated with regard to favorable spin states. In general, low spin states for the metal cations were favored in contrast to high spin configurations. This is also not too surprising, since the spectrochemical series predicts a rather high ligand field splitting. On top of that, the EC molecule was chosen as a test system to investigate the interactions between surface and the electrolyte. Three distinct initial configurations were chosen, while using an initial distance of 2 Å, because this separation was found to be favorable. These test cases resulted in rather planar final orientations towards the surface. However, it could not be decided with high certainty, which configuration was the most stable one. Due to self-interaction effects, such as hydrogen bonds in one test case, the data are insufficient to show which configuration can be regarded as the most probable. The highly planar configuration resulted in hydrogen bonds in contrast to the other test cases due to the geometrical orientation. Therefore, the results are qualitative in nature.

P19

Arresting the cubic metastable phase in HfO_2 nanoparticles as a model compound for 3-dimensionally confined resistive switching

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The development of new nanomaterials is driven by everchanging demands in the IT sector. Just in the year 2007, HfO_2 was introduced as gate material in complementary metal oxide semiconductors (CMOS) and still is one of the state-of-the-art materials as of today. More recently, HfO_2 was also introduced as a promising material for novel non-volatile memory devices based on resistive switching, so called Resistive Random Access Memories (ReRAMs). [1]

We report a facile one-pot hydrothermal microwave synthesis that allows us to tune the crystal phase of HfO_2 sub-10 nm nanoparticles without the necessity to introduce dopant elements. In doing so, we can adjust synthesis parameters that either yields the monoclinic (space group $P2_1/c$, 14), cubic (space group $Fm\bar{3}m$, 225) or mixture of these crystal phases. Our recent experiments give strong evidence that HfO_2 in the cubic phase indeed facilitates the migration of O^{2-} ions, which is considered of eminent importance concerning resistive switching processes. [2]

We try to rationalize the phase formation in our wet-chemical approach using various methods. In order to determine the particle size distribution and crystallinity of the samples, transmission electron microscopical analyses are predominantly used, while the crystal phase ambiguities itself were analyzed via in -situ X-ray diffraction and neutron diffraction methods, solid-state ^{17}O NMR and Raman spectroscopy.

With these findings we strive for the integration of nanoparticles into nanoelectronics circuitry in order to address scalability and concomitant limitations with respect to switching capability, stability and speed.

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P20

Investigation of Localized Reduction Phenomena in Yttria Stabilized Zirconia Electrolytes

P21

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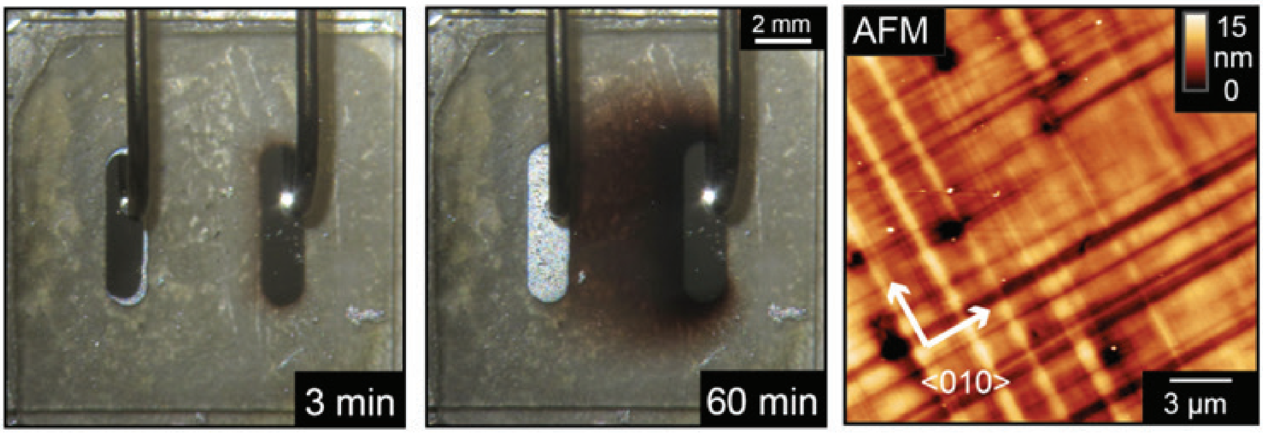
Solid oxide cells (SOCs) are key components of a future hydrogen-based, emission-free energy system. In electrolyser mode, they can be used to convert the electrical energy generated, *e.g.*, by wind turbines or solar cells into chemical energy via electrochemical water splitting. The resulting hydrogen can then be stored and converted back into electrical energy in fuel cell mode, thus overcoming the intermittency problem of renewable power sources. In order to design and optimize SOCs and avoid premature degradation, a fundamental understanding of the processes taking place in an electrical potential gradient is needed.

Here, we investigate the stability of yttria-stabilized zirconia, which is one of the most common SOC electrolyte materials. We perform Hebb-Wagner polarization experiments under vacuum conditions inducing electro-reduction thus emulating the conditions of long-term electrolyser operation. By performing optical and thermal microscopy on single crystals during the application of an electric field, the blackening effect, which is a consequence of the local reduction of the material, is analyzed. We follow the propagation of the reduction by optical microscopy revealing that the electro-reduction has an inhomogeneous nature related to the formation of dendrite-like finger structures and the evolution of several reduction fronts subsequently travelling from cathode to anode.

The progression of the blackening fingers follows preferentially the electric field lines and thus is in-fluenced by the electrode geometry and distortions in the electric field, *e.g.*, by the presence of metal particles in the oxide. While the first stage of the reduction process is only related to an enhanced concentration of oxygen vacancies in the electrolyte, we show by XPS that after prolonged electro-reduction, phase transformations towards highly oxygen-deficient ZrO_x phases occur leading to a change of the valence of the Zr ions from 4+ to 0 indicating the presence of metallic zirconium. This phase transformation results in the formation of dislocation-rich zones and characteristic checkered topography patterns at the microscale level, which might indicate the built-up of strong strain fields. Our results demonstrate that local structural and chemical inhomogeneities are of significant relevance for electro-reduction processes and may therefore help to understand and prevent degradation and decomposition of oxide devices operating at high temperatures.



Left: Progression of the blackening from cathode to anode; right: surface after heavy electro-reduction.

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A- and B-site doping of perovskite oxides enables microwave-assisted catalysis: A case study on CO oxidation

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We explored microwave-assisted catalysis as a method for direct CO oxidation employing multiple doped ABO_3 perovskite-oxides. This reaction serves as model for the evaluation of individual catalyst materials as potential candidates for engine exhaust gas aftertreatment. The materials were partially substituted on the A- and B-site during synthesis and have been tested for both, their activity towards microwave-induced heating and catalytic activity. It was shown that the powdered catalyst could be rapidly and selectively heated to conversion temperature in a matter of seconds to minutes. It was found that the materials could be tuned to specifically increase their microwave susceptibility, which in turn was also found to increase their catalytic performance. Additionally, some of the compositions under examination showed step-change behavior in MW-susceptibility and catalytic activity when certain experimental conditions were met, after which their catalytic activity dramatically increased. The results from this study may contribute to the deeper understanding of direct microwave-activation of solid materials and promote the development of chemical processes utilizing this quick and efficient source of heating.

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P22

Preparation, characterization and conductivity of NASICON-type $Li_{1+x}M^{(III)}{}_xTi_{2-x}(PO_4)_3$ ($M^{(III)}$ = Al, Cr, Fe; $0.5 \le x \le 2.0$) materials via modern, scalable synthesis routes

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NASICON structured materials are a promising class of solid-state ion conductors for application in electrochemical storage devices. The NASICON structure consists of a skeleton of vertex-sharing PO_4 tetrahedra and MO_6 octahedra, which provides a network of three-dimensional pathways for the alkali metal ions. This skeleton allows for the high degree of stability and flexibility of NASICON materials and a multitude of compositions. The highest ionic conductivities are found for $M^{(III)}$ cation substituted $LiTi_2(PO_4)_3$ derivates. While aluminum substituted compositions are mostly researched as electrolyte-materials the chromium and iron containing compounds are reported to be mixed conductors and thus suitable materials for cathodes.

Conventional synthesis routes of these materials include the highly energy consuming solid-state reaction and the sol-gel method in organic solvents. Unfortunately, the literature the conductivity trends in substitution series is rather scattered as one must include data from widely varying synthesis and preparation techniques and conditions. In addition, only a very small part of the sources includes information on porosity or verification of the intended stoichiometry.[1]

Samples of $Li_{1+x}M^{(III)}{}_xTi_{2-x}(PO_4)_3$ ($M^{(III)}$ = Al, Cr, Fe; $0.5 \le x \le 2.0$) were created by two recent synthetic routes with less environmental impact and high scalability.[2][3] The Samples were characterized regarding stoichiometry, crystal- and microstructure, density. And the conductive properties were investigated via electrochemical impedance spectroscopy.

The preparation yielded dense samples of the known NASICON- and secondary phases with no significant deviation from the intended stoichiometry. And the ionic conductivities of the resulting NASICON-materials are mostly within the upper range of comparative literature.

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P23

Multi-Scale Investigation of Na^+ Migration in doped $NaZr_2(PO_4)_3$ NASICONs

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Derivates of NASICON structure $NaZr_2(PO_4)_3$ are promising candidates as solid electrolyte in electrochemical devices due to their 3D structural framework of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra with multiple sodium sites which provides high mobility of the sodium ion charge carrier. The flexible framework allows great compositional diversity that leads to many possible applications. Si-doping on P-sites in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ introduces additional sodium ions resulting in high ionic conductivity in the range of some mS/cm at room temperature for compositions with $x = 2 – 2.5$.

On the atomistic scale the conductivity is determined by the local site energies and migration energies of the mobile sodium ions. The knowledge of the atomic scale energy landscape enables the understanding of migration processes. In order to elucidate the conductivity maximum, we investigate the influence of the cation environment on the sodium site energies as well as the migration mechanism of the sodium ions in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ using density functional theory (DFT). The results reveal that the site energies strongly depend on electrostatic effects. Furthermore, it is shown that a correlated migration of mobile sodium ions on regular lattice sites is favorable. Three different migration pathways are considered defined by their angles. The migration energy decreases with increasing angles and doping fraction because of increasing coulombic repulsion and opening of the bottleneck along the migration pathway.

Based on the results, we generate an energy model to predict configurational and migration energy in Kinetic Monte Carlo (KMC) simulations with 10000 steps per particle (MCSP) between 300 – 598 K of composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ with $x = 0.2 – 2.8$. Four different models are applied to differentiate the effect of different energy contributions and to reveal the origin of the conductivity maximum at high sodium content that was observed in previous studies. We show that sodium ions are trapped due to introduced silicon ions but percolate in the system for $x \geq 2.0$, which greatly increases the ionic conductivity.

Furthermore, we study the ionic conductivity by force-field molecular dynamic (FFMD) simulations to support the previous findings. Force-field parameter are generated using structural reference data obtained by high-precision first-principal MD (FPMD) simulations based on DFT. An implementation of the metaheuristic cuckoo search (CS) optimization is applied for $Na_2Zr_2Si_1P_2O_{12}$ to fit the set of parameters. Subsequent FFMD simulations of 1 ns are performed of supercells with around 4000 – 5000 atoms for the entire compositional range between 298 – 798 K. The diffusivity of the ions is investigated based on the mean squared displacements (MSDs) of the ions showing that only Na ions are mobile in the structure. Obtained ionic conductivities and activation energies of sodium ion migration are in good agreement with previous results of KMC simulations as well as literature values.

P24

Proton migration and interactions in doped barium zirconate: review of DFT data and simulating of conductivity

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Barium zirconate is a promising material for application as solid electrolyte in ceramic fuel cells due to its high protonic conductivity when doped with trivalent oxides such as yttria. On the atomic level, the transport behaviour can be elucidated using density functional theory and energy parameters controlling the mobility have been calculated by several researchers in the last years. In this work, we give a summarizing overview of the available literature data. We consider the interaction energies between protons and dopant ions and the migration barriers of proton motion for individual jumps in bulk $BaZrO_3$ with the focus on Y-doping. Generally, there is a large spread of energy values, which is related to the variations in the calculation parameters and variable distortions in the ionic lattice introduced by defects. Especially the cell size has a paramount influence on the results. In comparison to other dopants, yttrium exhibits a similar trapping of protons in both nearest and second nearest neighbour positions. This seems to be beneficial for conductivity as it leads to overlapping trapping zones and probably moderate barriers for the detrapping jump to a third nearest neighbour position.

Based on the collected data, we estimated the protonic conductivity using kinetic Monte Carlo simulations. We varied the energy parameters from a low to a high limit reflecting the range of the literature values. Additionally, different models were applied varying the radius of interactions considered for the calculation of the migration barriers. The simulations show that the variation of the energy values within the range of the literature data has a larger impact than the choice of the specific model.

P25

Unification of Bulk Storage and Supercapacitive Storage

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Bulk storage of Lithium or Sodium in electrodes is comparatively well investigated and understood though the principles of defect-chemistry for treating mixed conductors are not fully acknowledged. On the other hand, supercapacitive storage is equally well experimentally addressed. However here defect-chemistry is even more poorly brought into the game (unlike in our concept of job-sharing storage [1]). As a result, the two fields appear to be unnecessarily separated. We show at the example of TiO_2 as electrode how storage can be described and understood as a function of position [2] (measured as distance to the interface to the current collector). In this way a generalization of bulk and boundary storage - in more loose terms of electrochemical and supercapacitive storage - is achieved. For this purpose we carefully measure the storage capacity of titania films as a function of thickness allowing us to separate bulk and boundary contributions. Using various techniques electric field and charge distributions from bulk to the interface region are investigated. In the same context we study the space charge behavior in a discretized manner rather than by using the analytical Poisson-Boltzmann function [3]. In this way a more precise definition and demarcation of electrode and double layer capacity is achieved. In terms of application this work is expected to lead to a better way of describing and utilizing energy density - power density relations.

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[3]. C. Xiao, C.-C. Chen, J. Maier, Phys. Chem. Chem. Phys., 2022, 24, 11945-11957, Discrete modeling of ionic space charge zones in solids

P26

Drawing a materials map with an autoencoder for all-solid-state Li-ion batteries

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Machine learning techniques have garnered considerable attention as effective means of discovering new materials with desired properties. According to previous research [1], there is excellent potential to discover new materials that are not registered in the current databases. In this study, compositional and structural descriptors, which are multidimensional vectors, were compressed into one-dimensional vectors using an autoencoder. Encoded compositional and structural descriptors were used as horizontal and vertical axes, respectively, to visualize the two-dimensional distribution of known materials, obtaining a "materials map". To demonstrate this method, structural datasets of 1635 Li-containing fluorides were extracted from the Materials Project [2] database and the Li-ion conduction properties of these fluorides were computed using the high-throughput force-field technique [3]. By feeding composition/structure/property data to the autoencoder (Fig. 1), a materials map for Li-F materials was constructed (Fig. 2). The regions corresponding to well-investigated or unexplored compositions/structures are visible at a glance, and the map may provide hints for the exploration of fast Li-ion conductors. Consequently, this technique may be beneficial for materials researchers by providing an intuitive understanding and enabling the rational design of materials.

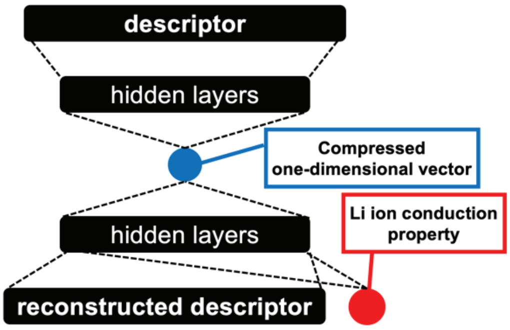

Fig. 1 Architecture of autoencoder
The model was trained by minimizing the sum of root mean absolute error (RMSE) of the descriptor and Li-ion conduction property.

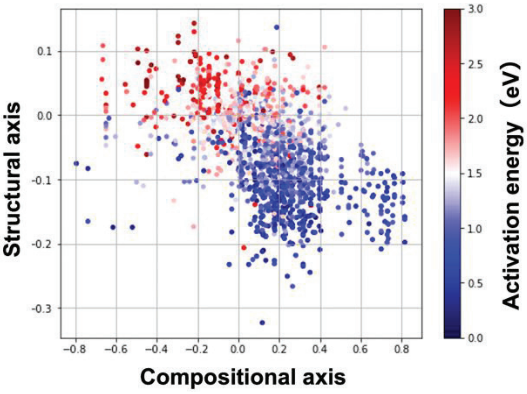

Fig. 2 Materials Map
Compositional and structural descriptors encoded by autoencoder are shown on the horizontal and vertical axes, respectively; the map is colored based on migration energy.

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P27

Tailored Indium Oxide Nanostructures for Efficient Charge Separation in Water Splitting Photoanodes

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Exploring new nanostructured heterojunctions with high photoactivity is an eternal pursuit of solar-driven water splitting. Here, we first introduce indium oxide (In_2O_3) nanorods (NRs) as a novel electron transport layer for bismuth vanadate ($BiVO_4$) with a short charge diffusion length. In_2O_3 NRs reinforce the electron transport and hole blocking of $BiVO_4$, surpassing the state-of-the-art photoelectrochemical performances of $BiVO_4$-based photoanodes. Also, a tannin-nickel-iron complex (TANF) is used as an oxygen evolution catalyst to quicken the reaction kinetics. The final TANF/$BiVO_4$/In_2O_3 NRs photoanode generates photocurrent densities of 7.1 mA cm^{-2} in sulfite oxidation and 4.2 mA cm^{-2} in water oxidation at 1.23 V versus the reversible hydrogen electrode. Furthermore, the "artificial leaf," which is a tandem cell with a perovskite/silicon solar cell, exhibits a solar-to-hydrogen conversion efficiency of 6.2% for unbiased solar water splitting. We reveal significant advances in photoactivity of TANF/$BiVO_4$/In_2O_3 NRs came from the tailored nanostructure and band structure for charge dynamics.

P28

Computational study of oxygen diffusion in the perovskites $CaTi_{1-x}Fe_xO_{3-\delta}$

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Perovskite-type oxides have the ability to stabilize high concentrations of defects, which is why they are utilized in a broad range of electrochemical applications. [1,2] While cubic calcium titanate exhibits a low conductivity, [3] higher ionic and electronic conductivities are found in the iron-substituted perovskite. [4]

Oxygen diffusion was examined in the mixed ionic-electronic conducting perovskite-oxides $CaTi_{1-x}Fe_xO_{3-\delta}$ (with $x = 0.1$, 0.2 and 0.3) by atomistic simulations. We carried out molecular dynamics and Metropolis Monte–Carlo simulations using one potential of Buckingham-type [5-12] and one potential based on a Morse-function [13].

With increasing iron content, a higher activation enthalpy for oxygen diffusion was derived. We employed coordination analysis to elucidate the role of interactions between iron and oxygen vacancies. Qualitatively, results from both types of potentials agree.

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