

# **Materials and Energy - New Directions for the "Energiewende"**

**773. WE-Heraeus-Seminar**

**23 – 27 October 2022**

**at the Physikzentrum Bad Honnef/Germany**

**WILHELM UND ELSE  
HERAEUS-STIFTUNG**



# Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see <https://www.we-heraeus-stiftung.de>

## Aims and scope of the 773. WE-Heraeus-Seminar:

"Energy" and "Materials" have an overarching importance for the future development of our society. They are coupled in multiple ways ranging from fundamental science to real-world applications. Analyzing their intricate relationship as energy-materials nexus, however, is a new approach. On the fundamental physics side, the control of quantum processes in real time under non-equilibrium conditions will have practical implications for bringing the understanding and discovery of materials and the development of process design concepts to the next level.

In the field of materials science, novel functional materials for energy conversion and storage and their processing towards usable devices (batteries, water splitting, fuel cells, catalysis) aims at efficient pathways for energy conversion and storage. This field benefits from a combination of fundamental understanding as well as combinatorial materials discovery and informatics to find new materials that combine application-related efficacy with availability on the level of raw materials.

Sustainability aspects require considering the entire chain of synthesis, processing, and application and thus finding optimum solutions through techno-economical multi-criteria analysis. In this context, novel energy- and resource-efficient materials processes are highly relevant for industry such as steel manufacturing, smelting, chemical industries as well as for the targeted production of high-performance materials by reduction of the number of processing steps, e.g., through additive manufacturing, and recycling.

Novel high-performance materials, finally, play an enabling role for the engineering of energy-efficient technologies, such as through lightweight high-strength materials for mobility and civil engineering, high-temperature materials for turbine blades, and corrosion-resistant materials for operation under extreme conditions.

This WE-Heraeus Seminar aims at connecting "Energy" and "Materials" in a new way and steering thinking and research in new directions.

## Scientific Organizers:

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# Introduction

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## Venue :

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## Registration:

Mojca Peklaj (WE Heraeus Foundation)  
at the Physikzentrum, Reception Office  
Sunday (17:00 h - 20:00 hrs) and Monday morning

**Program**

# Program (CEST)

**Sunday, 23 October 2022**

17:00 – 20:00 ARRIVAL and REGISTRATION

18:00 *BUFFET SUPPER*

## Start of the Scientific Program

20:00 Klaudia Seibel **KEYNOTE:**  
**Materials and Energy in Science  
Fiction: New Directions for Thought**

**Monday, 24 October 2022**

08:00 *BREAKFAST*

## Session 1: Fundamental Physics – Concepts that Define Demand for Materials

09:00 – 10:00 Christian Jooß **Energy Conversion in Advanced  
Materials – from Single Excitations to  
Correlated Dynamics**

10:00 – 11:00 Alfred Ludwig **High-throughput Experimentation for  
Discovery of Future Energy Materials**

11:00 – 11:30 *COFFEE BREAK*

11:30 – 11:50 Gabi Schierning **Current Status on the Interplay of  
Electronic Instabilities and  
Functionality in Martensites: Common  
Motifs in Charge Density Wave  
Materials, Shape Memory Alloys,  
Ferroelectrics, and Superconductors**

11:50 – 12:10 Hongbin Zhang **In-silico Design of Magnetic Materials  
for Energy Applications**

12:10 – 12:20 **Conference Photo (outside at the main entrance)**

12:20 – 13:30 *LUNCH*

# Program (CEST)

## Session 2: The Materials' Space

13:30 – 14:30	Rossitza Pentcheva	<b>Tailoring the Functionality of Transition Metal Oxide Surfaces and Interfaces for Energy Conversion Applications</b>
14:30 – 15:30	Tejs Vegge	<b>Transforming Computational Discovery of Energy Materials and Interfaces</b>
15:30 – 16:00	<i>COFFEE BREAK</i>	
16:00 – 16:20	Steven Angel	<b>Nanoscale High-entropy Oxides (HEO) from Spray-flame Synthesis for Oxygen Evolution Reaction (OER) in Water Splitting</b>
16:20 – 16:40	Vineetha Vinayakumar	<b>Pilot-scale Preparation of Nickel-cobalt Based Anode Materials for Alkaline Electrolysis</b>
16:40 – 17:30	<b>Poster Slam</b> (2 min per poster)	
17:30 – 19:00	<b>Poster Session 1</b>	
19:00 – 20:00	<i>DINNER</i>	
20:00	<b>Round Table Discussion</b>	

# Program (CEST)

Tuesday, 25 October 2022

07:30            *BREAKFAST*

## *Session 3: The Materials' Function in Energy Technologies*

08:30 - 09:30    Jeffrey Bergthorson    **Using Metals as Carbon-free Fuels and Energy Carriers**

09:30 - 10:30    Linda Nazar            **Materials for High-Energy Batteries**

10:30 - 11:00    *COFFEE BREAK*

11:00 - 12:00    Kerstin Schierle-Arndt    **An Industrial View on the Development of Materials for Energy Technologies**

12:00 - 13:30    *LUNCH*

13:30 - 14:30    Hubert Gasteiger        **Catalyst Development Approaches for Sustainable Proton Exchange Membrane (PEM) Fuel Cells and Electrolyzers**

14:30 - 14:50    Jian Duan                **Elucidation of Failure Mechanism and the Importance of Stack Pressure in the Li Metal Solid State Battery**

14:50 - 15:10    Hanyu Huo               **Interfacial Engineering of Solid-state Batteries**

15:10 - 15:30    Florian Strauß          **High-Entropy Multi-element Substituted Lithium Argyrodite Superionic Solid Electrolytes**

15:30 - 16:00    *COFFEE BREAK*

16:00 - 17:00    **Poster Slam** (2 min per poster)

17:00 - 18:30    **Poster Session 2**

18:30 - 19:30    *DINNER*

19:30            **Panel Discussion**  
(Christian Hagelüken, Umicore; Dierk Raabe, MPI Eisenforschung; Kerstin Schierle-Arndt, BASF; Peter Viebahn, Wuppertal Institut)

# Program (CEST)

Wednesday, 26 October 2022

07:30            *BREAKFAST*

## *Session 4: Old Materials – New Perspectives*

08:30 – 09:30	Dierk Raabe	<b>The Materials Science behind Sustainable Metals</b>
09:30 – 10:30	Martin Schneider	<b>The Building Materials Industry in the Changing Values of our Times</b>
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:20	Morteza Abedini	<b>Materials Degradation by the Interaction of Wear and Corrosion: A Survey of Tribocorrosion Processes</b>
11:20 – 11:40	Volker Weiser	<b>On the Combustion of Silicon as a Carbon-free Fuel for Power Generation</b>
12:00 – 13:00	<i>LUNCH BREAK</i>	
13:00	<b>Excursion:</b> <b>Hike in the mountains around Bad Honnef</b>	
17:30 - 18:30	<b>Poster Slam</b> (2 min per poster)	
18:30 - 19:30	<i>HERAEUS DINNER</i> at the Physikzentrum (cold & warm buffet, with complimentary drinks)	
19:30	<b>Poster Session 3</b>	



# Program (CEST)

Thursday, 27 October 2022

07:30                    *BREAKFAST*

## ***Session 5: The Materials' "Economy"***

08:30 – 09:30	Christian Hagelüken	<b>Resources, Recycling and Circular Economy: The Case of Metals</b>
09:30 – 10:30	Peter Viebahn	<b>Critical Materials of the Transition in the Energy and Industry Sector – Status, Assessment and Perspectives</b>
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:20	Johannes de Boor	<b>Lightweight and Sustainable Thermoelectric Generators for Waste Heat Recovery</b>
11:20 – 11:40	Jannik Neumann	<b>Preliminary Techno-Economic Assessment of Iron as an Energy Carrier</b>
11:40 – 13:00	<b>Moderated Final Discussion</b>	
13:00 – 14:00	<i>LUNCH</i>	

***End of Seminar / Departure***

## Posters

## Poster Session 1: Monday, 24 October, 17:30 h (CEST)

- |    |                     |  |
|----|---------------------|--|
| 1  | Benjamin Zimmermann | High Entropy Oxides as New Materials for Energy Applications   |
| 2  | Lei Zhang           | Exploring WC-based Electrocatalysts for Robust Hydrogen Evolution Reaction via Energy-Saving Method                        |
| 3  | CANCELLED           |  |
| 4  | Tingting Yang       | Biphasic Layered Material Strengthened by Tenon-and-Mortise Structure for Robust Sodium Ion Batteries Cathode              |
| 5  | Da Xing             | Insertion / De-insertion of Magnesium into the Bi Modified Au Electrode: DEMS and EC-STM Study                             |
| 6  | Philipp Winstermann | Steam-Iron Process for Storage and Transport of Hydrogen   |
| 7  | Yu Wang             | Self-activation of Exsolved LaFe <sub>0.9</sub> Ru <sub>0.1</sub> O <sub>3</sub> Perovskite in Propane Combustion Reaction |
| 8  | Janika Wagner       | Kinetic Monte Carlo Simulation of the Growth of SEI at the Li/Electrolyte Interphase                                       |
| 9  | Timo Wagner         | Increasing the Microscopic Surface Area of Nickel Surfaces by Plasma Application with Industrial Scalability in Mind       |
| 10 | Martin Underberg    | A Pilot Plant for Gas-phase Nanoparticle Synthesis: Products for Future Energy Applications                                |
| 11 | Laura Tropf         | Flow and Bubble Investigations in the Vicinity of In-Liquid Plasmas for Graphene Synthesis                                 |

## Poster Session 1: Monday, 24 October, 17:30 h (CEST)

- 12 Jonas Spielmann **Iron as Fuel – Investigating the Thermochemical Oxidation of Iron Particles via Mössbauer Spectroscopy**
- 13 CANCELLED
- 14 Mohammed-Ali Sheikh **Doped NaSICON-Type Solid Electrolytes for Sodium-Ion Batteries from Scalable Spray-Flame Synthesis**
- 15 Doris Segets **New Materials for Electrocatalysis: Their Design, Implementation and Characterization to Make Academic Developments Relevant**

## Poster Session 2: Tuesday, 25 October, 17:00 h (CEST)

- |    |                         |  |
|----|-------------------------|--|
| 16 | Patrik Schuehle         | Transition Metal Phosphide Catalysts for the Chemical Storage of Renewable Hydrogen  |
| 17 | Franziska Scheffler     | Manufacturing of Flexible High-performance Thermoelectric Microlayers  |
| 18 | Ahmad Saylam            | An HCCI-engine Concept as a Conversion Process of Gaseous Hydrocarbon Feedstock  |
| 19 | Haroon Christopher Sam  | Fundamental Studies on the Development of Hydrogen Traps in Ferritic Steel and their Influence on Hydrogen Embrittlement during Long Term Exposure |
| 20 | Paul Peter Paciok       | Heat-treated RhMo-doped PtNi/C Catalysts for the Oxygen Reduction Reaction   |
| 21 | Pierfrancesco Ombrini   | An Advanced Model for Solid-State Batteries  |
| 22 | Bich-Diep Nguyen        | Combustion of Individual Iron Micro-particles with Resolved Boundary Layers  |
| 23 | Harshita Naithani       | Electronic Transport Modelling of High efficiency Thermoelectric Mg <sub>2</sub> (Si,Sn) Solid Solutions   |
| 24 | Johannes Mich           | A Comparison of Mechanistic Models for the Combustion of Iron Microparticles and their Application to Polydisperse Iron-air Suspensions.           |
| 25 | Faria Huq               | Influence of PTFE Membrane Thickness in Gas Diffusion Electrode for CO <sub>2</sub> Electroreduction   |
| 26 | Claudia F. Lopez Camara | Exploring the Si-precursor Composition for Inline Coating and Agglomeration of TiO <sub>2</sub> via Modular Spray-flame and Plasma Reactor         |

## Poster Session 2: Tuesday, 25 October, 17:00 h (CEST)

- |    |               |   |
|----|---------------|---|
| 27 | Teo Lombardo  | <b>Secondary Ions VS Secondary Electrons for Electrode Microstructures Characterization: Advantages and Perspectives</b>                            |
| 28 | Tao Li        | <b>Visualization of Single Iron Particle Combustion in Laminar Flow Conditions</b>  |
| 29 | Thomas Lange  | <b>Sonochemical Modification of Highly Conductive Carbon Blacks and its Effect on the Performance of a Proton Exchange Membrane Fuel Cell</b>       |
| 30 | Thomas Krenn  | <b>Investigation of Iron Particle Combustion Behavior in the Exhaust Gas of a Methane Bunsen Flame</b>  |
| 31 | David Kitsche | <b>ALD-derived Zirconia Coatings on Ni-rich Cathodes in Solid-State Batteries: Correlation between Surface Constitution and Cycling Performance</b> |

## Poster Session 3: Wednesday, 26 October, 19:30 h (CEST)

- 32 Leonhard Karger Low Temperature Ion-exchange Based Synthesis of Highly Ordered LiNiO<sub>2</sub> Single Crystals
- 33 Jacob Johnny Deposition and Characterization of Ru@SILP on Si Wafer Substrates as Designer Catalysts
- 34 Patrick Hutterer Influence of Composition on Structural Evolution and Material Properties of High Entropy Zirconates
- 35 Ricardo Alonso Martinez-Hincapie Experimental Pitfalls in the Electrochemical Evaluation of Energy-related Materials
- 36 Janik Hebel Particle Velocity Measurements of Gas-assisted Iron Dust Flames in a Swirl Stabilized Combustion Chamber
- 37 Sebastian Grimm Gas-phase Reactions of Ferrocene: New Insights from Microreactor Studies Using Synchrotron Radiation
- 38 CANCELLED
- 39 Jaime Andres Gallego Marin An Easy Method to Obtain High Surface Area Perovskite-like Oxides. LaFe<sub>0.9</sub>Ru<sub>0.1</sub>O<sub>3±δ</sub> as Example
- 40 Markus Sebastian Friedrich Correlation of Phase Transitions and Diffusion in Polycrystalline WO<sub>3</sub> Films during electrochemical Ion Insertion and Extraction
- 41 Michal Fedoryk Laminar Combustion Wave Velocity and Structure Investigation in Bunsen Type Iron Dust Burners
- 42 Moritz Exner Observation of the Co-intercalation of Solvated Sodium Ions in Graphite by In-situ Characterization Techniques

## Poster Session 3: Wednesday, 26 October, 19:30 h (CEST)

- |           |                     |  |
|-----------|---------------------|--|
| <b>43</b> | Jan Luka Dornseifer | <b>Impedance Spectroscopy of Microstructured Ceria Thin Films</b>  |
| <b>44</b> | Johannes Döhn       | <b>Computational Screening of Oxide Perovskites as Insertion-Type Cathode Materials</b>                            |
| <b>45</b> | Simon Daubner       | <b>Modeling Battery Intercalation Materials on the Nano- and Micro-scale</b>                                       |
| <b>46</b> | Samira Boukachabia  | <b>Study of CsBX<sub>3</sub> Perovskites (B = Pb, Sn, Ge / X = Cl, Br, I) by TDDFT Method</b>                      |
| <b>47</b> | Usman Ali           | <b>Physisorption Studies about Tuning of Mesoporosity in Silica Monoliths Controlled by Hydrothermal Treatment</b> |
| <b>48</b> | Md Yusuf Ali        | <b>Gradient Ceramics in Polymer hybrid electrolyte for solid state Li-ion batteries</b>                            |
| <b>49</b> | Isnaldi Souza Filho | <b>Green Steel via Hydrogen Plasma Reduction of Iron Oxides</b>  |



# **Abstracts of Lectures**

(in alphabetical order)

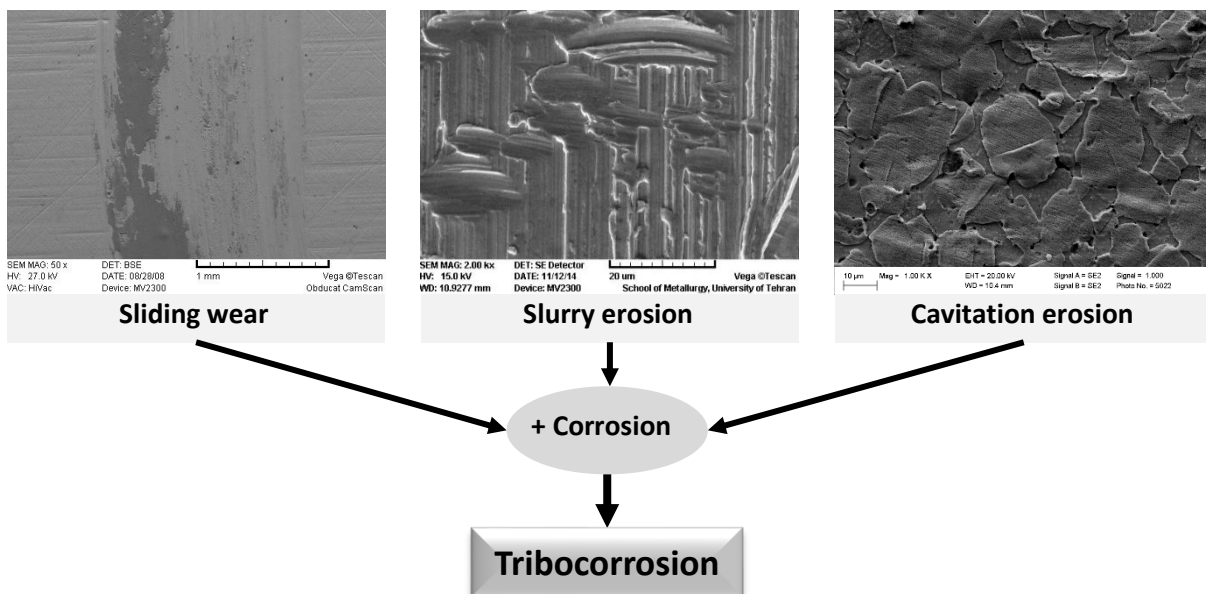
# Materials degradation by the interaction of wear and corrosion: a survey of tribocorrosion processes

Morteza Abedini

<sup>1</sup>Materials Science and Engineering, Institute for Metal Technologies, University Duisburg-Essen, 47057  
Duisburg, Germany

<sup>2</sup>Department of Metallurgy and Materials Engineering, Faculty of Engineering, University of Kashan, Kashan,  
Iran

A part of global energy loss is directly stemmed from the failure of the metallic components that should be repaired or replaced. The replacement of components would also increase the demand for metals which means higher consumption of the limited materials resources and emissions of more greenhouse gases. Therefore, not only the energy and resources can be saved by increasing the service life of the components, but also the environment will be protected. To enhance the component's life, it is essential to know about the damaging mechanisms and the root causes. Among the other destructive mechanisms, mechanical wear and electrochemical corrosion are two main surface-damaging processes that attack various metals and alloys. Wear is the removal of material from a solid surface under repeated stresses that can happen through three main modes: sliding wear, slurry erosion, and cavitation erosion. On the other hand, corrosion as a result of surface interaction with the environment damages the surface of solids through a variety of mechanisms; mainly anodic dissolution, hydrogen embrittlement, and high-temperature oxidation. While wear and corrosion each have unique complexity, their simultaneous occurrence makes it even more challenging to study the process called tribocorrosion. Here in this research, some results on sliding wear-corrosion, slurry erosion-corrosion, and cavitation erosion-corrosion will be presented to explain the effect of corrosion on wear and vice versa. The findings have revealed that eliminating the corrosion could largely decrease the removal rate and therefore, increase the life of metallic materials under tribocorrosion damage, though the removal rate by corrosion alone can be negligible.



# Nanoscale high-entropy oxides (HEO) from spray-flame synthesis for oxygen evolution reaction (OER) in water splitting

**Steven Angel<sup>1</sup>, Vimanshu Chanda<sup>2</sup>, Ignacio Sanjuán Moltó<sup>2</sup>, Corina Andronescu<sup>2,3</sup>, Christof Schulz<sup>1,3</sup>, Hartmut Wiggers<sup>1,3</sup>**

<sup>1</sup> IVG – RF, University of Duisburg-Essen, Duisburg,

<sup>2</sup> Technical Chemistry III, University of Duisburg-Essen, Duisburg, Germany

<sup>3</sup> CENIDE, Center for Nanointegration, University of Duisburg-Essen, Germany

HEOs have recently gained much attention as novel, e.g., anode/cathode materials for Li-ion batteries or fuel cells. HEOs are compounds counting with a configurational entropy higher than  $1.609 R$  ( $R$ : gas constant) which are stabilized above a critical temperature (e.g.,  $>850$  °C). Thus, the synthesis techniques of these compounds typically require high temperatures, which can be achieved using a calcination step after, e.g., a co-precipitation step of the required precursors as in conventional methods. Alternatively, the spray-flame synthesis method – in which temperatures higher than  $1300$  °C are typically obtained – offers the option to continuously synthesize HEOs in a single step. In this work, the spray-flame synthesis of three HEOs, HEO1:  $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ , HEO2:  $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})_3\text{O}_4$ , and HEO3:  $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.1}\text{Mg}_{0.05}\text{Al}_{0.05}\text{Cu}_{0.2})_3\text{O}_4$  – is explored. While the spray-flame synthesized HEO1 crystallizes as a single phase in the rock-salt structure, the HEO2 and HEO3 samples were stabilized in the single-phase spinel  $Fd-3m$  structure. Based on TEM/EDX measurements, particles from the HEO1 were found to have a predominantly cubic morphology ( $d_p = 7\text{--}10$  nm) and a homogeneous element distribution on the atomic scale with local fluctuations of Mg and Zn. In contrast, the HEO2 and HEO3 samples presented particles with polyhedral morphologies and spherical particles ( $d_p = 5\text{--}12$  nm) with uniform elemental distributions. The samples were further characterized by TGA/DSC, FTIR, and XPS. All spray-flame-synthesized HEOs were tested as OER catalysts in the electrochemical water splitting. HEO1 presented a promising activity, reaching a current density of  $\sim 70$  mA/cm<sup>2</sup> at a potential of  $\sim 1.65$  V vs. RHE.

## References

- [1] H. Xu et al., Nature Comm. **11**, 3908 (2020).
- [2] B. L. Musicó et al., APL Mater. **8**, 040912 (2020).
- [3] S. J. McCormack et al., Acta Mater. **202**, 1 (2021).
- [4] A. Sarkar et al., J. Europ. Ceramic Soc. **37**, 747 (2017).
- [5] F. Schneider et al., Rev. Sci. Instr. **90**, 085108 (2019).
- [6] C. Schulz et al., Proc. Combust. Inst. **37**, 83 (2019).

# Using Metals as Carbon-free Fuels & Energy Carriers

J.M. Bergthorson<sup>1</sup>

<sup>1</sup>*McGill University, Montreal, Canada*

In order to address climate change, we must transition to a low-carbon economy. Many clean primary energy sources, such as solar panels and wind turbines, are being deployed and promise an abundant supply of clean electricity in the near future. The key question becomes how to store, transport, and trade this clean energy in a manner that is as convenient as fossil fuels. The Alternative Fuels Laboratory (AFL) at McGill University is actively researching the use of recyclable metal fuels as a key enabling technology for a low-carbon society. Metal fuels, reduced using clean primary energy, have the highest energy density of any chemical fuel and are stable solids, simplifying storage, transport, and trade. This presentation will overview the concept of using metals as circular carbon-free fuels and the methods to harness the chemical energy contained in the metal fuels. Metals can be burned with air to produce heat in flames similar to traditional hydrocarbon fuels and, specifically, coal. Some metals can also be reacted with water to release hydrogen and heat in exothermic reactions. In both cases, the products are solid metal oxides that can be recycled with renewable energy in carbon-free processes, closing the loop and enabling metal fuels to be a sustainable energy carrier for the long term.

# Lightweight and sustainable thermoelectric generators for waste heat recovery

**J. de Boor<sup>1,2</sup>, J. Camut<sup>1</sup>, P. Ziolkowski<sup>1</sup>, C. Stiewe<sup>1</sup>, E. Müller<sup>1,3</sup>**

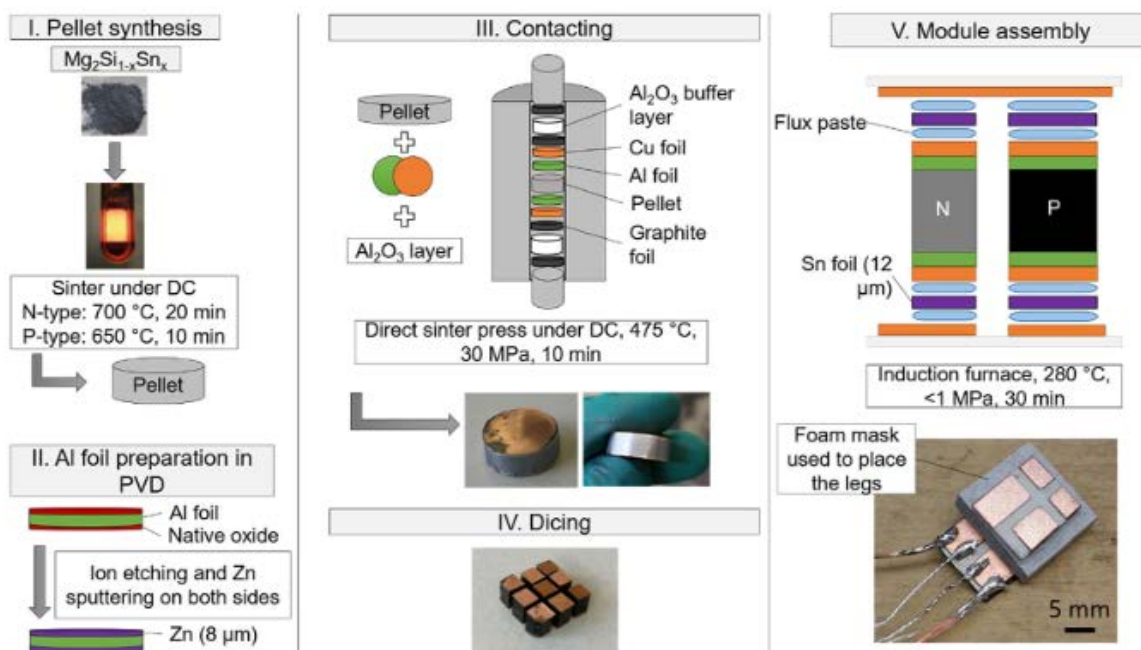
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Thermoelectric (TE) devices enable data transmission from outside the solar system (Voyager probes), move rovers on Mars (Curiosity) and constitute an integral part in industrial technologies, enabling e.g. CoViD PCR tests by genome sequencing and autonomous sensors. While conceptually simple, robust and with broad potential of **generating electricity from ubiquitous waste heat**, their practical implementation has yet remained limited. The reasons for this are a lasting dependence on toxic and scarce elements.

Magnesium silicide based solid solutions  $Mg_2X$  ( $X = Si, Ge, Sn$ ) are among the most promising thermoelectric (TE) materials for the temperature range of 500 K to 800 K, where a large fraction of the reusable heat is available. Very good TE properties combined with a high material availability, low cost of raw materials and environmental compatibility, makes these materials preferred candidates for large scale applications. I'll discuss milestones and challenges on the successful fabrication of one of the first  $Mg_2X$  based TEG prototypes.



## Elucidation of failure mechanism and the importance of stack pressure in the Li metal solid state battery

Jian Duan, Till Fuchs, Anja Henss, Juergen Janek,

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Solid state battery is long regarded as a promising candidate for a safer electrochemical energy storage device and intensive research has been conducted in recent years. Coupled with Li metal anode, achieving high energy density could be possible. Among the solid electrolyte, the sulfide solid electrolyte shows comparative Li-ion conductivity with non-aqueous electrolyte. However, the critical current density (CCD) is relatively low in the sulfide-based Li metal solid state battery (LMSSB), which is a big issue at present. Although the dendrite issue has been under investigation for a long time, there is still a lack of fundamental understanding and solutions for long stable performance are limited.

Here multi-characterization methods, including *operando*, *in-situ* scanning electron microscopy, and *ex-situ* focus ion beam scanning electron microscopy were employed to investigate the failure mechanism in  $\text{Li}_6\text{PS}_5\text{Cl}$  based LMSSB. The *Operando* method is a straightforward way to give us an insight view of the failure mechanism. Cracking of the solid electrolyte was identified as the dominant failure reason. Furthermore, we found that cracking was initiated during the plating process and the situation would be worse when an inhomogeneous plating occurred.

Due to a solid-solid contact of the Li/solid electrolyte interface, stack pressure is one vital parameter. In this report, we further give details of the relationship between the stack pressure and the battery performance, and some design principles. Our results unambiguously demonstrate that cracking could cause a disastrous effect on LMSSB, indicating that more attention should be paid on the mechanics of the solid electrolyte.

## **Catalyst Development Approaches for Sustainable Proton Exchange Membrane (PEM) Fuel Cells & Electrolyzers**

*Hubert A. Gasteiger*

*Chair of Technical Electrochemistry, Chemistry Department, Technical University of Munich*

Driven by climate change, the global community is seeking to expand renewable energy generation and to decarbonize the transportation sector, which has a significant share in the world-wide CO<sub>2</sub> emissions. This can partially be addressed by the development and deployment of light-duty battery electric vehicles (BEVs). On the other hand, hydrogen is envisioned as fuel for mid- and heavy-duty applications (SUVs, trucks) using fuel cell electric vehicles (FCEVs) based on proton exchange membrane (PEM) fuel cells.

In the latter case, hydrogen must be produced from renewable electricity (wind, solar), which can also be used for decarbonizing chemical processes like steel and ammonia production as well as for temporary large-scale energy storage. PEM based water electrolyzers are promising candidates for the generation of high-pressure hydrogen. However, both PEM fuel cell and water electrolyzer technologies currently require significant amounts of costly and supply-limited precious metals, which could restrict their large-scale implementation, so that improved catalyst and electrode concepts must be devised. These challenges will be discussed.

# Resources, Recycling and Circular Economy: The case of Metals

Christian Hagelüken

*Umicore AG & Co KG, Hanau, Germany*  
*christian.hagelueken@eu.umicore.com*

Resource efficiency, energy and mobility transition are crucial strategies to both mitigate climate change and to reduce Europe's dependency on (fossil) raw material imports. While raw materials are the basis of our material world, their excessive consumption over the last decades has also contributed significantly to climate change. However, raw materials, and here especially metals, play a key enabling role as well for climate protection technologies, such as electro mobility, the hydrogen economy, and solar and wind power plants, and also for digitalization. Accordingly, it is necessary to make the utilisation of raw materials much more resource-efficient than before and to *use* them as purposefully as possible instead of *consuming* them.

A key approach to this is the circular economy, because metals can basically be reused "infinitely," mostly without any loss of quality. If modern recycling technologies are applied consistently, pure metals are available again at the end of the processes that are identical in their chemical and physical properties to those from mining. But how can metals such as cobalt, nickel and lithium in electric car batteries; platinum group metals in catalysts; or precious metals, copper, tin and other technology metals in electronic components be used and recycled as efficiently as possible?

Advanced circular economy systems and sophisticated recycling technologies build the backbone for the development of a resource efficient and sustainable society. Closed metal cycles contribute for to this by securing relevant parts of the material supply for high-tech products and by reducing CO<sub>2</sub> emissions in their production at the same time. Interacting steps in multistage treatment processes are challenging but will give a competitive advantage for networks of industry and science that are able to handle that. In this context, high-quality recycling means the economically viable recovery of many relevant metals and materials with high yields, in marketable quality and in compliance with high environmental and social standards.

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# Interface Engineering of Solid-state Batteries

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The solid-solid interfacial contact is a critical issue during the studies of solid-state batteries (SSBs), which greatly affects the electrochemical performance of SSBs, such as the coulombic efficiency, and cycle life. For flexible polymer/garnet electrolytes (PGEs), the interfacial issue mainly comes from the interactions between the inorganic fillers and the polymer matrix. The slow Li<sup>+</sup> transport through the polymer/garnet interface can lead to the low ionic conductivity of PGEs. While for garnet ceramic electrolytes (GCEs), the ceramic bulk with a relative density over 99% shows no obvious grain boundary, leading to the ionic conductivity over 10<sup>-3</sup> S cm<sup>-1</sup> at room temperature. Under this circumstance, the interfacial issue could be attributed to the poor interfacial contact between the GCEs and Li metal anodes. It can induce the large interfacial resistance as well as the lithium dendrite growth. In this presentation, I'll focus on the aforementioned interfacial issues, various targeted strategies will be introduced to construct the excellent interfacial structure, thus significantly improving the performance of SSBs [1-3].

**Keywords:** Garnet; Solid-state batteries; Interfacial engineering; Li dendrite suppression

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# Energy Conversion in Advanced Materials – From Single Excitations to Correlated Dynamics

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Energy conversion in materials is based on interacting excitations that develop after the primary stimulation. The fundamental understanding to which energy channels excitations are transformed e.g. in photovoltaic or electrochemical devices is very well developed in materials, where excitations and interactions can be described using rigid states populated by single particle approximations. However, despite of progress the fundamental understanding of the elementary processes is still very limited in advanced materials with dynamic electronic or atomic structure or in systems with strong correlations in interacting excitations [1-4]. This can lead to qualitatively new behavior, where established models break down. At the same time, such systems open up new paths for control of energy conversion and thus to achieve higher performance.

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# High-throughput Experimentation for Discovery of Future Energy Materials

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Discovery of new materials for sustainable production/storage/conversion of energy carriers is necessary to enable future energy systems and can be addressed by thin-film high-throughput experimentation [1]. This approach is useful for validation of theoretical predictions (e.g. from high-throughput computations) as well as exploration and exploitation of large compositional search spaces such as e.g. high entropy alloys. The approach comprises fabrication and processing of thin-film materials libraries by combinatorial sputter deposition and optional post-deposition treatments, followed by high-throughput characterization (composition, structure, properties) of the libraries, and finally the organization of the acquired multi-dimensional data in adequate databases as well their effective computational analysis and visualization. Results for up to quinary systems are visualized in the form of composition-processing-structure-function diagrams, interlinking visually compositional data with structural and functional properties. The talk covers discovery examples with a focus on compositionally complex materials (e.g. [2]). A new approach to accelerate atomic-scale measurements for alloys [3] is presented as well as applications of materials informatics to accelerate and improve materials discovery [4, 5].

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# Materials for High Energy Batteries

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The widespread integration of renewable, intermittent energy sources such as wind or solar is dependent upon the development of efficient large-scale energy storage systems for load-levelling the electric grid. Similarly, the acceptance of electric vehicles hinges on the availability of intermediate scale, safe, low-cost high energy density storage batteries that can provide long driving ranges. In this context, it is widely acknowledged that traditional Li-ion batteries are starting to approach their limits.

This talk will present a perspective on the challenges, and opportunities for future strategies for electrochemical energy storage from a materials perspective. The topics will encompass promising new developments in Li metal batteries, solid state batteries, and holistic approaches towards advances in Li-sulfur batteries that increase the cell capacity and provide close-to-theoretical reversible electron transfer. Such step-changes require tailor-designed materials for the electrodes, and new electrolyte strategies for both liquid and solid state configurations. These topics will be the subject of the presentation along with our unfolding understanding of the underlying material and battery chemistries.

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# Preliminary Techno-Economic Assessment of Iron as an Energy Carrier

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The sixth IPCC Assessment Report clearly shows that climate change is progressing more rapidly than originally expected. In addition to the development of new CO<sub>2</sub>-free technologies, the climate-neutral retrofitting of existing infrastructure, which is feasible in the short and medium term, is therefore becoming increasingly important in order to achieve the 1.5°C target.

On the way to a climate-neutral electricity economy, the sustainable generation of electrical power from renewable energies plays a pivotal role. However, the widespread use of renewable energy faces several challenges, especially its intermittency and locally limited availability. Addressing this temporal and geographic mismatch between renewable energy supply and demand is therefore crucial for a successful carbon-neutral electricity economy. Large-scale, transportable, and storable energy carriers are a key element in redressing this imbalance.

Besides hydrogen-based fuels, metal fuels and iron in particular are promising alternatives to serve this purpose: Electrical energy from renewable sources is stored by thermochemical reduction of iron oxides with green hydrogen and can be converted back into electricity by thermochemical oxidation (e.g., in retrofitted coal-fired power plants) spatially and temporally separated from the storage process.

A meaningful evaluation of the energy-iron cycle requires a comprehensive analysis of the overall system. This holistic system approach has to consider all sub-processes and promising variants, divers evaluation criteria (e.g., efficiencies, costs, environmental impact), and various deployment scenarios.

Preliminary energetic and economic analyses of iron as energy carrier show comparable to superior energy and cost efficiencies compared to hydrogen as energy carrier. The additional cost and energy requirements for the recycling of the iron oxides compared to the direct use of hydrogen are overcompensated by favorable transport and storage capabilities, as well as the retrofit potential of existing infrastructure. Iron as a chemical energy carrier may enable a CO<sub>2</sub>-free climate-neutral circular energy economy.

This research is conducted within the framework of the Clean Circles project. For more information see: [www.tu-darmstadt.de/clean-circles](http://www.tu-darmstadt.de/clean-circles)

Tailoring the functionality of transition metal oxide surfaces and interfaces for energy conversion applications

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Due to their abundance, chemical and thermal stability and, in particular, to the interplay of orbital, spin and lattice degrees of freedom, transition metal oxides emerge as prospective candidates for energy conversion applications, e.g. as thermoelectrics or catalysts for the (photo-) electrocatalytic water splitting. Nanostructuring and reduced dimensionality can lead to further intriguing functionalities that are not available in the bulk compounds. Based on density functional theory calculations with a Hubbard  $U$  term, I will discuss several examples how to model, understand and tailor the thermoelectric properties of oxide superlattices by exploiting the effect of interface polarity, confinement and strain [1-5] or to tune the catalytic activity of anode materials for the oxygen evolution reaction (OER). By comparing iron and cobalt spinels [6-7] vs. perovskites [8] we disentangle the role of structural motifs, crystallographic orientation and dopants on the OER overpotential. Analysis of the underlying electronic and magnetic properties indicates dynamic variation of oxidation state during OER and points towards potential active sites.

Funding by the German Research Foundation DFT within CRC TRR80 (Projects G3, G8) and TRR247 (Project B04) as well as computational time at the Leibniz Rechenzentrum and the supercomputer MagnitUDE at UDE is gratefully acknowledged.

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## The Materials Science behind Sustainable Metals

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The presentation is about the sustainability of metallic alloys, specifically steels and aluminium alloys. Only metallic materials encompass such diverse features as strength, hardness, workability, damage tolerance, joinability, ductility and toughness, often combined with functional properties such as corrosion resistance, thermal and electric conductivity and magnetism [1-4]. Today we produce and consume about 2 billion tons of metals every year, with steels alone standing for an annual production of currently 1.85 billion tons. The huge and accelerating demand for load-bearing and functional metallic alloys in key sectors such as green energy supply, infrastructures, health, durable construction, robotics, passenger safety and modern transportation is resulting in predicted production growth rates of up to 200% until 2050. Most of these materials, specifically steel, aluminium, nickel and titanium, require a lot of energy when extracted and manufactured and these processes emit large amounts of greenhouse gases and pollution. This means that the huge success of metallic products and industries also brings them into a position where they have an essential role in addressing environmental aspects. The vast availability of metals, efficient mass producibility, low price and amenability to large-scale industrial production (from extraction to the alloy) and manufacturing (downstream operations after solidification) have become a substantial environmental burden: worldwide production of metals leads to a total consumption of about 8% of the global energy used and 35% of all industrial CO<sub>2</sub>-equivalent emissions when counting only steels and aluminium alloys. This lecture presents several aspects related to this field, with a focus on methods for improving the sustainability of steels, in areas including reduced-carbon-dioxide primary production, recycling and scrap-compatible alloy design. The lecture also discusses the effectiveness and technological readiness of individual measures and also shows how novel structural materials enable improved energy efficiency through their reduced mass, higher thermal stability and better mechanical properties than currently available alloys.

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# **An Industrial View on the Development of Materials for Energy Technologies**

Kerstin Schierle-Arndt

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BASF – we create chemistry for a sustainable future. The world is changing at a rapid pace – more and more urgently than ever, solutions are needed for a more sustainable future. Chemistry plays a key role here. In almost all areas of life, it can help overcome pressing global challenges with innovative products and technologies – from climate change and using resources more sparingly to feeding the world's population.

Inorganic materials are key drivers for energy technologies. New and improved materials enable transformations towards renewable energy, energy storage and energy efficiency. However, in development of these technologies to market maturity, the challenges go beyond the material itself. The integration of the material into the system and the overall system development go hand in hand with material development in interdisciplinary teams. Partnerships along the value chain and between academia and industry are key to success.

Along BASF examples, this talk will give insights into the interplay between material and system development. In addition to technology, economic considerations are decisive: market needs, competing technologies and cost. Only if a new product or a new technology meets all requirements in this complex interplay, it will succeed in the market.



# **Current status on the interplay of electronic instabilities and functionality in martensites: Common motifs in charge density wave materials, shape memory alloys, ferroelectrics, and superconductors**

**A. Grünebohm<sup>1</sup>, A. Hütten<sup>2</sup>, A. E. Böhmer<sup>3,4</sup>, J. Frenzel<sup>5</sup>, R. Drautz<sup>1</sup>, I. Ennen<sup>2</sup>, L. Caron<sup>2</sup>, T. Kuschel<sup>2</sup>, I. Eremin<sup>3</sup>, F. Lechermann<sup>3</sup>, D. Anselmetti<sup>2</sup>, T. Dahm<sup>2</sup>, K. Rossnagel<sup>6,7</sup>, G. Schierning<sup>2</sup>**

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Many materials used for energy applications exhibit displacive phase transitions, such as (magnetic) shape memory alloys, ferroelectrics, or superconductors. Since the pioneering work of Verwey, Mott and Peierls on electronic driving forces of displacive structural phase transitions, there is now ample experimental and theoretical evidence that electronic and phononic instabilities, as well as microstructural features, accompany the formation of fascinating functional properties in these different classes of materials. They manifest as (giant) Kohn anomalies, phonon softening, Fermi surface nesting and anomalies in the transport behaviour as well as twinning and (nano)domain formation. Within this contribution, in particular, the role of conduction electrons in the martensitic phase transition of the shape memory alloy NiTi is discussed based on transport experiments that can be interpreted in terms of the formation of a charge density wave during this phase transition [1]. This contribution then attempts to discuss the common electronic and structural features at such phase transitions that occur similarly in these different materials.

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# The Building Materials Industry in the Changing Values of our Times

**Dr. Martin Schneider**

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Cement is the most used material on a global scale and is indispensable for a wide range of buildings, infrastructures and transport systems. In the time to come cement will also in many respects play an important role for modern societies and their sustainable development. Global cement production has constantly and significantly increased due to rising populations, continuing urbanisation and infrastructure development. The total annual cement consumption in 2016 was 4.13 Gt and it is expected to grow by up to 4.68 Gt/year by 2050. Cement production is inevitably accompanied by a significant demand for energy and by high CO<sub>2</sub> emissions. This is due to the physical and chemical processes when converting limestone-based raw materials into Portland cement clinker, which cannot be avoided even if the overall production process is optimised as much as possible. Today the cement industry is the third largest industrial energy consumer, and cement production accounts for up to 6 - 7 % of global anthropogenic CO<sub>2</sub> emissions.

Against the background of global climate change, the cement industry has embarked on its biggest transformation ever. The different pathways to decarbonise the sector are an essential part of the many roadmaps on a global, regional or company levels which define how to reach net-zero CO<sub>2</sub> by 2050. Taking the German cement industry's roadmap as an example, different measures have been addressed. They require an active role of the industry itself as well as a technical and political framework but – most importantly – the partnership with policymakers and society.

While cement was already used in Roman times, industrialised cement production has a history of around 200 years. The values which have been important to the cement producers have always continued to develop, as they have for all societies, organisations or cultures. Growing from a sense of togetherness, pride, and setting the rules for high qualitative cements, this development has continued into strategically operating companies, many of them vertically integrated and operating globally. Today, in a post-modern society, the cement industry proactively advocates for the decarbonisation of its value chain, taking the initiative to implement the necessary technical measures to achieve full carbon neutrality by 2050.

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# **“Materials and Energy – New directions for the ‘Energiewende’”**

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We all live in a material world. But the future consists of ideas before it materializes in the here and now; ideas that are formed by scientists, but also ideas that are envisioned by science-fiction writers. Their imagination boldly goes where no-one has gone before, pushing the boundaries of what is thinkable ever further: From the manifold ways little details are presented in science-fiction worlds to the bold vision of Star Trek’s smooth conversion of energy into matter, from the vastness of planet-size star-ships to smallest-scale nanotech materials, the visions of science fiction challenge the scientist’s mind to ponder how much of it is mere fantasy and how far we can actually go along the path presented to us.

The keynote “Materials and Energy in Science Fiction: New directions for thought” will introduce into the way science fiction explores the realm of what is possible and present a wide variety of examples of how science fiction imagines new forms of and uses for matter and energy.

# High-Entropy Multi-element Substituted Lithium Argyrodite Superionic Solid Electrolytes

**F. Strauss<sup>1</sup>, J. Lin<sup>1</sup>, G. Cherkashinin<sup>2</sup>, S. Indris<sup>3</sup>, J. Janek<sup>1,4</sup>, A. Kondrakov<sup>1,5</sup> and T. Brezesinski<sup>1</sup>**

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Solid-state batteries (SSBs) are attracting great attention because of potentially higher energy and power densities than conventional Li-ion batteries based on liquid electrolytes. Yet, they are plagued by the development of advanced solid electrolytes (SEs), mainly lacking in ionic conductivity and electrochemical stability; thus, the ongoing quest for exploration of new materials and compositions. Despite increasing research interests in high-entropy materials, the effect of configurational entropy on charge transport properties and electrochemical stability remains largely elusive. Recently, we have shown that high-entropy argyrodites can be achieved via polyanionic/cationic substitution, showing a low activation energy ( $E_A = 0.22$  eV) and moderate r.t. ionic conductivity ( $\sim 1$  mS/cm) [1]. However, the possibility of polycationic substitution and the resulting structure-property relationships have not been explored yet. Within this context, we herein report about the polycationic substitution in argyrodite SEs, namely  $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$  [2]. Using electrochemical impedance spectroscopy and  $^7\text{Li}$  pulsed field gradient nuclear magnetic resonance (NMR) spectroscopy, it is found that polycationic substitution leads to a very low activation energy ( $E_A = 0.19$  eV) and a high r.t. ionic conductivity ( $\sim 13$  mS/cm). These findings are rationalized via neutron powder diffraction in combination with magic angle spinning NMR spectroscopy. The  $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$  SE was also employed in high-loading SSB cells with a Ni-rich layered oxide cathode and found by X-ray photoelectron spectroscopy to suffer from interfacial side reactions during cycling. Overall, the results of this study indicate that optimization of conductivity is equally important to optimization of stability, and that high-entropy lithium argyrodites represent a new playground for rational design of advanced solid electrolytes.

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# Transforming Computational Discovery of Energy Materials and Interfaces

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**Keywords:** Solid-liquid interfaces, energy materials, density functional theory, machine learning

Understanding and controlling the complex and dynamic processes at solid-liquid interfaces in electrochemical devices like batteries, fuel cells, and electrolyzers holds the key to developing more efficient and durable technologies for the green transition. Fundamental and performance-limiting interfacial processes like the oxygen evolution/reduction reactions (OER/ORR) in electrocatalysis [1] and the formation of the Solid-Electrolyte Interphase (SEI) in battery cells span numerous time- and length scales [2]. Despite decades of research, the fundamental understanding of structure-property relations remains elusive. Computational modeling at the scale of density functional theory (DFT) and ab initio molecular dynamics (AIMD) generally provides sufficient accuracy to describe the making and breaking of chemical bonds at these interfaces [3]. Still, the calculational cost is often prohibitively high to reach sufficiently long time- and length-scales to ensure proper statistical sampling [4]. Machine learning (ML) potentials offer a potential solution to this challenge. Still, the training of ML-based potentials capable of handling liquid (organic or aqueous) electrolytes remains a fundamental challenge since the potential must capture both intra- and intermolecular interactions in the electrolyte and during chemical reactions at the interface [5]. Here, we present new approaches for machine/deep learning models to predict the spatio-temporal evolution of electrochemical interphases in batteries, e.g., Li-dendrite formation [6], and electrocatalytic systems such as the platinum-water interface [7]. We also discuss the development of methods for uncertainty quantification training and evaluating neural network ensemble models [8] and AI-based optimal experimental design [9] using models trained on multi-sourced and multi-fidelity data from multiscale computer simulations operando characterization, high-throughput synthesis, and laboratory testing. Finally, we will give our perspectives on a path towards better and smarter batteries by combining AI with multisensory and self-healing approaches [10].

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# **Critical Materials of the Transition in the Energy and Industry Sector – Status, Assessment and Perspectives**

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The transformation towards a climate-neutral energy and industrial system requires in particular the switch to renewable energies and the implementation of energy efficiency measures. Turning away from fossil energies means, on the one hand, both a reduction in greenhouse gas emissions and a massive decrease in the (fossil) consumption of primary energy resources. On the other hand, there is a not inconsiderable consumption of non-energy resources, including metals in particular. If their worldwide occurrence is limited or if the supply is dependent on only one or a few countries, these are also referred to as critical materials. Moreover, they often compete with other applications such as from the IT sector. Since they are usually also functional materials, they cannot be replaced at will in the event of a possible shortage situation.

It is therefore essential to address the climate-energy-resource nexus, i.e. to analyse negative or positive trade-offs between climate change mitigation and the consumption of critical materials. This should include both technologies already on the market (such as wind turbines) and technologies in development status. In the case of the latter, the challenge is to identify possible resource restrictions already in the basic research stage, which could arise later in commercial use.

The presentation will use examples to present methods and concepts that can be used to determine the resource consumption of long-term climate protection scenarios in Germany and the EU.

# Pilot-scale preparation of nickel-cobalt based anode materials for alkaline electrolysis

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In recent years, the demand for renewable energy has grown rapidly due to the depletion of conventional sources. Water electrolysis can produce hydrogen and oxygen, which is becoming increasingly desirable and experiencing rapid advancements at this moment. Research focuses on stable and high-efficiency anodes for alkaline water electrolysis. However, upscaling these electrodes into pilot-scale synthesis allows direct property-performance correlations in industrial settings which remains challenging (Kang, Yang et al. 2018). We aim to bridge this gap by using commercial powder catalysts and developing well-dispersed inks through various techniques and preparing electrodes by spray coating to demonstrate catalytic activity. In the first step, commercial micropowders are characterized for their size and composition using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). Using analytical centrifugation and Hansen parameter determination (Bapat, Doris 2020), dispersion of the well-characterized micropowder in organic solvents is systematically evaluated as a function of their stability. The selected dispersions will be then coated on Ni plates through simple spray deposition where the effect of surface treatments such as plasma on the substrates will also be investigated. By combining various complementary techniques, the electrodes will be characterized in-depth in terms of their structure, composition, surface topography, and porosity. These electrodes will then undergo catalytic testing and their physicochemical properties will be correlated. By optimizing various electrode material properties, we will facilitate the first step in large-scale electrode depositions more relevant for the chemical industry where the catalytic performance can still be tuned.

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# On the combustion of silicon as a carbon-free fuel for power generation

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Solar power and wind energy are not available all the time. To guarantee a continuous power supply, it will hardly be possible without stationary electricity power plants. In the sense of a CO<sub>2</sub>-free power supply, coal must be replaced as an energy carrier. Hydrogen can only fill the gap to a limited extent, since its low volumetric energy density makes it difficult to store in large quantities. The production of green hydrogen in large amounts is still a challenge. Metal particles, or especially silicon, are suitable as storable and carbon-free fuels. Silicon is the most abundant element in the earth's crust after oxygen and is ubiquitous as stone. Like carbon or hydrogen, it has the distinct advantage that the combustion products do not have to be collected for direct recycling. It is quite conceivable that silicon particles could be used in a combustion process like coal to generate electricity in a power plant. The transport and operational safety of silicon particles is not critical. The energy required for production can now be provided by environmentally friendly or regenerative methods. Silicon reacts strongly exothermically with air and water. The diffusion-controlled combustion process may be realized in a classical particle burner. The most important difference to coal is that mainly condensed combustion products are formed. The characteristics of the combustion of silicon with respect to the burning behaviour, the combustion temperature and the particle size-dependent combustion time of silicon particles are currently being investigated at the Fraunhofer ICT as quasi-stationary combustion stabilized with a hydrogen-oxygen flame. The results provide parameters for the design of combustion chambers and exhaust gas cleaning. The resulting combustion products are also being characterized. Further investigations are concerned with the potential use of the main combustion product SiO<sub>2</sub>, for example as construction sand.



# In-silico design of magnetic materials for energy applications

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As it is said, “die Energiewende ist eine Materialwende” (the energy transformation is a materials transformation), the engineering and employment of advanced materials are of pivotal importance for the sustainable development of our society. In contrast to the conventional ways based on the trial-and-error experimentation, accelerated materials design following the Materials Genome initiative provides valuable solutions to map out the composition-processing-(micro)-structure-property relationships of various functional materials. In this work, I am going to demonstrate the implementation of two major approaches for design materials, i.e., high-throughput calculations and machine learning modelling. Taking magnetic materials as an example, a fully-fledged high-throughput workflow has been designed and applied to screen for promising candidate materials as permanent magnets and magnetocaloric as well as spintronic materials [1]. It covers both the thermodynamic and transport properties, and can be easily extended to optimise the other classes of functional materials. The application of such a workflow will be demonstrated on antiperovskite [2], all-d-metal Heuslers, and carbides/nitrides with nano-laminated structures [3]. In the second part, I will demonstrate how various machine learning techniques can be applied to tackle the current challenges in materials science, such as forward inference using random forest [4], inverse design using generative deep learning [5], and closed-loop optimization based on Bayesian optimization [6] to perform multi-objective optimisation of materials.

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# **Abstracts of Posters**

(in alphabetical order)

# Gradient Ceramics in Polymer hybrid electrolyte for solid state Li-ion batteries

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Polymer electrolytes are attractive candidates to boost the application of lithium metal batteries. Single ion conducting polymers can reduce polarization and lithium dendrite growth, though these materials are eventually mechanically overly rigid, thus requiring mobilizers such as organic solvents to transport Li ions. Inhomogeneous distribution of the solvent and resulting preferential Li transport pathways might yield favored spots for Li plating, imposing additional mechanical stress and even premature cell short-circuits. Here, we explored a ceramic-in-polymer hybrid electrolyte consisting of a polymer blend of single-ion conducting polymer and PVDF-HFP, including EC:PC as swelling agent, and silane-functionalized LATP particles. The hybrid electrolyte features an oxide-rich layer that notably stabilizes the interphase toward Li metal, enabling single-side lithium deposition for over 700 hours at a current density of  $0.1 \text{ mA cm}^{-2}$ . Also, the incorporated oxide particles significantly reduce the natural solvent uptake from 140 to 38 wt.-% despite maintaining reasonably high ionic conductivities. Its electrochemical performance was evaluated in  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NMC622)||lithium metal cells, exhibiting impressive capacity retention over 300 cycles. Notably, very thin  $\text{LiNbO}_3$  coating of the cathode material further boosts the cycling stability, resulting in capacity retention of 78 % over more than 600 cycles, clearly highlighting the potential of the hybrid electrolyte concept.

## **Physisorption studies about tuning of mesoporosity in silica monoliths controlled by hydrothermal treatment**

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Hierarchical silica monoliths with macro-mesopores have high potential as support for catalysis and adsorbents with fine efficiency and productivity for a number of applications. In this study, we performed detail physisorption studies of mesoporosity in silica monoliths treated at various hydrothermal temperatures. Basic aim of this study was to investigate the possibility of controlled tuning of mesoporosity and understanding the connectivity of mesopores in silica monoliths by using series of hydrothermal treatments. We systematically increased the temperature from 80°C to 95°C by varying 3°C and 95°C to 110°C by varying 5°C. Comparative studies by two different adsorptive (Ar87K and N<sub>2</sub>77K) confirmed the pore blocking at lower hydrothermal temperature and open mesoporous system at higher temperature with increase in mesopore size. Adsorption and desorption hysteresis scans further explored the type of connectivity in mesoporous silica monoliths that somehow reflects the data from NLDFT pore size distribution of different adsorptive. This study successfully concluded that the lower hydrothermal temperature leads to pore blocking in mesopores space, but there is no cavitation found in silica monoliths and higher hydrothermal temperature leads towards open mesopores space, but overall pore volume remains same. A systematic increase in pore size distribution with orderly increase of temperature confirmed the controlled tuning of mesopore space over wide range of hydrothermal temperatures. By every 3°C increase in temperature leads to an increase of by 1 nm in average pore size distribution till 95°C. The higher temperature from 95°C to 110°C leads to open mesoporous system with systematic change in mesoporosity by 4nm having a lower surface area. Further more we are studying the effects of tuned mesopore space on flow catalysis.

# DFT, TDDFT investigation of the structural, electronic, and optical properties of lead-free perovskite

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The density functional theory (DFT) and time-dependent density-functional theory (TDDFT) have been used in this work to investigate the structural, electronic and optical properties of the inorganic perovskite CsBX<sub>3</sub> (B = Pb, Sn, Ge; X = I, Br, Cl) using both the Perdew–Burke–Ernzerhof parameterization of the generalized gradient approximation and the screened hybrid functional of HSE non-local approximation.

The commercialization of photovoltaic devices has increased the focus on lead (Pb) free, non-toxic perovskite solar cells. In this study, Special attention is paid on how the lead's substitution affects the compound's electronic and optical performance.

Electronic calculations show perovskites exhibit semiconducting behavior with direct bandgap, respectively. Optical properties were calculated and discussed, including real and imaginary parts of dielectric functions indicate that these materials can be the effective candidates for the photovoltaic applications.

# Modeling battery intercalation materials on the nano- and micro-scale

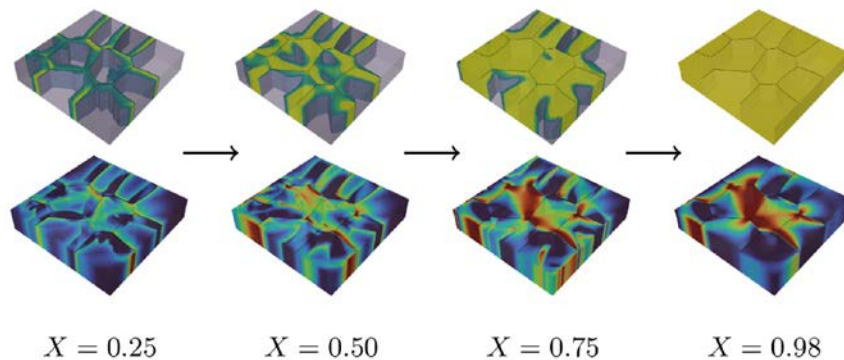
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The research of new electrode materials such as sodium ion intercalation compounds is key to meet the challenges of future demands of sustainable energy storage. Work in the lab is accompanied by computational methods on various scales to increase the knowledge gain about crucial material characteristics. The interplay of chemical, electrical and mechanical forces strongly drives the intercalation behaviour on the microscale and, thus, influences the overall cell performance. The multiphase-field method [1] is a suitable tool to study these multi-physics on the nano- and micro-scale to identify the dominant processes and hopefully guide research towards batteries with longer lifetime and improved performance [2].

Our work [3] highlights the importance to consider pre-existing grain boundaries for nucleation at higher-order junctions, heterogeneity of the intercalation fluxes and grain-by-grain filling behaviour. Anisotropic elastic deformation leads to high stresses at the evolving phase boundaries, especially at high misorientations between neighbouring grains. The maximum principle stress is used as an estimate for degradation by fracture in polycrystals.



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# Computational Screening of Oxide Perovskites as Insertion-Type Cathode Materials

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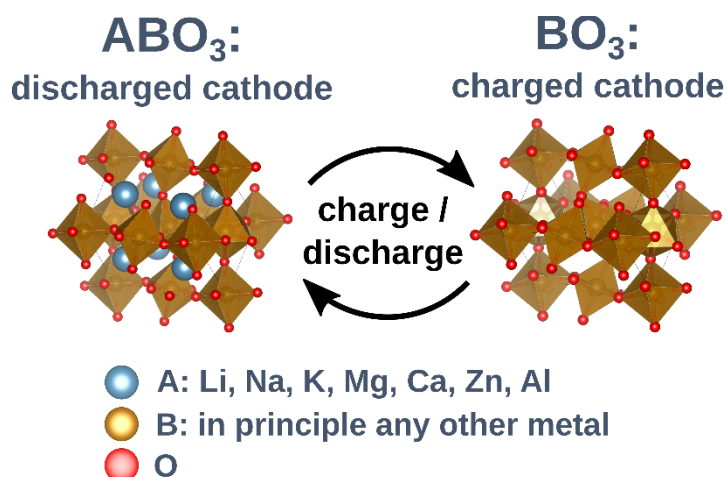
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The intermittency of wind and solar power – the solely sustainable energy sources which are considered to be abundantly available – leaves only one consequence: For the transition towards renewable energy systems, efficient and reliable storage technologies are needed. Batteries are one of the most widely used storage devices but current technology based on the transfer of Li-ions faces several challenges including their dependence on critical materials with respect to both, scarcity and toxicity.

In our contribution we will discuss atomic-scale investigations of potential future battery materials carried out using density functional theory (DFT). We employed a high-throughput approach in order to screen the well known material class of oxide perovskites as insertion-type cathode materials and we derived several crucial battery properties including voltage, volume change during charge/discharge, theoretical energy density and chemical stability for in total 161 compounds. For those candidate materials with promising properties, we evaluated additional features such as voltage profile, the band gap, and diffusion barriers for ionic transport.

Such in silico investigations significantly narrow down the potential materials space for experimental coworkers and thereby contribute to finding green, cheap and reliable battery devices which may support further progress of the Energiewende.



# Impedance Spectroscopy of Microstructured Ceria Thin Films

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Polycrystalline thin films with mixed electronic and ionic conductive properties play a key role in many devices for energy conversion and storage. These devices and their applications require in addition to a careful materials selection an optimized microstructure. A prominent representative of mixed conducting materials is cerium (IV)-oxide (ceria) which is used as functional material in solid-oxide fuel cells and applications for catalysis, gas storage, and gas sensing. Characterization of charge transport properties in novel mixed conducting materials is often done by impedance spectroscopy (IS). In IS measurements, individual transport processes within the material can be distinguished in the spectrum if their characteristic frequencies differ. The IS data is evaluated by using models to correlate the macroscopic properties to the microscopic transport processes. Thereby the correlation, between the microstructure and the macroscopic properties, is often approximated by simple models since the real correlation is not known yet. Here, we show that the microstructure in polycrystalline ceria thin films has a significant impact on the impedance. An experimental approach has been developed to prepare ceria microstructures with an extension of 70 – 200  $\mu\text{m}$  on top of sapphire substrates. Utilizing a lithographic process, single ceria microstructures were electrically contacted and investigated by IS. The ceria microstructures consist of several grains and have defined transport pathways that can be easily identified by optical microscopy. Furthermore, novel computer-aided simulations based on an impedance network model are used to analyze the experimental IS data. In these simulations, the ceria microstructure is accurately mapped and implemented. The results show that the influence of the microstructure on the impedance is stronger than previously thought. Further investigations are promising for establishing a new correlation model.



# Observation of the co-intercalation of solvated sodium ions in graphite by in-situ characterization techniques

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Sodium-ion batteries (SIB) have attracted wide interests as a good alternative to Lithium-ion batteries (LIB), especially for local energy storage. But different to lithium, sodium can only intercalate into graphite, which is the most used anode material for LIBs, in form of co-intercalation in a solvation complex in an ether-based solvent.<sup>1</sup>

The co-intercalation process is not fully understood yet, therefore, the co-intercalation of sodium with different electrolyte solvents was investigated by in-situ characterization techniques.

The received data by in-situ Raman spectroscopy, optical microscopy, and in-situ X-ray diffraction were combined, and the changes in the spectra, images, and patterns were aligned with the co-intercalation and staging process of the ternary graphite intercalation complex (t-GIC). Large differences in the co-intercalation mechanism could be observed between the linear glymes monoglyme, diglyme, and tetraglyme in comparison to triglyme and the intercalation of lithium.

The in-situ measurements were placed into a reference to evaluate the suitability of the in-situ Raman technique for the studies of battery materials and give an insight into the possibilities and hindrances of the technique.

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# **Experimental investigation of the laminar combustion wave velocity of iron-air flames in a tube burner**

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This poster presents the results of experimental measurements of the laminar combustion wave velocity of iron-air-flames in a model tube burner. The carbonyl iron powder with an average Sauter diameter of about 13  $\mu\text{m}$  was mixed with air at ambient temperature and pressure in an air knife seeder and fed to the tubular burner. The iron-air-flame was stabilized without additional fuel, air preheating, or increasing the amount of oxygen in the gas phase. The stabilization range of the cone flames is quite limited in order to measure constant combustion wave velocities without flame flashback. The measurements were performed using an optical camera with a short exposure time. Analysis of the averaged photos shows that the wave velocity of laminar combustion is about 8 to 12 cm/s for the experimental conditions studied. In addition, the results show a low dependency of the global equivalence ratio on the combustion wave velocity.

# Correlation of Phase Transitions and Diffusion in Polycrystalline WO<sub>3</sub> Films during electrochemical Ion Insertion and Extraction

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The International Energy Agency stated in its “European Union 2020 Energy Policy Review” that in 2016 in the European Union alone 152 TWh were consumed for air conditioning, despite only six percent of the global stock of AC units is operated in the European Union.<sup>1</sup>

The installation of windows with switchable optical properties, so called “smart windows”, e.g. windows based on electrochromic (EC) materials, such as WO<sub>3</sub>, are promising candidates to reduce this kind of energy consumption. The coloration and bleaching of the EC material is based on the reversible insertion and extraction of small ions like H<sup>+</sup> or Li<sup>+</sup> into the material. The diffusion of ions plays a key role in this process and therefore needs to be understood in depth in order to enable the optimization of future devices. Burkhardt et al. found, that the diffusion coefficient in this material is dependent on the concentration of already incorporated ions.<sup>2</sup> We suggest, that this originates from changes in the crystal structure of the WO<sub>3</sub> thin films. To substantiate this suggestion spatially and temporally resolved in situ transmission and in situ Raman spectroscopic experiments were performed during potentiostatic ion insertion and extraction to correlate the diffusion of small ions inside the material with changes of its crystal structure.

The Raman experiments reveal that the WO<sub>3</sub> undergoes structural transitions during hydrogen insertion, from its initial structure to a tetragonal structure. We found, that there is a strong correlation of changes in the crystal structure of the thin film and the acceleration of ion diffusion in the material.

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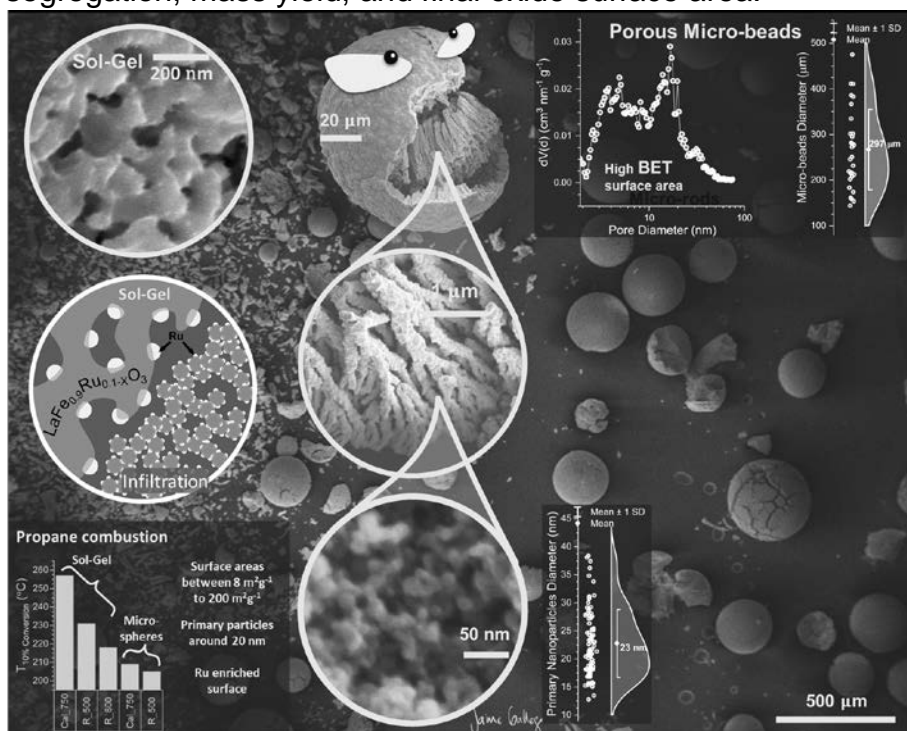
# An easy method to obtain high surface area perovskite-like oxides. $\text{LaFe}_{0.9}\text{Ru}_{0.1}\text{O}_{3\pm\delta}$ as example

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Perovskite-like materials have shown high performance for several physical and chemical applications, including catalytic ones. However, oxides with this structure present a low surface area which limits some real applications. This work shows preliminary results of a simple, reproducible, and extrapolating methodology to prepare high surface area perovskite-type oxides. This case study evaluated  $\text{La}_1\text{Fe}_{0.9}\text{Ru}_{0.1}\text{O}_{3\pm\delta}$  as a first example. Polymeric commercial microspheres were used as hard templates in an infiltration/calcination methodology to obtain those mixed oxides [1-3]. We found that the polymer's thermal stability and the calcination procedure affected the surface area (SA) and crystalline phase purity. Exsolvable  $\text{La}_1\text{Fe}_{0.9}\text{Ru}_{0.1}\text{O}_3$  were obtained with SA between  $8 \text{ m}^2\cdot\text{g}^{-1}$  and  $200 \text{ m}^2\cdot\text{g}^{-1}$ . SA affects the behavior during the Ru exsolution, final Ru/parent-oxide surface composition, and its catalytic behavior in propane combustion. We used different analytical techniques such as gas sorptometry, XRD, TGA-MS, XPS, and SEM. This preparation methodology is being developed to produce several mixed oxides, focusing on perovskite-like ones. As preliminary findings, it is worth mentioning that the thermal treatment of freshly infiltrated micro-spheres strongly influences the oxide phase segregation, mass yield, and final oxide surface area.



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# Gas-phase reactions of ferrocene: New insights from microreactor studies using synchrotron radiation

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Ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) is among the most widely used precursors for the gas-phase synthesis of carbon nanotubes (CNTs) and iron oxide thin films [1]. Previous studies have shown that the morphology, crystallinity, and growth kinetics of CNTs depend significantly on the decomposition products of the precursor, which requires a comprehensive knowledge of the gas-phase mechanism for synthesis [2].

To address this, we studied the thermal decomposition of ferrocene between 356 and 1250 K in a resistively heated microreactor at a short residence time  $< 40 \mu\text{s}$  experimentally and evaluated the flow field using computational fluid dynamics methods [3]. For analysis, the decomposition products were sampled in a molecular beam, ionized by tunable vacuum ultraviolet (VUV) synchrotron radiation and examined using double imaging photoelectron photoion coincidence spectroscopy ( $i^2\text{PEPICO}$ ).

At temperatures around 900 K, the precursor molecule first breaks down in a homogeneous surface reaction, producing byproducts such as cyclopentadiene and cyclopentadienyl radicals that are rapidly released into the gas-phase. At higher temperatures, ferrocene quickly decomposes in the gas-phase, losing iron and two cyclopentadienyl radicals. When hydrogen is added to the reaction mixture, the decomposition temperature is reduced and the product's branching ratio changes. The primary cause of this variation is the surface-based H-addition reaction of cyclopentadienyl radicals, which leads to the release of cyclopentadiene into the gas-phase. Our approach allows the detection of short-lived gas-phase species and has proven to be useful not only to determine and characterize elusive reactive intermediates, but also to delimit surface and gas-phase chemistry [3].

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# Particle velocity measurements of gas-assisted iron dust flames in a swirl stabilized combustion chamber

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The transition from a fossil fuel-based to a CO<sub>2</sub>-neutral energy sector is associated with many challenges. Renewable energy sources are subject to short- and long-term fluctuations in electricity generation. Large energy storage facilities are needed to compensate for these fluctuations. The storage of excess energy in metals holds great potential in this respect. Iron in particular has a high volumetric energy density and can be used in a redox cycle [1]. To use iron as an energy carrier, fundamental research is required in the field of iron combustion on an industrial scale.

In this study, particle velocities of iron dust flames within a turbulent solid fuel combustor (SFC) are measured using Particle Image Velocimetry (PIV). The SFC is an optically accessible gas-assisted combustion chamber that operates with a thermal output in the range of 20 kW<sub>th</sub> and 60 kW<sub>th</sub>. A swirled flame is stabilized featuring a characteristic strong inner recirculation zone. The flame and flow configurations share essential similarities with industrial burners, which typically have poor visual accessibility. As the glass walls of the burner provide perfect optical accessibility, a variety of non-invasive laser-optical diagnostics can be used to gather detailed information about the stabilization of turbulent iron dust flames.

PIV of the dispersed phase is used to measure the velocity of iron particles in the region that is important for flame stabilization. Particle size, oxygen concentration, and thermal power are varied to evaluate their effects on the particle flow field and flame stabilization. Three different particle sizes were investigated with corresponding diameters (D<sub>50</sub>) of 7.7 μm, 17.4 μm, and 30.7 μm. Results show that smaller particles inside and outside the inner recirculation zone exhibit higher velocities under the same operating conditions. In addition, smaller particles are more likely to be transported back towards the burner head by the inner recirculation zone as a result of their lower slip velocities with respect to the surrounding gas phase. While the inlet volume flows are kept constant for an operating condition with higher oxygen concentration, the iron particle velocity increases significantly. This is in contrast to the flow field of the underlying methane combustion, where hardly any changes in the flow field can be seen. This indicates enhanced heat release in the early stages of the iron combustion with increasing oxygen concentration.

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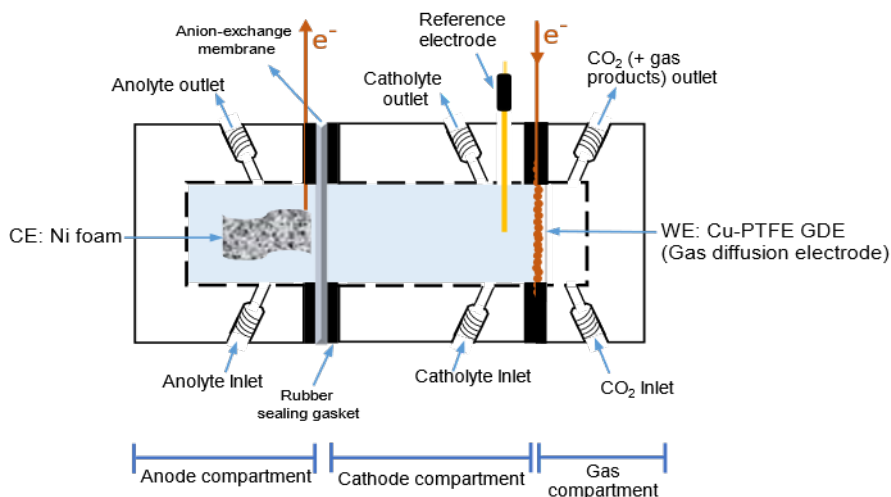
# Influence of PTFE membrane thickness in Gas Diffusion electrode for CO<sub>2</sub> electroreduction

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Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is an excellent way to store green energy in chemical bonds while providing fuels or chemicals. The CO<sub>2</sub>RR in gas diffusion electrodes uses a gas diffusion layer (GDL) to enhance the mass transport towards the catalyst layer, which enables the reduction of CO<sub>2</sub> at high current densities (> 100 mA cm<sup>-2</sup>). The porosity and hydrophobicity of GDL are essential to ensure gaseous CO<sub>2</sub> transport to the solid catalyst layer and prevent electrolyte flooding. When electrolyte enters the catalyst layer and the GDL, the CO<sub>2</sub> transport to the catalyst layer is hindered due to its low solubility in the electrolyte.<sup>[1]</sup> Polytetrafluoroethylene (PTFE) based membrane as GDL shows high hydrophobicity even at negative potentials, whereas carbon-based GDL are flooded due to electrowetting effects and H<sub>2</sub> formation is promoted over the CO<sub>2</sub>RR.

Here, gas diffusion electrodes (GDEs) were fabricated via sputter deposition of Cu with a thickness of 730 nm on PTFE membranes with thicknesses of 25-51 μm, 75 μm, and 203-305 μm. The CO<sub>2</sub>RR on the Cu – PTFE GDEs was performed in a flow cell having three compartments (figure 1).<sup>[2]</sup> The thickest membrane showed the lowest activity for CO<sub>2</sub>RR, due to a decreased transport of CO<sub>2</sub> to the three-phase boundary where the CO<sub>2</sub>RR occurs. The total Faradaic efficiencies considering the liquid and gaseous CO<sub>2</sub> products were higher for the membrane with a thickness of 75 μm.



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# Influence of composition on structural evolution and material properties of High Entropy Zirconates

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High Entropy Oxides (HEOs) have attracted great interest in recent years due to their unique properties and are promising for future energy applications. Analogous to high entropy alloys (HEAs), they consist of five or more different cations on one or more cation sublattices in approximately same amount. Regarding the application for future thermal barrier coating (TBC) materials for gas turbines, HEOs are promising since the high configurational entropy results in improved phase stability at high temperatures and low thermal conductivity is obtained due to increased phonon scattering. This allows higher process temperatures and will lead to higher efficiency and lower CO<sub>2</sub> emissions of gas turbines. Furthermore, due to the flexibility in composition, the properties of the HEOs can be tuned to obtain corrosion resistant materials with good mechanical properties. However, little is known about the structural evolution of these materials as well as the structure-properties relationships.

In this work, HEOs with the general formula  $A_2Zr_2O_7$  and up to 10 different cations on the A-site have been successfully synthesized by using reverse co-precipitation. The composition has been varied systematically to evaluate its influence on crystal structure and material properties. Chemical and structural characterization was performed using X-ray diffraction, scanning electron microscopy, electron backscatter diffraction and electron microprobe. Differential scanning calorimetry, HT-XRD and long-term annealing experiments were conducted to assess the thermal stability as well as thermodynamic and thermophysical properties of the compounds. The results were compared to the single element counterparts and an easy indicator for single phase prediction of High Entropy Zirconates is given.



# Deposition and characterization of Ru@SILP on Si wafer substrates as designer catalysts

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Selective catalytic hydrogenation is of paramount interest for the conversion of renewable feedstocks into valuable chemicals [1, 2]. Nanoparticles (NPs) immobilized on supported ionic liquid phases (SILPs) have been found as adaptive and multifunctional catalysts for selective hydrogenation of different substrates due to synergistic effects between NPs and SILPs, affecting e.g., the morphology and catalytic properties [3]. Knowledge about the spatial distribution of NPs on the SILP and, the electronic interaction between the SILP and the NPs are of great interest to optimize such catalysts. Most of the NPs@SILP studies so far focused on powder-based supports, however, are not compatible with certain characterizations due to the undefined geometry and high surface roughness of the powder supports.

Herein, heterostructures made of anchored SILPs decorated with Ru NPs are synthesized on atomically flat Si wafer surfaces. The synthesis involves two steps where first the SILP is grafted onto the pre-cleaned Si wafers via chemisorption followed by a deposition of Ru NPs via an organometallic approach. Multiple complementary techniques such as contact angle, SEM-EDX, AFM, and XPS were applied to characterize the SILPs and NPs on the surface of the Si wafers. Finally, these RuNPs@SILP systems were successfully used as catalysts for the hydrogenation of phenylacetylene. Our recent results demonstrate that these systems perform as active catalysts, similar to their powder-based counter systems, with a defined selectivity towards styrene and ethylbenzene as the conversion products.

Future analysis on these systems aims to explore the interaction between SILPs and NPs by characterizing the RuNPs@SILPs systems *ex-situ* before and after the catalytic reaction using techniques such as XPS. Furthermore, element selective characterization via X-ray-based *operando* spectroscopy is planned to shed light on the interaction between NPs and SILPs during operation.

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# Low temperature ion-exchange based synthesis of highly ordered LiNiO<sub>2</sub> single crystals

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Due to the demand of high energy density materials for lithium ion batteries, cathode active materials with high nickel content are being pursued in an effort to achieve higher energy densities for application in electric vehicles. Particularly the ternary phase LiNiO<sub>2</sub> is a promising candidate, but brings with it various issues including poor structural stability during storage, cycling and synthesis. When prepared *via* solid-state synthesis, the material is prone to form with disorder of Li and Ni on the 3a and 3b sites, leading to residual occupancy of Ni<sup>2+</sup> in the Li layer. These point defects severely hinder full lithiation during discharge, thus massively reducing the practically available capacity. Here we present an alternative, two-step synthesis approach that avoids the formation of Ni on the Li site occupational defects. First, NaNiO<sub>2</sub> is synthesized, which features no Ni occupancy in the alkali layer due to the larger difference in radius between Ni<sup>2+</sup>/Ni<sup>3+</sup> and Na<sup>+</sup> ions. It is then subjected to a Na/Li ion exchange reaction under mild conditions. We thereby obtain a LiNiO<sub>2</sub> material without interlayer Ni occupancy defects and confirm the previously empirically predicted stabilization of highly delithiated states during electrochemical cycling.<sup>[1]</sup> Furthermore, this method also allows for the size-tailored low-temperature synthesis of de-agglomerated monolithic LiNiO<sub>2</sub> particles, a strategy that may be used to gain fundamental insights into the size-property relations of single crystalline LiNiO<sub>2</sub>.

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# ALD Zirconia Coatings on Ni-rich Cathodes in Solid-State Batteries: Correlation between Surface Constitution and Cycling Performance

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While the shift to battery-powered mobility, as one essential part of the energy transition, is gaining increasing significance, there is an ongoing push to improve vehicle range and safety. As the technologically mature lithium ion batteries are expected to approach their performance limits in the not too distant future, solid-state batteries have been drawing considerable attention based on the hope for potentially increased energy density and safety.

Composite electrodes made from Ni-rich layered oxides and lithium thiophosphate solid electrolytes are one of the most promising material combinations for high energy and power density SSB applications. However, protective coatings are required to address their interfacial incompatibility.

The proposed contribution showcases the deposition of nanometer-thin, conformal ZrO<sub>2</sub> layers onto LiNi<sub>0.85</sub>Co<sub>0.10</sub>Mn<sub>0.05</sub>O<sub>2</sub> (NCM85) using atomic layer deposition (ALD). Special emphasis is put on the structural, morphological and chemical evolution of the ZrO<sub>2</sub>-coated NCM85 upon heat treatment, a processing step often required to boost battery performance. The coating properties have a strong effect on cyclability of high-loading SSB cells. After “mild” annealing (at ~400 °C), the NCM85 cathode material delivers high specific capacities (~200 mAh/g at C/10) and exhibits improved rate capability (~125 mAh/g at 1C) and stability (~78 % capacity retention after 200 cycles at 0.5C), enabled by effective surface passivation. However, annealing temperatures above ~500 °C lead to the formation of an ionically insulating layer that negatively affects the cycling performance. Overall, this contribution highlights that the preparation conditions for a given material combination need to be tailored carefully for the application in SSBs and that ALD is a useful surface-engineering technique towards this goal.

# Investigation of iron particle combustion behavior in the exhaust gas of a methane Bunsen flame

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The combustion behavior of iron particles in a variety of different combustion scenarios is a current topic of high interest for sustainable energy systems. Phenomena, such as the formation of nanoparticles, can be investigated for a fundamental understanding of iron combustion in various combustion scenarios. This investigation aims to deepen the understanding of particle transport and combustion in a methane Bunsen flame.

Within this experimental work, iron particles are in-situ measured as they move through the methane flame front and oxidize in the exhaust gas. Here, iron particle with a median diameter ( $d_{50}$ ) of 8  $\mu\text{m}$  are used. The methane Bunsen flame is operated at a equivalence ratio ( $\Phi$ ) of 0.54 corresponding to a oxygen content in the exhaust gas of 20%. During the measurements, particle concentrations of 25  $\text{g}/\text{m}^3$  (A) and 150  $\text{g}/\text{m}^3$  (B) were used and measured prior to ignition using extinction measurements. Recorded Mie-scattering signals of the particles within a laser sheet recorded at 20 kHz are applied to evaluate the transport and combustion behavior of the iron particles.

Using particle tracking velocimetry (PTV), the particle dynamics are investigated following the trajectory from the unburnt gas to the post-flame zone. Based on this, particle velocity profiles are evaluated, which are spatially conditioned on the reconstructed methane flame front. Furthermore, the formation of nano oxides in the exhaust gas is visualized. In the present work, the effects of the gas phase- and particle phase velocity on the nanoparticle cloud topology is evaluated.

This research is conducted within the framework of the Clean Circles project. For more information see: [www.tu-darmstadt.de/clean-circles](http://www.tu-darmstadt.de/clean-circles)

# **Sonochemical modification of highly conductive carbon blacks and its effect on the performance of a proton exchange membrane fuel cell**

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Highly conductive carbon blacks (CBs) are becoming increasingly important for applications in the field of energy storage (e.g. battery) and energy conversion (e.g. PEMFC). CBs are mostly used in electrocatalysis as supports for anchoring nanoparticulate electrocatalysts. For battery electrodes, CBs serve as conductive additives and are used in various anode and cathode structures. In both fields, CB together with other components (e.g. catalyst and proton conductive polymers) undergo a homogenization process in a colloidal state before electrode layer coating. However, the interactions between these components and the surface of the CB particles are highly complex. Hence the surface properties of CB particles play a crucial role in the engineering and resulting design of the electrode layer and later on in the performance of the PEMFC. In general, ultrasonication is a common laboratory method to homogenize such ink slurries. When ultrasound is used, apart from the physical effects induced by acoustic cavitation, further chemical effects such as the dissociation of water molecules into radicals (sonolysis) could occur, through which other chemical reactions will follow. To this date and from the authors' knowledge, there are no detailed studies on the effects of ultrasound on highly conductive CBs such as Vulcan XC72R, Ketjen Black, and Super C65. To leverage our understanding of the effect of ultrasound treatment, physicochemical properties of commercial CBs were investigated, including electrical conductivity, particle size distribution, isoelectric point, and oxygen-containing surface groups. Finally, the influence of ultrasonication on PEMFC performance was investigated. It was found that the effect of ultrasound intensity strongly depends on the surface structure of the CB used. High surface CB (~ 1000 m<sup>2</sup>/g) preserved its initial basicity after intense sonication and the effect of sonication on PEMFC performance is negligible. In contrast, both (initially basic) medium- and low-surface-area CBs exhibit an acidic surface after intense sonication (< 250 m<sup>2</sup>/g) and showed a decrease in PEMFC performance. It is assumed that the sonochemically formed free radicals form acidic groups on the surface by oxidation, but due to their short lifetime, they are unlikely to reach the surface of the pore system of high surface area CBs.

In conclusion, several methods were proposed and studied to identify the physicochemical properties of different CBs and to portray the importance of monitoring the processing step and characterizing potential modifications during processing.

# Ignition of single iron particles in oxygen-rich laminar flows

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The transition toward a climate-neutral energy system requires chemical energy carriers and innovative thermochemical energy conversion processes [1]. As carbon-free chemical energy carriers, metals, especially iron (Fe), reveal a high potential to store and transport energy produced by wind and photovoltaic power plants. The combined reduction-oxidation concept [2] using recyclable iron as energy carriers reveals great potential for future energy systems enabling carbon neutrality but raises a lot of open challenges concerning the combustion characteristics and thermodynamic efficiency that request extensive fundamental research [1].

In the current work, the ignition behavior of single micrometer-sized iron particles is experimentally investigated in a laminar flow reactor (LFR) by using optical diagnostics. The LFR utilizes premixed CH<sub>4</sub> flat flames to generate high-temperature and oxygen-rich atmospheres in the post-flame zone. Boundary conditions such as gas temperatures and gas velocities were carefully examined in previous experiments. Single iron particles were sieved to four size classes from 25 to 125 µm. This study is performed in five gas atmospheres with 0 to 40 vol% oxygen content, with similar gas temperatures at about 1800 K. The particle size and irregular shape are in-situ measured by a diffuse backlight-illumination (DBI) system at high temporal (i.e., 5 kHz) and spatial resolution (50 lp/mm). Simultaneously, broad-band luminosity imaging (LU) with a CMOS camera is applied to determine the particle ignition at 5 kHz. The ignition delay time is defined as the first instant when particles emit visible luminosity signals above the background. By tracking the change of the sphericity, the melting time can be determined in the time-resolved DBI images, providing essential information on the mean particle heating rates. The results show that the heating rates increase with decreasing particle diameter. By correlating multi-parameter data from DBI and LU, the ignition is delayed as particle diameter increases. In addition, particles ignite faster with more oxygen, showing the importance of oxygen diffusion for ignition behavior. This study enables a better understanding of single particle combustion and, more importantly, provides a novel data set for advanced numerical simulations.

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## Secondary Ions VS Secondary Electrons for Electrode Microstructures Characterization: Advantages and Perspectives

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Electrodes are a key component of modern Li-ion and solid-state batteries, and their microstructure is recognized to be critical for ions and electrons pathways, (in)homogeneous (de)lithiation, and the localized formation of hotspots and degradation products, among others. All the above affects the most relevant features of batteries, from their energy and power density to their safety and cycle life, underlying the importance of characterizing the 3D organization of the different electrode components, and their correlations with electrochemical performance.

Among the different techniques used to characterize the electrodes microstructure, Secondary Electrons Microscopy (SEM) and Focused-Ion Beam SEM (FIB-SEM) are widely used for acquiring 2D and 3D information, respectively. Despite the advantages of these techniques, one main limitation is that chemically different species, but having similar atomic components or weights, are often not distinguishable.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is based on the analysis of the secondary ions generated through the impact between an accelerated primary ion and the sample. From one side, this technique allows obtaining chemically-specific information and acquiring images of sizes in the order of hundreds of  $\mu\text{m}$ , with a resolution down to 150 nm. On the other side, this technique is strongly surface sensitive, the reason for which it is typically not associated with microstructure characterization.

In this work, we would like to illustrate why we believe that ToF-SIMS can be applied to microstructure characterization thanks to a devoted experimental setup and computational procedures, showing the first results obtained for a case study focused on Si-graphite composite anodes, which are currently at the forefront as next anode generation for commercial Li-ion batteries.

# Exploring the Si-precursor composition for Inline Coating and Agglomeration of TiO<sub>2</sub> via Modular Spray-Flame and Plasma Reactor

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Inline particle coating after the particle formation process to preserve its specific properties is hardly investigated scientifically. Tackling that issue, we have studied the use of three different vaporized organo-siloxanes (tetraethyl orthosilicate TEOS, hexamethyldisiloxane HMDSO, and octamethylcyclotetrasiloxane OMCTS) as precursors for direct inline coating of pristine titanium dioxide (TiO<sub>2</sub>) nanoparticles made via spray-flame synthesis. The inline silica (SiO<sub>2</sub>) coating of the formed titanium dioxide nanoparticles is achieved by vaporizing and sending the chosen organo-siloxane precursors into a cylindrical coating nozzle downstream the particle formation zone of the spray-flame. To further explore the effects on morphology and the quality of the resultant TiO<sub>2</sub>|SiO<sub>2</sub> core-shell nanoparticles, a plasma discharge – i.e. dielectric barrier discharge source – is applied after the coating step. The TiO<sub>2</sub>|SiO<sub>2</sub> core-shell nanoparticles are characterized using Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM), X-Ray Diffraction (XRD), Fourier-Transform InfraRed spectroscopy (FTIR), Brunauer-Emmett-Teller surface area analysis (BET), elemental analysis, and dynamic light scattering (DLS).

Results showed distinct core-shell nanoparticles with shell thicknesses of around 1.5 nm alongside the formation of unattached SiO<sub>2</sub> nanoparticles due to homogenous nucleation of SiO<sub>2</sub>. As the precursor silicon content increased (TEOS < HMDSO < OMCTS), the homogenous nucleation rose to generate materials with high BET surface areas. When employing OMCTS, the high homogeneous nucleation rate led to SiO<sub>2</sub> agglomeration, which resulted in large TiO<sub>2</sub>|SiO<sub>2</sub> agglomerates. Morphologically, the phase composition of anatase/rutile of the produced coated nanoparticles did not vary significantly when compared with the reference uncoated TiO<sub>2</sub> nanoparticles, indicating that the SiO<sub>2</sub> coating is purely a surface phenomenon. Plasma discharge was shown to reduce coated particle agglomeration up to certain extend. Based on these findings, we conclude that the best studied parameters to benefit the synthesis of homogeneously coated TiO<sub>2</sub>|SiO<sub>2</sub> nanoparticles are (i) using TEOS as a coating precursor to minimize SiO<sub>2</sub> homogeneous nucleation and (ii) applying a plasma discharge to slightly reduce coated particle agglomeration.



# Experimental Pitfalls in the Electrochemical Evaluation of Complex Energy-Related Materials

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Electrochemical energy conversion and storage technologies are expected to have a decisive role in a net-zero-emissions scenario. However, rigorous electrochemical evaluation of electrode/solution interfaces is a challenge. For example, the ammonia detection and quantification in the N<sub>2</sub> electroreduction is overestimated because of nitrate or nitrite impurities or other contamination [1]. Another common problem is the correct determination of the electrochemical active surface area in complex materials since in most of the cases it is underestimated which causes apparent high activities. The problems in the reported activity/selectivity/durability could delay the development of the electrochemical devices in a market-scale. This work points out some of the common pitfalls and proposes some possible solutions to overcome the problems found in the electrochemical evaluation of complex materials [2].

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# **A comparison of mechanistic models for the combustion of iron microparticles and their application to polydisperse iron-air suspensions**

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Despite global efforts to reduce CO<sub>2</sub>-emissions, a large share of countries relies on coal-fired power plants for significant proportions in their energy mix. While several countries have passed policies to phase-out of coal, coal-fired power plants are still planned and constructed in other parts of the world, and they are scheduled to run for decades. In this context, iron is a promising energy carrier which could eventually be utilized in retrofitted coal power plants to produce CO<sub>2</sub>-free energy in the framework of a circular energy economy.

The burning velocity of iron dust flames is a crucial factor in the design of such facilities. Recently, several models for the combustion of micron-sized iron particles and their suspensions in air were developed. However, the models differ greatly in their modeling of the particles' ignition behavior and chemical kinetics.

Real iron dust is polydisperse, which means it is composed of particles with many different sizes. In a propagating flame front, the conversion of the particle fractions starts sequentially according to their size-dependent ignition temperatures and thermal inertia. Therefore, modeling of chemical kinetics and ignition behavior are of fundamental importance in polydisperse iron dust flames.

In our work we apply different particle models with representative ignition behaviors in multiphase, one-dimensional, numerical simulations of polydisperse iron dust flames. The sequential conversion of the iron particles is depicted, which depends on their size and the used particle model. It is demonstrated that the individual particles burn in completely different combustion environments, depending on their position in the polydisperse flame during conversion. This affects their respective overall conversion and contributions to the flame's heat release. In turn, the flame propagation is found to be greatly influenced by the particle size distribution.

This research is conducted within the framework of the Clean Circles project. For more information see: [www.tu-darmstadt.de/clean-circles](http://www.tu-darmstadt.de/clean-circles)

# Electronic transport modelling of high efficiency thermoelectric $\text{Mg}_2(\text{Si},\text{Sn})$ solid solutions

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Thermoelectric (TE) materials generate electricity when subjected to a temperature gradient and vice versa. They have a promising future in applications for converting waste heat into electricity. Improving TE generator performance requires a thorough understanding of a material's electronic and thermal properties. Electronic band structure modelling within the framework of the Boltzmann Transport Equation is a powerful tool to understand the electronic transport properties of a material as it does not require dedicated software, is computationally cheap and utilizes experimental data to estimate relevant band structure parameters. Most TE materials are narrow band gap and heavily doped semiconductors. Usually, the assumption that a single parabolic band, i.e. a single carrier type (majority carriers) is governing the electronic transport is made. But most TE materials have their best properties at temperatures where this assumption loses validity as minority carriers also affect the transport properties significantly. Therefore, multiband modelling of TE materials is required. In this work, we systematically model the electronic transport of  $\text{Mg}_2(\text{Si},\text{Sn})$  solid solutions – a high performance, cheap and non-toxic class of TE materials. We first develop a general methodology to obtain a two-band model and apply this methodology to  $\text{Mg}_2\text{Sn}$  and  $\text{Mg}_2\text{Si}$  – the end members of the solid solution. With our methodology we obtain the density of states masses, scattering potential constants and most importantly the band gap for the TE material. Next, we develop a multiband model for the entire solid solution range and obtain relevant band structure parameters. Our model can be used for optimization of TE materials for better generator performance by identifying optimum carrier concentrations and/or chemical compositions depending on the application scenario.

# Combustion of individual iron microparticles with resolved boundary layers

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Recently, metal fuels are gaining importance as green energy carriers, since they have a higher volumetric energy density than liquefied hydrogen, are recyclable and widely available [1, 2]. Iron, in particular, is the focus of interest for many researchers, since it has low production costs, is expected to form only small amounts of nano-sized oxide particles and has similar burning velocities compared to hydrocarbon fuels such that existing combustion devices can be retrofit to burn with iron [2, 3]. There are only few studies on the oxidation of iron/air mixtures and the micro/macro structures of iron dust flames. Iron differs significantly from other solid fuels such as coal and thus, previous modeling approaches cannot be transferred directly. Unlike existing fuels, which form a continuous flame front, iron particles act as point-like heat sources and therefore can burn in a discrete flame regime [4]. The goal of our work is to understand influencing factors on the flame regime and its implication on flame propagation. The flame propagation is investigated on particle arrays with increasing complexity. Under certain circumstances, iron particles can burn entirely kinetic limited. However, under realistic conditions, iron particles mostly burn in a diffusion limited regime, hence the conversion rate is controlled by heat and mass transfer between the particle and the surrounding gas. Therefore, the heat and mass transfer in the boundary layer and between the particles are fully resolved to provide a detailed assessment of particle interactions. To reduce computational costs, the solid phase is not resolved and instead represented by a 0D combustion model, whereby the heat and oxygen transfer inside the particle is realized through boundary conditions at the particle surface. The combustion model was successfully validated on a single particle using experimental data. Furthermore, the model can capture particles burning in a kinetic limited as well as diffusion limited regime. This research is conducted within the framework of the Clean Circles project. For more information see: [www.tu-darmstadt.de/clean-circles](http://www.tu-darmstadt.de/clean-circles).

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# An Advanced Model for Solid-State Batteries

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## Abstract

All-Solid-state batteries gain increasing interest due to the higher promised energy densities without the use of flammable liquid electrolytes. Two main challenges for solid-state batteries are contact loss and interphase formation, playing a central role in the quality of the solid electrolyte-electrode interfaces. Here, we present a modular phase-field model that is generally applicable for solid-state batteries with different electrodes and corresponding microstructures. The model is based on Multiphase Porous Electrode Theory (MPET), where Li-ion diffusion in solid electrolytes and electrode materials is integrated through a regular solution free energy functional. Modules for contact loss, diffusive interlayers, SEI formation, coatings, and liquid interphases are also implemented, providing numerous modeling options for a comprehensive understanding of electrochemical systems. A thorough comparison between the solid-state and conventional liquid electrolyte models for phase separating electrodes reveals the optimal conditions and bottlenecks of solid-state diffusion and failure mechanisms. The predictions underline contact loss and interphase formation as the crucial mesoscopic morphological characteristics of solid-state systems, setting the ground for in-depth understanding and optimized performance in all-solid-state batteries.

# Heat-treated RhMo-doped PtNi/C Catalysts for the Oxygen Reduction Reaction

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Bimetallic octahedral PtNi nanoparticles are one of the most active electrocatalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cell (PEMFC) cathodes, though they suffer from Nickel corrosion and particle shape degradation. Strategies for increasing the stability of octahedral PtNi particles are alloying with elements such as rhodium or molybdenum and heat treatments in a reducing atmosphere. <sup>[1,2]</sup> Here, the preparation of highly active and long-term stable catalysts is demonstrated by combining both strategies. A solvothermal one-pot strategy was developed for the synthesis of octahedral-PtNi catalysts doped with Rh and Mo. After heat treatment, the quaternary octahedral PtNi(RhMo) catalysts show exceptionally high ORR performance accompanied by improved shape integrity after stability tests.

By means of in situ X-ray diffraction (XRD), in situ scanning transmission electron microscopy (in situ STEM) and identical location scanning transmission electron microscopy and energy dispersive X-ray analysis (IL-STEM-EDX) experiments the structural changes were revealed and correlated to changes in the electrochemical performance of the heat-treated catalyst systems. Our studies show that doping octahedral PtNi catalysts with small amounts of Rh and Mo in combination with heat treatment mitigates Pt diffusion and reduces the amount of nickel oxides on the octahedral surfaces, which induces an increase in activity and stability. Our results show a promising new approach for Pt alloy catalysts for use in PEMFCs.

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# **Fundamental studies on the development of hydrogen traps in ferritic steel and their influence on hydrogen embrittlement during long term exposure**

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Ferritic microstructure with same chemical composition but different degree of defects is prepared to study the development of hydrogen traps in the defect's sites and their influence on hydrogen embrittlement. The influence of hydrogen activity, in-situ hydrogen charging with mechanical loading and exposure time has been studied. Presence of potential hydrogen trapping sites like dislocations, lattice microstrain, high angle, low angle, sigma three and sub grain boundaries, coherent/incoherent inclusions, interface boundaries, grain size, deformed grains among others have been identified. Higher hydrogen activity charging showed higher content of hydrogen loaded into the sample as well as more degradation of mechanical properties with short exposure time while long exposure time with lower hydrogen activity showed less degradation. Higher activity hydrogen charging showed crack nucleation and crack propagation from inclusion interface boundaries. However, higher hydrogen activity charging influences the microstructure by increasing the vacancies concentration <sup>1</sup> and inducing twin boundaries <sup>2</sup> in the microstructure. In-situ hydrogen charging with mechanical loading state showed the evolution of hydrogen peak with lower hydrogen activity charging in thermal desorption spectroscopy of the annealed structure which was not found before. In-situ hydrogen charging with mechanical loading is attributed to bond stretching, flow/evolution of dislocations and vacancies which enhance the intake of hydrogen. Applied stress of 0.80 Re or over Re promotes hydrogen diffusion in steel <sup>3</sup>. Hydrogen charging under mechanical loading states facilitates and stabilizes the trapping of hydrogen.

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# Modelling study of an HCCI-engine concept as a conversion process of gaseous hydrocarbon feedstock

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## Abstract

The purpose of this work is to present a Homogeneous Charge Compression Ignition (HCCI)-engine concept as a process for converting a hydrocarbon gas feedstock, here *n*-alkanes from methane to *n*-heptane, to produce fuels blend/chemicals (oxygenated hydrocarbons, hydrogen peroxide, formaldehyde, and alkenes). This conversion process was studied by a single zone modeling of a four-stroke HCCI-engine. The main production of the target species is generated under portions of the low- to intermediate-temperatures chemistry regimes, which start at nearly 680 K to about 1000 K depending on the *n*-alkane. This maximum production is achieved during the maximum reactivity of the mixture near Top Dead Center (TDC) and survives the rest of the cycle when auto-ignition is avoided. The engine speed of 400 rpm is the favorite for the studied C<sub>1</sub>-C<sub>7</sub> *n*-alkanes [1]. A compression ratio of 5 is nearly optimal for maximum conversion of C<sub>4</sub>-C<sub>7</sub> *n*-alkanes, but higher values are required for the lower-reactivity alkanes of C<sub>1</sub>-C<sub>3</sub> [2]. The synthesis process of fuels blend/chemicals using an HCCI-engine conversion process, with yields up to 85% for *n*-heptane, is now theoretically justified and needs to be experimentally validated. The production of high yields of Syngas (CO and hydrogen) using this concept requires moving from the partial oxidation region of lean *n*-alkane/air mixtures  $\phi \leq 1$  to rich mixtures  $\phi > 1$  [3-5].

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# Manufacturing of flexible high-performance thermoelectric microlayers

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The growing interest in more efficient thermoelectric generators (TEG) for the direct conversion of (waste) heat is not only fuelled by the development of novel thermoelectric compositions but also by the investigation of the influence of processing parameters on the thermoelectric (TE) performance (figure of merit). It could be shown, that the preparation of antimony telluride micro layers by the process of Doctor-Blading led to an improvement of the material properties, when special conditions for the milling and dissolving process were applied.

The manufacturing consists of the following steps: (i) homogenization and structuring of the  $\text{Sb}_2\text{Te}_3$  with a solvent which finishes with a thermoelectric ink; (ii) film coating via doctor blading and (iii) compaction of the sheets via sintering. The obtained flexible thermoelectric sheets have a thickness of about 139  $\mu\text{m}$ .

By physicochemical measurements the following thermoelectric properties of the produced sheets were obtained: Seebeck coefficient of 117  $\mu\text{V}/\text{K}$  and electrical conductivity of  $15 \cdot 10^4$  S/m, resulting in a power factor of 2097  $\mu\text{W}/\text{m} \cdot \text{K}^2$ . These results will be compared to the performance of TE layers obtained by inkjet-printing [1], screen-printing [2, 3], dispenser-printing [4] and stereolithography [5].

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# Transition metal phosphide catalysts for the chemical storage of renewable hydrogen

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Future production of chemicals and energy must be realized without the use of fossil raw materials. Therefore, the provision of renewable H<sub>2</sub> from catalytic water electrolysis is inevitable. Green hydrogen will most likely be converted into liquid chemicals like methanol or LOHC, enabling safe and efficient H<sub>2</sub> storage and transportation. At place and time of energy demand, H<sub>2</sub> can be released and applied in fuel cells to generate electricity. This future scenario requires a variety of efficient catalysts for (de)hydrogenation and electrocatalytic reactions. Today's catalysts consist of expensive and low abundant noble metals like Pt or Pd. Goal of my research is to develop novel catalysts for H<sub>2</sub> activation and production, using low cost materials that are not strategically limited or reducing the required amount of noble metals. In recent studies, transition metal phosphides (TMP), sulfides and nitrides or mixtures thereof were shown to be such efficient alternatives.<sup>[1,2]</sup> However, performance of these catalysts depends on their structure and composition, requiring innovative synthesis routes to tailor their specific properties. Therefore, I follow a novel method to synthesize highly promising TMP-catalysts, that is characterized by the application of organic phosphonium salts (PS) with highly variable composition as catalyst precursor. Application of PS offers several advantages in comparison to state-of-the-art precursors (e.g. PH<sub>3</sub>, Phosphates) as it allows overcoming drawbacks of classical methods, such as high temperatures, limitations in choice of metal species and catalyst supports and the need for explosive and toxic gases. In detail, my contribution presents the development of an effective phosphonium-based TMP-synthesis method, the analysis of the materials and their application in (de)hydrogenation reactions. The general procedure is transferable to the synthesis of metal nitride and sulfide catalysts by applying sulfonium and ammonium salts instead of PS.

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# **New Materials for Electrocatalysis: Their Design, Implementation and Characterization to Make Academic Developments Relevant**

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New, micron and nano-sized functional materials play a key role for future technologies that are currently developed in the field of energy conversion (electrolysers, fuel cells) and electrocatalysis (N<sub>2</sub> fixation, CO<sub>2</sub> reduction). While new materials with outstanding properties are continuously developed, they rarely find their way into – urgently needed – large scale production and industrial applications. Overcoming and bridging this “valley of death” is an interdisciplinary endeavour for which chemical engineering and in particular, particle technology is indispensable. To fulfil this bridging function, the field needs to develop in such a way that we i) collect and make efficient use of more data and develop standard procedures that allow us to better understand process-structure and structure-property relationships, ii) replace idealized conditions and model formulations by technically relevant scenarios (testing at application concentration, full complexity of a formulation mixture) and iii) apply relevant processes (scalable dispersion, R2R-coating) already on lab-scale as integrating research tools. In my talk, I will introduce concepts that we developed and apply in my team and in collaborations with colleagues across the Rhine-Ruhr area to generate hierarchically structured electrode layers that can be integrated into full cells.

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# Doped NaSICON-Type Solid Electrolytes for Sodium-Ion Batteries from Scalable Spray-Flame Synthesis

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Solid-state sodium ion batteries are a viable alternative to lithium ion batteries due to the high availability of raw materials and low costs. Sodium Super Ionic Conductors (NaSICON) are promising candidates for solid electrolytes in such application due to their high ionic conductivity and compatibility with sodium metal based anodes, enabling high energy density [1]. One of the best studied NaSICON materials is  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  (NZSP) with a high ionic conductivity in the order of  $1 \text{ mS cm}^{-1}$  at room temperature [2, 3]. We present spray-flame synthesis (SFS) as a new approach for the synthesis of NZSP. In SFS, metal salts dissolved in organic solvents are combusted resulting in fine metal oxide particles. They are characterized by transmission electron microscopy (TEM) and X-Ray diffraction (XRD) for morphological and structural investigation. Elemental information is obtained via energy-dispersive X-Ray spectroscopy (EDX). Ionic conductivities of sintered NZSP pellets are measured by impedance spectroscopy.

In our approach, nanoparticles with a median diameter of around 5 nm are obtained. The pristine particles consist of crystalline  $\text{ZrO}_2$ , homogeneously covered with an amorphous layer consisting of the elements Na, Si, P and O. After a short annealing step for 1h at  $1000^\circ\text{C}$ , this mixture can be converted almost quantitatively into the desired rhombohedral NZSP phase. Moreover, Mg and Ca were successfully added as aliovalent dopants substituting Zr. Pellets sintered at  $1100^\circ\text{C}$  for 3h to a relative density of ~90% showed – for a material sintered for such a short period of time – a surprisingly high ionic conductivity of up to  $0.79 \text{ mS cm}^{-1}$  (Mg-doped).

In conclusion, a novel approach for the preparation of NZSP allowing the phase formation at relatively low temperatures is demonstrated. SFS is a promising possibility for the scalable production of solid electrolytes, which also holds great potential, especially regarding further improvement of ionic conductivity through targeted doping.

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# Green steel via hydrogen plasma reduction of iron oxides

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Steel is the backbone material of modern civilization. While it enables sustainability via its high recyclability rates or when used in efficient devices for energy conversion (wind turbines), its primary production has strong negative impacts on the environment. This is because, currently, iron is extracted from its oxides through redox chemical reactions that employ C-carrier substances as reducing agents, leading CO<sub>2</sub> as the major by-product. On average, each ton of produced crude steel is accompanied of a staggering amount of ~2.1 tons of CO<sub>2</sub>. This enormous number represents ~7% of all CO<sub>2</sub> emissions on the planet and qualifies ironmaking sector as the heaviest individual industrial CO<sub>2</sub> emitter [1]. To render iron and steelmaking more sustainable, the hydrogen plasma reduction of iron oxides (HyPR), a fully electrified route whose by-product is water, is an attractive alternative. The procedure consists of igniting a hydrogen plasma arc between an electrode of an electric arc furnace (EAF), slightly modified to support small partial pressures of H<sub>2</sub> (e.g. 10%), and the ore to be processed. Inside the arc zone, the mutual collisions between electrons and hydrogen molecules (H<sub>2</sub>) allows for creating high densities of highly energetic hydrogen species, such as the proton (H<sup>+</sup>) [2]. These particles are more reactive than H<sub>2</sub>, thus they help to overcome the reaction's activation energy, enhancing the reduction kinetics. During HyPR, melting and reduction occur simultaneously, allowing the production of liquid iron in one single step without the need for intermediate agglomeration processes of the input ore. We investigated the reduction kinetics and chemical changes of hematite (Fe<sub>2</sub>O<sub>3</sub>) reduced via HyPR, from macroscopic dimensions down to the atomic scale [2]. Full metallization is obtained within 15 min exposure to the hydrogen-containing plasma. Using a broad set of microstructural and local chemistry characterization techniques, including high-resolution scanning electron microscopy, energy dispersive spectroscopy and atom probe tomography, we found that the gangue-related impurities partition preferably to the slag domains. Si-enrichment was observed at the FeO/Fe interfaces and in the interdendritic silicate domains. However, with the progress of the reduction process, the gangue constituents are gradually eliminated from the samples via evaporation, resulting in a final iron product nearly free of impurities.

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# Iron as fuel – Investigating the thermochemical oxidation of iron particles via Mössbauer spectroscopy

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With the increase of installed power of renewable energies, it is possible to phase out the majority of fossil fuels of the worldwide energy mix. However, storing energy from renewable sources in TWh quantities remain challenging <sup>[1]</sup>. Therefore, the *Clean Circles* <sup>[2]</sup> initiative investigates iron as potential energy carrier. Iron is particularly well suited based on its physicochemical properties <sup>[1],[3]</sup>.

Kinetic modelling of iron oxidation and reduction requires precise structural investigation under various condition. Thus, in this work, the oxidation behavior of an iron powder is investigated via <sup>57</sup>Fe Mössbauer spectroscopy, thermogravimetry and x-ray diffraction.

Within the *Clean Circles* project, it is intended that the oxidation and reduction cycles take place in fluidized bed reactors. Therefore, for oxidation experiments a pure commercial iron powder with average particle size of 23 µm was investigated.

During oxidation, sintering was observed at much lower temperatures than expected ( $\geq 300$  °C). Sintering is undesired in later reactor operation, since it changes diffusion lengths and heat transport in the sample <sup>[4]</sup>, as well as the optimal conditions for the reactor. Thus, it directly influences the thermochemical oxidation behavior. The issue of sintering is, to the best of our knowledge, not readily addressed in studies of oxidation behavior of iron powder present in literature but biases the transferability from lab-based investigations to technical applications.

In order to overcome this issue the iron powder was diluted, and the phase composition development was investigated during isothermal oxidation in air for reaction times ranging from 1 min to 24 h.

The reported results greatly aid in understanding the oxidation behavior of the iron powder of interest and set a starting point for further studies.

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# Flow and Bubble Investigations in the Vicinity of In-Liquid Plasmas for Graphene Synthesis

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Graphene proves to be a versatile and promising material in the context of fuel cells and electrolyzers, e.g. for use as selective barriers hindering undesirable crossover in proton exchange membrane fuel cells.[1] In order to achieve commercial breakthrough, large-scale and low-cost synthesis routes for high quality graphene are required. Plasma-in-liquid processes (PiL), which synthesize graphene from hydrocarbon precursors allow for easy upscaling. However, the quality of the produced graphene is sensitive to experimental conditions and therefore not very homogeneous.[2]

Within the presented project, we are developing a continuous-flow reactor to synthesize graphene from ethanol via PiL. The flow configuration aims for a better control of the synthesis process and the graphene quality while allowing for an upscaling of the production. The reactor geometry was designed with the help of CFD simulations. The in-house built reactor allows for variations in the flow of the precursor – both in quantity and direction –, and the gas and for control of the plasma conditions by regulation of the electrode distance, pulse width and repetition rate. This large parameter space enables us to find the best synthesis condition for graphene in the developed reactor. Moreover, we applied laser-optical methods to gain insight into the synthesis process of graphene. Using the shadowgraphy and particle image velocimetry (PIV) techniques, the effect of the plasma on bubble formation and motion and on the flow field inside the reactor has been investigated. Specifically, we aim to understand the relation between the operating conditions on the reactive zone inside the reactor and hence, how the immediate two-phase environment affects the crystallization of the carbon product.

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# A pilot plant for gas-phase nanoparticle synthesis: Products for future energy applications

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The production of nanoparticles in the gas phase is a so called bottom-up method. Advantages of this synthesis route are process control, high purity products and the opportunity to design a continuous processes. In contrast to top-down processes (e.g. milling), the particles are formed from atoms or molecules in an oversaturated atmosphere. Condensation in the form of nucleation and particle growth lead to the formation of solid particles directly from the gas phase. If the condensation is interrupted rapidly, nano-sized particles will be formed and a particle laden gas flow is created.

Actually, the gas-phase synthesis of highly sophisticated particles suffers from limited knowledge of scale-up processes to increase the production rate from grams per hour to kilograms per hour to allow the continuous use in industrial applications. The Pilot-plant for particle synthesis at the IUTA bridges the gap between lab scale and industrial application and aims on one hand for material quantities for first industrial testing and on the other hand to work out up-scaling rules. As a first step, successful synthesis routes from the laboratory scale are transferred into the pilot plant at IUTA and as a next step towards industrial scale. Consequently, process understanding and material synthesis (e.g. for energy applications) are the main research fields during the experimental work. The pilot plant facility consists of three reactor types and a total number of six reactors. In addition, a wet electro scrubber process, which allows to transfer the produced particles directly from the gas phase into the liquid phase, is investigated.

**Flame reactors** use the combustion of liquid or gaseous energy carriers to provide the energy required for the decomposition of the precursor materials. Typically, metal oxides are produced which can be used as catalyst material or electrolyte in solid oxide fuel cells.

**Hot-wall reactors** consist of a tube with electrically heated walls, in order to decompose the precursor. A typical product is a composition of highly pure silicon nanoparticles. Crystalline and amorphous, un-doped and doped, silicon materials can be produced. Silicon nanoparticles are a promising candidate for the use in Li-ion batteries as anode material.

Within **Plasma reactors** a microwave supported Argon/Hydrogen plasma is used for the decomposition of precursor materials. The process features extremely high temperature and quenching rates generate particles with a low degree of aggregation. For example, Graphene is a promising material for electrolyser applications due to its corrosion persistency and high conductivity.



# Kinetic Monte Carlo simulation of the growth of SEI at the Li/electrolyte interphase

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The transition from state-of-the-art graphite anodes to pure lithium metal anodes is considered a promising option to significantly increase the reachable energy density of energy storage devices [1]. However, the high surface reactivity of the pure metal towards liquid electrolytes leads to the formation of a solid electrolyte interphase layer (SEI) and still hinders the commercial application. Although there have been great efforts to understand and stabilize the SEI formation [2], the underlying processes as well as their interplay with the electrolyte composition are still not fully elucidated. This can be mainly attributed to a gap between theoretical models and experimental studies. Atomistic modelling approaches cannot reach realistic length- and time scale while experiments fail to reproduce the key processes that led to the formation of the SEI.

Here, we present an innovative multiscale approach that helps to close this gap. Thereby, stochastic models based on the kinetic Monte Carlo method are parameterized on the basis of molecular calculations. Their comparatively high efficiency leads to significantly increased time- and length scales [2]. In this study we applied the modeling approach to investigate SEI formation on lithium metal in an EC/EMC + LiPF<sub>6</sub> electrolyte. In doing so, we showed a high dependence of the initial SEI formation on the local Li<sup>+</sup>-ion concentration. Furthermore, we identified a layered, mainly inorganic initial SEI which consists of Li<sub>2</sub>CO<sub>3</sub> and LiF and could identify the limiting processes of SEI formation: A reaction limitation in the case of the EC decomposition and a diffusion limitation for the decomposition of the conducting salt. Overall, our approach narrows the gap between simulation and experiment, leads to a fundamental understanding of electrochemical interfaces and thus supports the knowledge-driven development of new energy materials.

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# **Increasing the microscopic surface area of nickel surfaces by plasma application with industrial scalability in mind.**

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Nickel foams provide a large specific surface area. Yet, compared to bulk nickel plates, they are less desirable for industrial applications due to their higher cost and more difficult handling. Ouyang et al. [1] proposed a method to increase the microscopic surface area of nickel foams by creating a coral like hierarchical structure with a plasma treatment.

As part of H2Giga, the hydrogen flagship project by the German Federal Ministry of Education and Research (BMBF), we developed a plasma treatment for industry relevant nickel plates. In our process, surfaces of nickel plates are exposed to a nitrogen plasma for a short amount of time. This leads to the formation of a sponge-like microporous structure and thus a considerable increase in microscopic surface area.

Various parameters have been identified as significant, while some others were found to be insignificant and thus eliminated.

One needs to keep in mind, that transferring plasma processes from geometrically different substrate systems is nontrivial, especially if the difference in topology is as pronounced as it is with foams and plates. Yet, the surface increase could be quickly achieved on simple nickel plates as well as nickel stretch metals. So the process can be easily used on various substrate geometries.

The process has been developed with both industrial compatibility and scalability in mind, as this is a key factor to bring newly developed processes to market.

The treated surfaces have also been examined for their chemical composition. By XPS measurements, it could be shown that some nickel at the surface has been transformed to nickel nitride.

A theoretical model to explain the underlying mechanics of this process is proposed.

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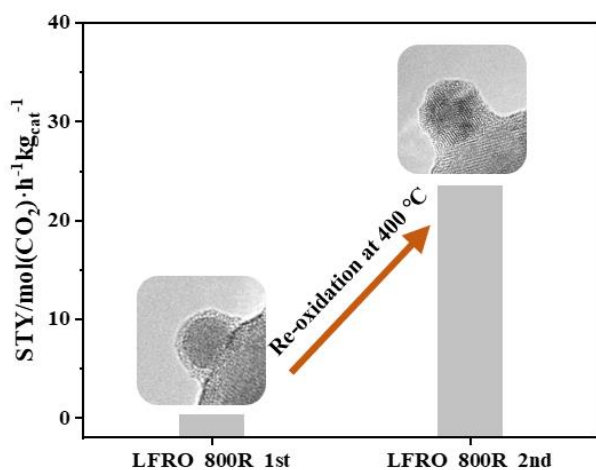
# Self-activation of Exsolved $\text{LaFe}_{0.9}\text{Ru}_{0.1}\text{O}_{3\pm\delta}$ Perovskite in Propane Combustion Reaction

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Precious metal / perovskite compositions prepared by in-situ exsolution from the parent perovskite have been intensively investigated due to the narrow size distribution and socketed structure, which have been used in a variety of chemical and energy conversion reaction.<sup>[1-2]</sup> Herein, we applied Ru doped lanthanum iron perovskite as a model to study the structure evolution during the reduction and re-oxidation process and its impact on the propane combustion reaction. The activity data shows that the rate of  $\text{CO}_2$  production at 210 °C of the reduced sample (LFRO\_800R) is as low as 0.27 mol( $\text{CO}_2$ )/(h·kg(cat)) in the first reaction cycle, while the STY value was dramatically enhanced to 23.5 mol( $\text{CO}_2$ )/(h·kg(cat)) when measured for the second time. The seemingly activation phenomenon was investigated by systematic characterization. It was revealed that  $\text{Ru@FeO}_x / \text{LaFe}_{0.9-x}\text{Ru}_{0.1-y}\text{O}_{3-\delta}$  structure was formed after reduction at 800 °C, where the



active Ru was covered by an inert  $\text{FeO}_x$ . The  $\text{FeO}_x$  layer will deform when treated at 400 °C in an oxidizing atmosphere, exposing more active sites for the propane combustion reaction. The present study therefore provides detailed insights into the structure evolution of the doped perovskite during the reduction and re-oxidation process, which may guide the preparation of highly efficient catalysts for practical application.

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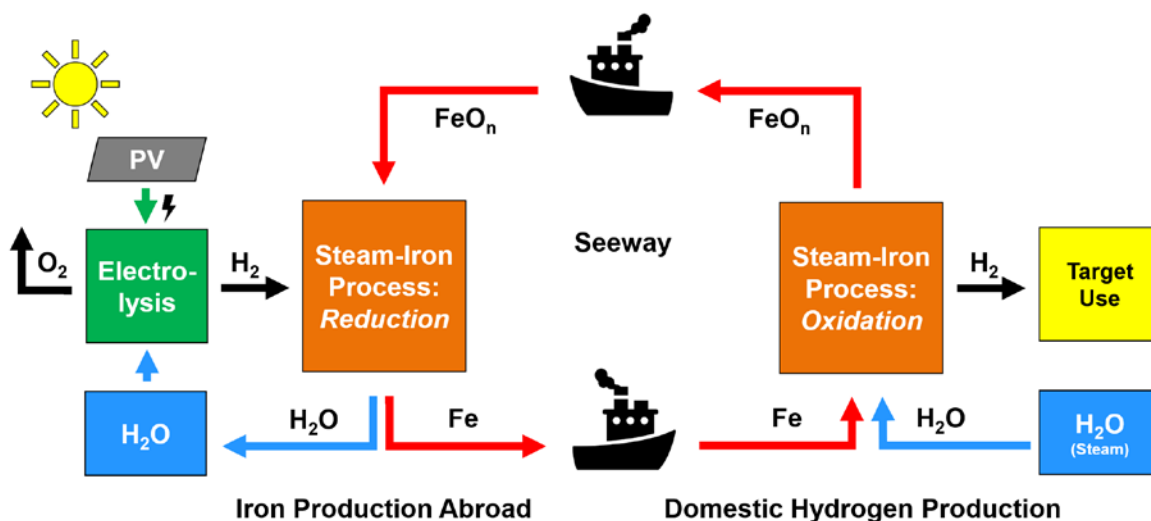
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# Steam-Iron Process for Storage and Transport of Hydrogen

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The strived decarbonization of the energy sector asks for regenerative energy sources. As a promising candidate, hydrogen comes into focus. The circumstance of the different local availability of wind and solar energy to produce “green hydrogen” asks for storing and transporting solutions. Present proceedings to store and transport hydrogen are posing various problems regarding safety and efficiency aspects. Utilizing the iron-steam process to store hydrogen in metal systems provides a promising approach to overcome mentioned problems. The idea is to reduce specially developed metal systems with hydrogen produced by electrolysis in a region with high availability of regenerative electrical energy. Using this process electricity is stored in the sense of a chemical battery in iron and can easily be transported. In the destination area the metal will be oxidized by steam to receive regenerative hydrogen. Main advantages of the researched process are the transport of hydrogen without special safety precautions and the presence of transport capacities in million tons scale.



## Insertion / De-insertion of Magnesium into the Bi Modified Au Electrode:

### DEMS and EC-STM Study

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Magnesium based secondary batteries have been regarded as a viable alternative compared to the immensely popular Li-ion systems owing to its high volumetric capacity.<sup>1</sup> In the past few years there has been great deal of interest in electrode with Sb and Bi as the anode for the rechargeable batteries.<sup>2,3</sup> Bi-nanotubes as an anode material for Mg alloying/de-alloying showed superior cycling stability and rate performance in 0.1 M Mg(BH<sub>4</sub>)<sub>2</sub>-1.5 M LiBH<sub>4</sub>-diglyme.<sup>4</sup> a high initial specific capacity of 180 mAh/g was observed Using electrodeposited Bi-CNT composite materials as magnesium battery anodes in Mg(ClO<sub>4</sub>)<sub>2</sub>/MeCN electrolyte.<sup>5</sup>

Magnesium deposition/dissolution on Au and Bi modified Au electrodes were investigated in 0.5 M MACC/TG electrolyte. The pre-cathodic peak at about 360 mV (vs. Mg/Mg<sup>2+</sup>) is related to the alloying of Mg with Bi adlayers to form Mg<sub>3</sub>Bi<sub>2</sub> alloy. The ratio of the amount of the alloyed Mg to that of the deposited Bi calculated from the corresponding peak charge is close to the theoretical value of 3:2 for Mg<sub>3</sub>Bi<sub>2</sub> formation. During the alloying process of Mg with Bi no ethylene formation was observed as opposed to the case of the Mg bulk deposition.

As observed by STM in MACC/tetraglyme electrolyte, the Bi bulk structure is similar to that in the aqueous solution. The Mg alloying and bulk deposition (big particles) were observed and almost all of these deposits could be dissolved reversibly. After the Mg alloying and bulk deposition, the surface of the electrode was smoother and the crystalline structure of Bi does not remain as observed at the beginning.

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# Defects strengthening by tenon-and-mortise-like interfaces in biphasic Mn-based layered cathodes for robust Na-ion batteries

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Layered cathode materials are commonly used in lithium and sodium ion batteries, but their structures prone to degradation during battery operation. The rigid fracture is the one of the key factors for degradation of functional materials, in particular the layered materials. Recently, the microstructure and defect engineering have broken a new ground in decreasing the rigid fracture and facilitating electrochemical performance of cathode materials. Herein, we introduced a buffer interface (tenon-and-mortise-like) in the biphasic layered oxides to construct an enhanced cathode for SIBs. As shown in Figure 1, this phases overlap is deemed to a tenon-and-mortise structure that has been widely served as the buffer structure in traditional Chinese wooden architecture. We revealed that the introduction of tenon-and-mortise-like interfaces results in a mild and “snake-shaped” evolution during Na<sup>+</sup> desodiation/sodiation processes, which was demonstrated by *in-situ* XRD. Through high resolution scanning transmission electron microscopy and neutron diffraction, the detailed structure of the high-density tenon-and-mortise-like interfaces in the materials are characterized before and after cycling. And they are stable during the long-term electrochemical cycling, leading to a superior cycling life for the retention of 84.2% after 1000 cycles at 8C. This work provides an artful defect engineering strategy to enhance the strength of layered cathodes for SIBs without adjusting the composition. The buffer mechanism of tenon-and-mortise-like interfaces may guide the optimization for the other electrode materials.

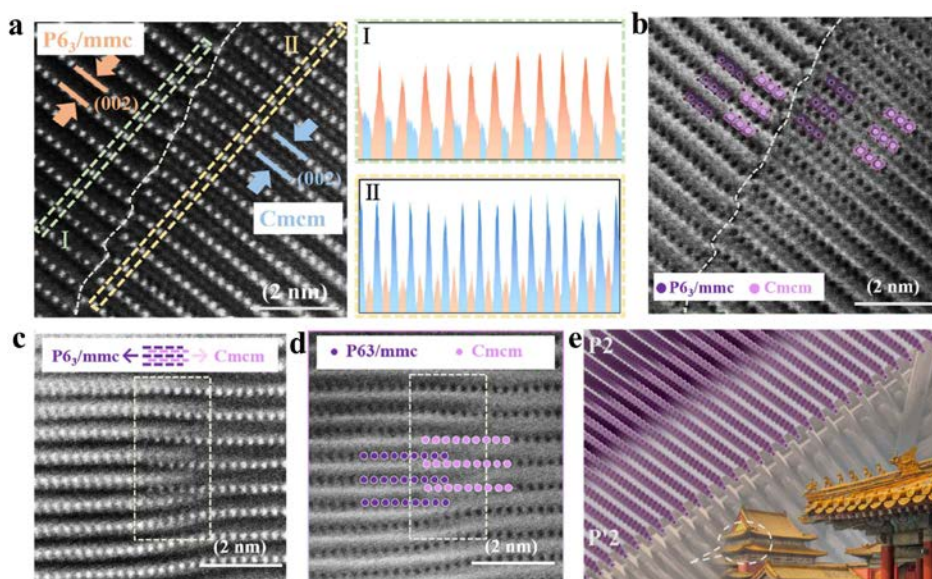


Figure 1. The atomic structure of the materials

Exploring WC-based Electrocatalysts for Robust Hydrogen Evolution Reaction via Energy-Saving Method

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Exploring high-performance and inexpensive electrocatalysts for hydrogen evolution reaction to substitute Pt-based compounds is important to sustain hydrogen production. Herein, WC-based self-supported catalysts doped with different concentration of nickel nitrate solution ( $\text{Ni}(\text{NO}_3)_2$ ) were synthesized on carbon fiber paper (CFP) by one-step molten salt method (abbreviated as  $x$  Ni-WC@CFP). The optimal 4M Ni-WC@CFP showed comparable catalytic ability in 0.5M  $\text{H}_2\text{SO}_4$  with a low overpotential of 73 mV at 10  $\text{mA cm}^{-2}$  and Tafel slope of 66.4  $\text{mV dec}^{-1}$ . The density functional theory simulations verified that the adsorption energy of hydrogen decreased with the rising amount of Ni doped in, while the W-H binding energy would change in an opposite direction as over doped Ni. This work provides an insight for the preparation of high-efficiency self-supported W-based electrocatalysts and expound the influence trend of Ni doping concentration on the performance of electrocatalysts.

With the help of new generation of information technology, the design process of energy materials can become faster and more energy-saving. In the next step, we will develop a model based on text mining of existing published research results by means of natural language processing and find the corresponding characteristics of WC-based electrocatalysts with high electrocatalytic activity in order to derive design rules, e.g., by measures of similarity and ultimately direct catalyst discovery. This model is envisioned to guide the choice of elements as well as the preparation process of electrocatalysts and provide effective support for further research in this field for both, experimentalists and simulation efforts, alike.

## High entropy oxides as new materials for energy applications

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High entropy oxides (HEOs) are a new class of materials that exhibit outstanding unique and tunable properties, making them promising for future efficient applications for energy conversion and storage. HEOs are complex single phase oxides consisting of five or more cations in approximately equal amounts. Thereby, the metal cations arrange randomly on the cation lattice of the crystal structure, resulting in high configurational entropy. Even compositions that have a positive enthalpy of formation can be stabilized at a certain temperature when the entropy term of the Gibbs energy becomes larger than the enthalpy term, so-called entropy stabilization, extending the materials engineering space.

Since the first publication in 2015 [1], many compositions and crystal structures have been synthesized and their properties have been studied. The investigated properties of HEOs range from surprisingly good electrochemical properties for the application in lithium ion batteries [2] as well as an exceptionally low thermal conductivity [3, 4], outstanding mechanical behavior [5] or promising electrical [6], (photo)catalytic [7] and magnetic [8] properties. By combining cations with different properties, e.g. different valences on the respective sublattices, the properties and electron structures can be specifically adjusted to the application needs.

This paper presents examples of the implementation of HEOs for energy-related applications and identifies potential future research directions.

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