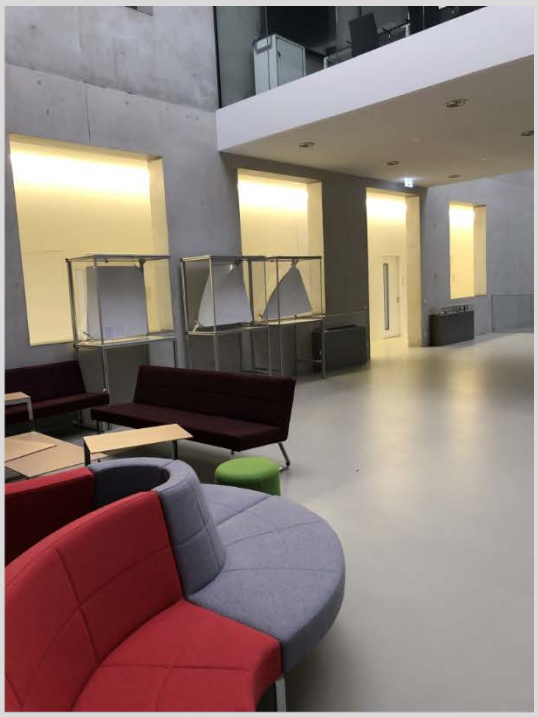

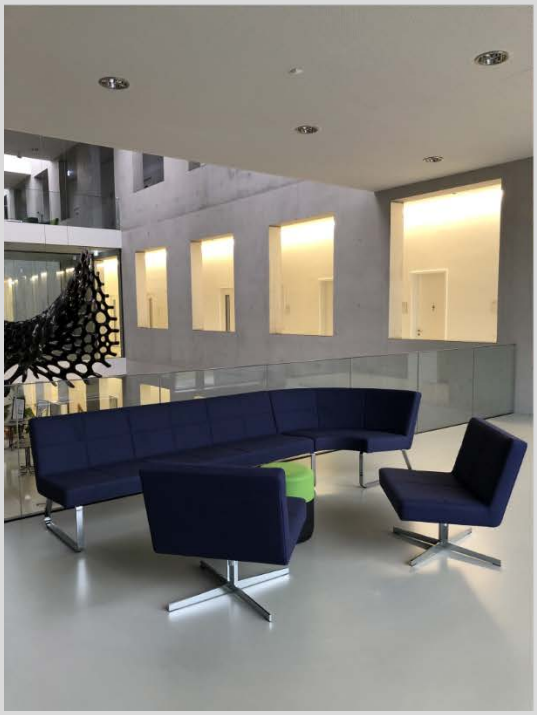

Das Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien
Freiburg Center for Interactive Materials and Bioinspired Technologies

FIT

Report 2022

universität freiburg

REPORT

2022

FIT

FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

FIT

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FOREWORD

FIT INTO THE FUTURE

The past year has once again brought new, major challenges for science and society. In addition to a wide range of political issues overshadowed by the war in Ukraine and its impact on society, the creation of a sustainable society that uses the world's resources responsibly continues to be an important topic. The sustainable use of materials and the reduction of energy use as well as the reduction of the CO2 footprint continue to be important research and development goals of FIT. In doing so, we must all work to create a society that not only tolerates and accepts the diversity of people in all aspects, but rather actively uses and promotes it to form a breeding ground for a colorful bouquet of creative research activities. Furthermore, it is an important task for all of us to promote the next generation of scientists and to introduce young people to research in order to prepare the next generation with all their enthusiasm and creativity for these key questions and for the challenges we all face.

In June 2022, for the first time since the FIT building opened, the regular five-year evaluation of our institute came to a close. In this evaluation, a highly interdisciplinary committee certified that FIT's research accomplishments are rated with the best possible grade of "outstanding." The FIT was confirmed to have achieved enormous visibility both nationally and internationally, and that the scientific quality of the FIT is excellent in both qualitative and quantitative terms. According to the reviewers' vote, FIT has achieved an impressive publication record and has created an excellent, unique materials research environment. The final rating was also "excellent" in terms of infrastructure and personnel-related aspects, as well as the area of training. The result of the evaluation underlines the important role that FIT plays in the development of the profile field of materials research and for the University of Freiburg as a whole. This very positive evaluation is a strong affirmation for us and our efforts, but also a strong incentive to continue to perform excellent work and to conduct and further develop future-oriented, world-class materials research.

In this foreword, I could refer to many attractive new research projects that were started or continued at FIT last year. However, in this short contribution I would like to focus on one aspect of the promotion of young researchers. Here, a high-light is certainly the implementation of the MasterLabs, which are carried out by the research clusters livMatS and IPROM who have their home in FIT. The aim of the MasterLabs is to introduce young, advanced students to research during their studies and to promote their interest in scientific work. This is achieved by the MasterLab participants working independently on so-called research challenges and at the same time being introduced to topics such as scientific ethics, communicating science and scientific publishing. The MasterLab has already received a great response and a very positive evaluation from the participants and the supervisors.

However, good science does not develop in a vacuum, but is driven by people. For all the outstanding achievements and services to the impressive development of our FIT, we would like to express our sincere thanks to all employees working at the FIT. Without the everlasting commitment of many hard-working hands (and heads), we would not be able to produce outstanding scientific work. Our special thanks go to all employees in administration and technology and to the FIT members, who constantly drive the FIT forward with new creative ideas by soliciting and carrying out projects. Furthermore, we would like to express our sincere gratitude to our scientific staff, our scientific advisory board and our many supporters and sponsors within and outside the university.

The current political situation and climate change present us all with major challenges that will certainly shape the coming year and the years to come. However, we at FIT do not want to join in the general lament and the

many doomsday scenarios so broadly discussed. Rather, we see and also should see that the current challenges offer many new opportunities to make an important contribution to the future of science through forward-looking and excellent scientific work. We at FIT will continue to tackle these tasks with energy and confidence in the coming year. I sincerely hope you enjoy reading our annual report.

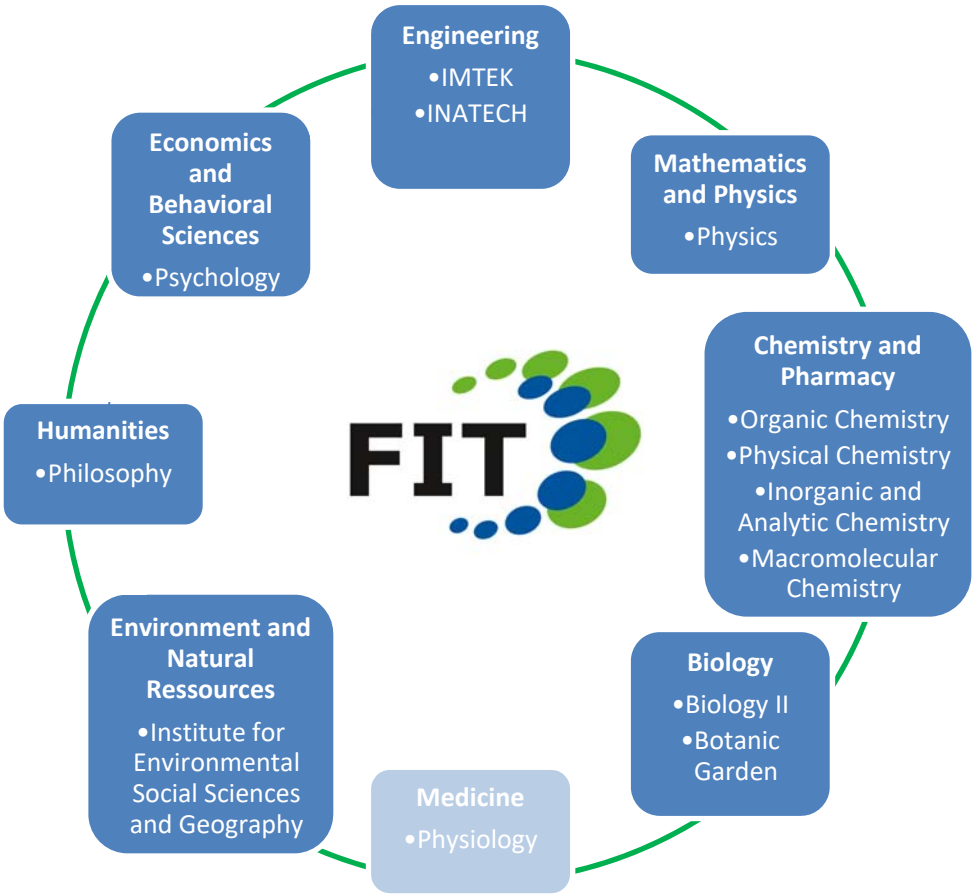
Jürgen Rühe

(Executive Director FIT)

The Center

Structure

The FIT is a research institution of national and international importance for the development of future-oriented, innovative materials and materials systems. Special focus is placed on materials systems that react to changes in the environment and thus, inspired by plants and animals, have life-like functions. Following the model of living nature, these "vital" materials systems are interactive, adaptive, energy-autonomous, self-repairing, self-improving or even learning. These extraordinary properties and functions make them a decisive advance in the sustainable development of technology and society.



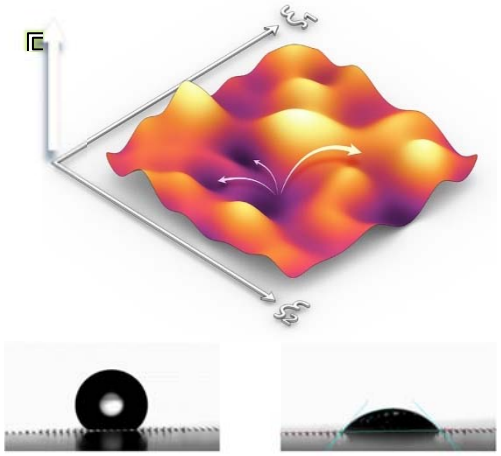
Overview of the various faculties and institutes that carry out disciplinary and interdisciplinary projects within the framework of basic research at FIT. A list of current and completed projects is available on the FIT website.

FUTURE FIELDS

Adaptive and Active Polymer Materials

Today's technical materials and materials systems are designed in such a way that they have more or less constant properties. These properties are given to them during the manufacturing process and should (apart from a little aging) not change in the course of time in the desired application. This immutability of material properties constitutes accordingly one of the core concepts of modern engineering and a rational systems design. In nature, on the other side, all living beings are designed to adapt as good as possible to their environment and to react to changes in environmental conditions with an appropriate response. A (young) sunflower, for example, moves its head according to the position of the sun in order to capture as much sunlight as possible, while a pine cone opens and closes depending on the ambient humidity to release its seeds under favorable conditions. Indeed one might rephrase Darwin's description of evolution by "Survival of the most adaptive".

The aim of the research program in the Future Field "Adaptive and Active Polymer Materials" is to develop new types of technical materials and advanced systems that do not have unchanging properties, but react to changing environmental conditions by adapting their shape and structure. This requires the generation of complex responsive systems, where the system can end up in different states depending on the nature of the stimulus, so that it can adapt to changes in the environment in a similar way as it is the case for living things. Fig. 1 gives an artist's impression for an energy landscape of such a multi-stimulus responsive system. Depending on the strength or type of the stimulus the system can end up in very different states represented by valleys in the energy landscape. This simplest case is observed, when the system responds to the stimulus only while the stimulus is still present. Such a behavior of the system is commonly called responsive. A simple example for responsive behavior is thermal expansion of a material. Switching, on the other side, occurs when the stimulus leads to reversible movement of the system between two states (example: photoisomerization of azo compounds). Here the system remains (at least for a while) in the second state and can return back to the original one through application of a different stimulus. Truly adaptive materials, however, can store these structural changes and retain the properties changed this way for further, later use. Taking the picture described above true adaptivity is only achieved when the stimulus leads to a reshaping of the energy landscape and thus keeps a memory of the conditions to which it had been exposed to. This way it resembles in a way a simple form of training / learning.



Artists impression of an energy landscape describing the effect of several stimuli acting on a materials system b) Wetting of a water drop on a mechanically actuated sample © Rajak, Rühe; unpublished results

Examples for such adaptive changes of materials, in which the outer appearance of the system is altered, are an origami-like folding of structures or the actuation of hair-like surface structures. But also the inner structure of a material can adapt to external stimuli as it is the case for auxetic materials which stiffen as a reaction to the application of a certain force. This adaptability of materials can be used to adjust properties of materials such as adhesion, wettability (see Fig. 1b) or mechanical properties, to environmental changes and thus opens up novel design spaces for the generation of complex objects. Materials systems with adaptive properties will allow breakthrough innovations in many different fields such as soft robotics, smart optical devices,

self-adaptive medical prostheses and orthoses, adaptive safety equipment, adaptive light guiding systems or interactive architectural components such as façade elements, which open and close with changes in the weather conditions.

In more complex systems not only one stimulus directs the behavior of a materials system, but usually several different stimuli act together, either subsequently or simultaneously. In this case the different signals need to be processed (and eventually weighed against each other). This weighing of different system responses leads to a gated behavior, not unlike logic gates in computer science (AND, OR, NOT). For example, systems can be designed which actuate in a certain fashion when either sufficient heat or humidity are present (OR condition). In another case bilayers systems can be generated where for example high humidity is required to “unlock” the system. An example could be here a lowering the glass transition temperature of a hydrogel layer rendering the layer much softer. This softening effect could then allow thermal or magnetic actuation of the bilayer system, where the movement is otherwise “frozen in”. Such a system requires for a successful actuation the presence of both stimuli, a typical AND condition. From a more general point of view, pathways to reach such complex adaptive behavior, which show features of an embodied intelligence, are the generation of reaction networks or the creation of complex metamaterials.

In nature, which serves as a great source of inspiration for the envisioned interactive and adaptive materials, the creation of such systems involves the integration of structures across many size scales, e.g., from the chemical structure of a cellulose molecule to the overall structure of a many meters high bamboo. Only when the components on the various length scales for cell to tissue and whole organism interact with each other in an appropriate way, adaptive behavior is observed. This is in a similar way true for artificial systems, where molecular changes e.g. by photoisomerization or swelling lead to macroscopic changes of an actuator.

However, the spatial domain is not the only one which needs to be addressed, but also timing can be crucial. In cases when the response to the signal relaxes with time (i.e. the system returns spontaneously, without the presence of an external stimulus back to the original state) also the time difference between the receptions of two separate stimuli will play an important role on the systems behavior. An example is a situation, where the first stimulus is needed to unlock the system and allow a response of the system to the second one. When relaxation after the first is faster than the application of the second stimulus, the “memory” of the occurrence of the first stimulus will be erased, the system remains locked and the presence of the second stimulus yields no systems response. However, when the arrival of the second stimulus, is faster than relaxation, the system is unlocked and can respond to this stimulus. Accordingly, complex adaptive systems might also require the consideration of different time scales ranging from rapid molecular changes, such as the closing or breaking of chemical bonds occurring within nano- to microseconds, to very slow processes such as thermal relaxation or creeping of materials that might take minutes or days. Successful development of interactive and adaptive materials thus requires a scale-bridging approach both from a theoretical and experimental point of view that extends all the way from a molecular oriented scale in time and space to that of a macroscopic object.

Jürgen Rühe

Biomimetic, Biobased and Bioactive Materials Systems

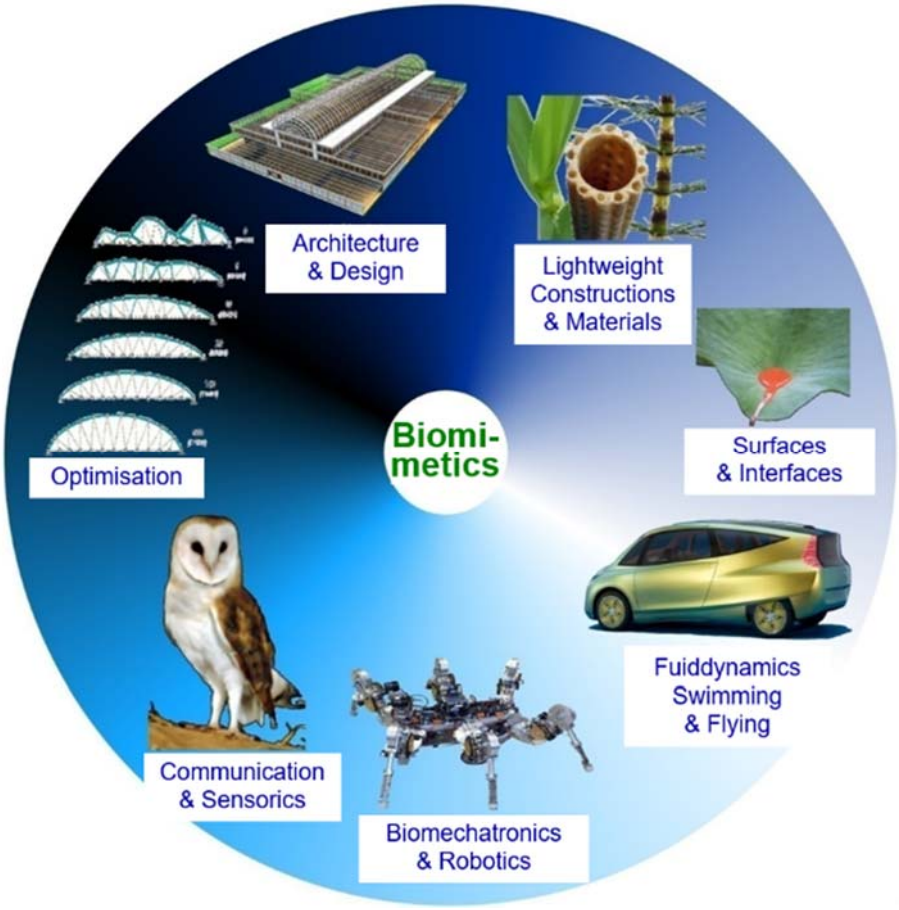


Fig. 1: Various fields of biomimetic research. © Plant Biomechanics Group Freiburg

In this future field the research focus lays on the development and construction of bioinspired, biomimetic, biobased and bioactive material systems. FIT projects cover the first two thirds of the value chain from basic research analyzing the biological role models and developing new materials systems to the production of functional demonstrators in lab bench dimensions. In addition to the transfer of functional principles from living nature to technical systems, this also includes the development of new active hybrids by the integration of synthetic and biological components, and the bioactive functionalization of materials and (micro)systems to enable them to interact with proteins, cells and tissues.

Biomimetic materials systems @ FIT

During the last decades biomimetics has attracted increasing attention as well from basic and applied research as from various fields of industry and building construction. Biomimetics has a high innovation potential and offers the possibility for the development of sustainable technical products and production chains. The huge number of organisms with the specific structures and functions they have developed during evolution in adaptation to differing environments represents the basis for all biomimetic R&D-projects. Novel sophisticated methods for quantitatively analyzing and simulating the form-structure-function-relation on various hierarchical levels, which is possible due to the various testing devices present at the FIT, allow new fascination insights in multi-

scale mechanics and other functions of biological materials and surfaces. Additionally, new production methods enable for the first time the transfer of many outstanding properties of the biological role models into innovative biomimetic products for reasonable costs (Fig. 1). In the FIT we concentrate on the development of biomimetic materials systems with various self-x-properties including self-repair, self-adaptation, self-cleaning and self-organization. Other research topics deal with bioinspired materials systems with pronounced energy dissipation, trainable materials systems, and the usage and development of 3D- and 4D-printing technologies for the production of novel bioinspired materials systems. Examples are plant inspired soft robots and soft machines and self-adaptive motile technical systems inspired by plant movements. For the latter especially hyromorphs, as e.g. Pine cones and scales (Fig. 2), are of increasing interest. The reasons for this interest are, that they: (1) harvest energy from the environment (no energy consumption), (2) are sensor, actuator, reactive movable element and support structure in one materials system, (3) show high level of structural and functional integration, and (4) display extraordinary high functional resilience and robustness[1].

Biobased materials @ FIT

In the biobased materials research @ FIT, we try to use biomimetic approaches to design novel materials from renewable resources. Our efforts particularly focus on the utilization of lignocellulosic biopolymers towards the design of advanced structural load carrying materials and materials systems, and of actuating materials for soft machines. One such project has attempted to develop novel processing approaches of lignin, the second most abundant biopolymer on earth, by utilizing a liquid crystalline cellulosic polymer as processing aid and lubricant. This processing approach is inspired by the biosynthesis and the morphogenesis of the plant cell wall. During the plant cell wall morphogenesis, a liquid crystalline cellulose / hemicellulose network serves as a host structure for the in-situ polymerization of monolignols. to finally deliver a high-strength, high toughness composite lignocellulosic material. The resulting lignocellulosic blends can be processed in solution by direct ink writing, which paves the way to new processing avenues for lignocellulosic polymers and thus novel applications.

In the framework of the Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (livMatS), which is located at the FIT, in 2021 the “livMatS Pavilion" was built in the Botanic Garden of the University of Freiburg as a model for a bioinspired sustainable construction. After the end of the Covid19 restrictions we started in 2022 to use very successfully the “*liv*MatS Pavilion” for activities in our outreach project “Learning from Nature in Nature”. The “*liv*MatS Pavilion” is inspired by the saguaro cactus (*Carnegia gigantea*) and the prickly pear cactus (*Opuntia* sp.), which are characterized by their special reticulated light-weight wood structure. Based on this bioinspiration civil engineers and architects of Cluster of Excellence “Integrative Computational Design and Construction for Architecture” (IntCDC) at the University of Stuttgart realized the “*liv*MatS Pavilion by using computer-aided design methods and robot-controlled production. The "*liv*MatS Pavilion" represents a prime example for a bioinspired sustainable construction with a light-weight biobased supporting structure [2].

References

[1] T. Speck, T. Cheng, F. Klimm, A. Menges, S. Poppinga, O. Speck, Y. Tahouni, F. Tauber & M. Thielen (2023): Plants as inspiration for material-based sensing and actuation in soft robots and machines. MRS Bulletin Impact. (in press)

[2] T. Speck, M.E. Schulz, A. Fischer & Jürgen Rühe (2023): Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (livMatS). – In: K. Dröder & T. Vietor (eds.), Future Automotive Production Conference 2022, Zukunftstechnologien für den multifunktionalen Leichtbau. Springer-Vieweg. (in press). DOI.org/10.1007/978-3-658-39928-3_18

Thomas Speck

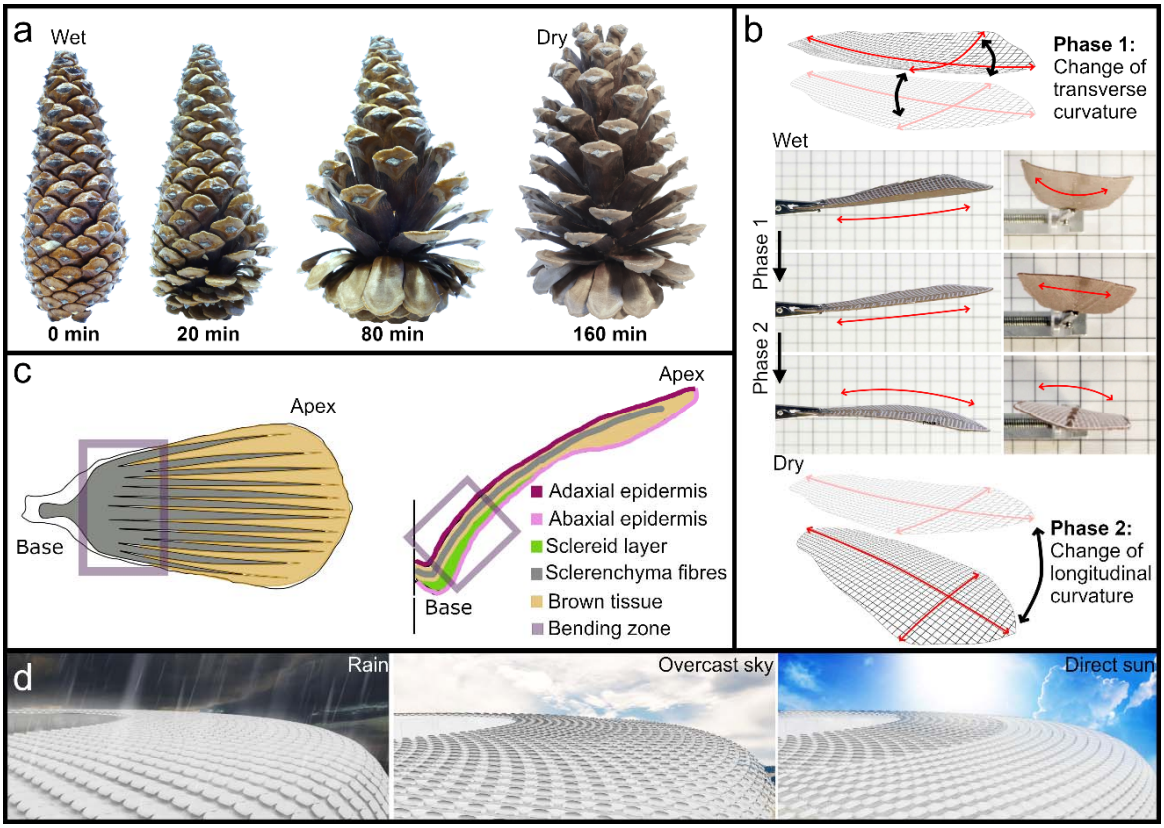


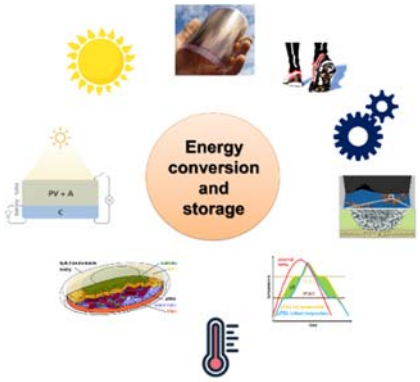
Fig. 2: Pine cone actuation, functional morphology and biomimetic self-sufficient compliant hygromorpic systems. (a) A pine cone shows sequential seed scale movements during the drying-induced opening sequence. (b) Multi-phase motion of a 4D-printed scale structure consisting of copolymer strands with embedded cellulose fibrils as the actuating layer and ABS polymer strands as the resistance layer. (c) Schematic top view (left) and longitudinal section (right) of a pine cone scale. (d) Vision of a modular smart-building skin consisting of shingle-like structures exhibiting tropistic behaviour for sun-tracking and nastic behaviour for fast hull closure upon an increase of environmental humidity. (Reproduced from [1] under CC BY-NC 4.0 license)

(Micro)Systems for Energy Conversion, Storage and Energy-autonomy

In this future field, the research focuses on the development and construction of material systems for energy conversion and storage. As such, inspired by nature, materials and systems are developed for the conversion of solar energy (solar cells and photoelectrochemical cells for artificial photosynthesis), chemical energy (fuel cells), thermal energy (thermoelectric generators) and vibrational energy (triboelectric generators). One aspect thereby aims to realize material systems with an embedded energy autonomy, i.e. materials systems which are ideally able to harvest the required energy from the ambient. In that sense, the materials and systems developed in this future field range from macro to highly embedded micro systems. As most ambient energy forms are intermittent, systems for energy storage must also be developed, so that the required energy is available on demand. Breaking with classical modular approaches, one vision is hereby to develop multifunctional conversion and storage systems at the highest level of integration, realizing a seamless integration of both functions. In this context, advanced multifunctional material processing techniques are of highest importance to realize this integration challenge.

Material systems for energy conversion and storage @ FIT

The largest activities in the future field are presently associated with the research activities in research area A of the livMatS Cluster in which novel concepts and systems for energy autonomous materials systems are developed.



Different forms of energy conversion and storage and associated materials and systems. © Area A of the *liv*MatS Cluster.

Solar energy conversion and storage

Solar energy is converted and stored as electrical charges in SolStore devices; devices, which fuse the function of light-induced charge carrier generation/separation and charge carrier storage at different levels of integrations, ranging from 3 electrode systems, in which a solar cell shares an electrode with an electrochemical energy storing system (supercapacitor or battery) to 2 electrode systems, in which the light-induced charge carrier generation/separation and charge carrier storage are truly embedded in one multifunctional material system.

This central *liv*MatS research is complemented by other FIT research projects in the future field related amongst others to a) solar energy conversion with novel tandem solar cells or photoanodes for photoelectrochemical water splitting, b) electrochemical energy conversion with bioinspired materials for Pt-free fuel cells as well as c) improved electrochemical energy storage with novel battery concepts and materials and interfaces.

Thermal energy conversion and storage

This area is anticipated by the development of highly efficient thermoelectric generators (TEGs) with integrated phase shift materials to be used as a storage unit for thermal energy. The corresponding project ThermoBatS is therefore again aiming at an intricate fusion of energy conversion and storage. The thermoelectric materials chosen are fabricated as highly nano-micro scale powders and formulated as thermoelectric inks or pastes. Fabrication of TEGs happens via dispensing or printing into flexible substrate materials, thus creating a versatile multi-material system suitable for the ambient temperature range. Other projects outside of livMatS will tackle the area of high-temperature energy harvesting using powder-pressed and sintered or electroplated thermoelectric materials. A third direction to be followed in all projects is the characterization of thermoelectric materials and systems.

Mechanical energy conversion

In *liv*MatS, triboelectric generators are the actual main topic of research in the project TriboGen. Here, we will do an extensive study on the fundamental physical effects of triboelectric charge generation, to gain more insight into this phenomenon, which is known for thousands of years but still a matter of scientific debate. As a result, optimized materials and suitable surface topologies will be developed for highly efficient triboelectric generators. Charge extraction will happen through innovative concepts and automatic frequency tuning will be performed through the mechanical design of self-adaptive triboelectric vibration harvesters.

These named projects are exemplary for the trend of energy research followed in FIT. Aside of the mentioned activities additional related projects are planned to widen the research platform with additional and highly innovative concepts for energy conversion, storage and transfer.

Anna Fischer & Peter Woias

New Materials: Societal challenges

Andrea Kiesel[1,2], Lore Hühn[1,3], Oliver Müller[1,3], Olga Speck[1], Rainer Grießhammer[1], Martin Möller[1], Julius Fenn[2], Philipp Höfele[1,4]

[1]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Department of Psychology, University of Freiburg; [3]Department of Philosophy, University of Freiburg; [4]Institute of Philosophy, Freie Universität Berlin, Germany

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2193/1 – 390951807

Technological advance promises to solve major problems. For example, in the context of new materials systems the development of sustainable, long-living materials systems that harvest energy from the environment might contribute to reduce human impact on climate change. Yet, technological advance challenges society and this challenge increases the faster and broader the technological advance is. On the one hand, technological advance is considered sceptical due to concerns that depend on the perception of risks and benefits as well as ethical concerns and trust in technologies per se. On the other hand, promises of technological advance are often misunderstood or misinterpreted. In the context of biomimetics, humans tend to believe that bio-inspired novel technologies are per se more sustainable, yet nature or to be more precise biological evolution is not goal-oriented and biomimetic products are not automatically sustainable[1].

Identifying and addressing the societal challenges of novel technologies requires interdisciplinary and transdisciplinary collaboration [2]. In this Future Field, philosophers, psychologists and sustainability researchers work together with material scientists (from several disciplines like chemistry, physics, engineering) and biologists to describe and characterice novel materials systems and identify their potential use as well as eventual risks and benefits. Novel tools are developed to assess and evaluate these materials systems and resulting novel technologies both from an empirical point of view in terms of societal acceptance [3] as well as from an analytical point of view in terms of sustainable development including aspect re-cycling [4]. Further, important concepts like "nature" and "life" are considered in the current discourse to increase inter- and transdisciplinary understanding and to identify misconceptions and narratives [5]. Feeding back the results helps material scientists to understand societal concerns and misconceptions and sustainability considerations and hopefully contribute to increase acceptance for the scientific approaches and novel technologies.

References:

[1] Möller, M.*, Höfele, P.*, Kiesel, A., & Speck, O. (2021). Reactions of sciences to the Anthropocene: highlighting inter- and transdisciplinary practices in biomimetics and sustainability research. Elementa: Science of the Anthropocene, 9(1). DOI: https://doi.org/10.1525/elementa.2021.03 (* = equal author contribution).

[2] Möller, M., Höfele, P., Reuter, L., Tauber, F.J., & Grießhammer, R. (2021). How to assess technological developments in basic research? Enabling formative interventions regarding sustainability, ethics, and consumer issues at an early stage. TATuP-Zeitschrift für Technikfolgenabschätzung in Theorie und Praxis, 30(1), 65-62. https://doi.org/10.14512/tatup.30.1.56

[3] Livanec, S., Stumpf, M., Reuter, L., Fenn, J. & Kiesel, A. (2022). Who's gonna use this? Psychological acceptance prediction of emerging technologies and transdisciplinary considerations in the Anthropocene. The Anthropocene Review, 9(2), 276-295. doi.org/10.1177/20530196221078924

[4] Möller, M., & Grießhammer, R. (2022). Prospective technology assessment in the Anthropocene: A transition toward a culture of sustainability. The Anthropocene Review. doi: 10.1177/20530196221095700

[5] Höfele, P., Müller, O., & Hühn, L. (2022). Introduction: The role of nature in the Anthropocene – Defining and reaction to a new geological epoch. The Anthropocene Review, 9(2), 129-138. doi/10.1177/20530196221110388

Andrea Kiesel

CORE FACILITIES

Imaging of Materials Systems

- Scientific head: Prof. Dr. Anna Fischer[1]
- Responsible manager and scientist: Dr. Yi Thomann[1] and Dr. Ralf Thomann[1,2]

[1] Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT);
[2] Institute of Macromolecular Chemistry

The core facility “Imaging of Materials System” (CF1) represents a specialized laboratory with various electron microscopes (200 kV HR-TEM/STEM, 120 kV TEM, SEM, FIB/SEM), a µ-CT, two atomic force microscopes (AFM) and a variety of peripheral devices.

The facility is accessible to all research groups within the university, as long as the projects are financed on a non-profit basis. Users can do measurements themselves or under supervision of the CF1 staff. We also provide service measurements, image processing methods and data analysis for various microscopic and tomographic applications.

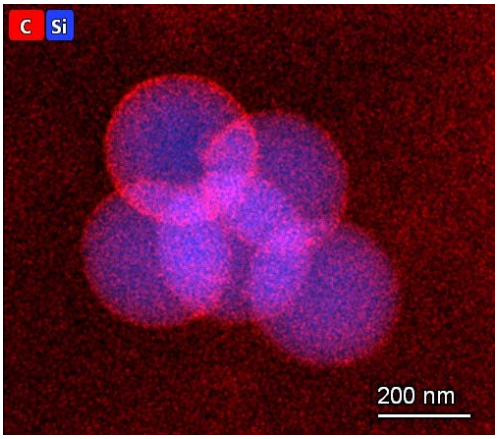


Fig. 1: EDX image of modified core-shell silica particles in an osteoinductive and biodegradable material for bone regeneration usage (Sample: group Seidenstücker / Bernstein). Image © Ralf Thomann

Our focuses are 2D and 3D-imaging on multiple length scales as well as microanalysis based on Electron Microscopy, X-Ray µ-Tomography and Atomic Force Microscopy. The following Figures show just a few results accomplished in the CF1 in the last year.

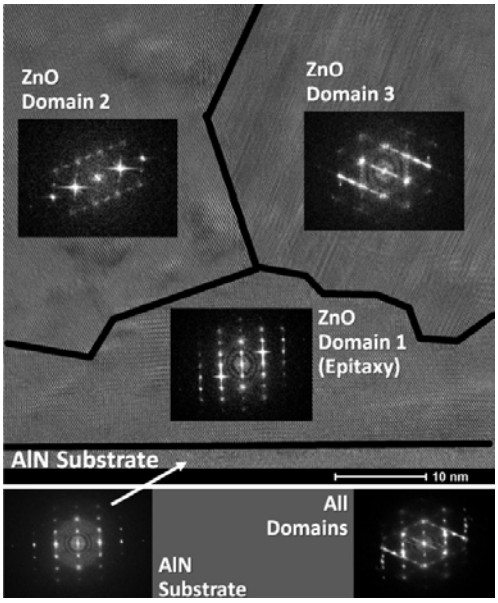


Fig. 2: HR-TEM and FFTs on a FIB/SEM lamella showing epitaxial crystal growth of ZnO (domain1) onto an AlN substrate. The above domains 2 and 3 show but different crystal orientations. (sample: Maximilian Kolhep / group Prof. Zacharias, IMTEK). Image © R.&Y. Thomann

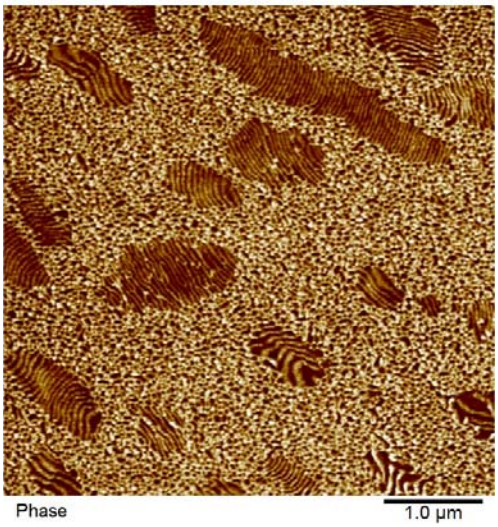


Fig. 3: Internal structure of a cryo microtomed amphiphilic PS/PDMS block-co-polymer network visualized by AFM phase mode. (sample Prof. Bela Ivan, university of Budapest). Image © Yi Thomann

For an overview of the instruments, methods, and the expertise in CF1 please refer to:

https://miap.eu/miap-unit/core-facility-imaging-of-materials-systems/

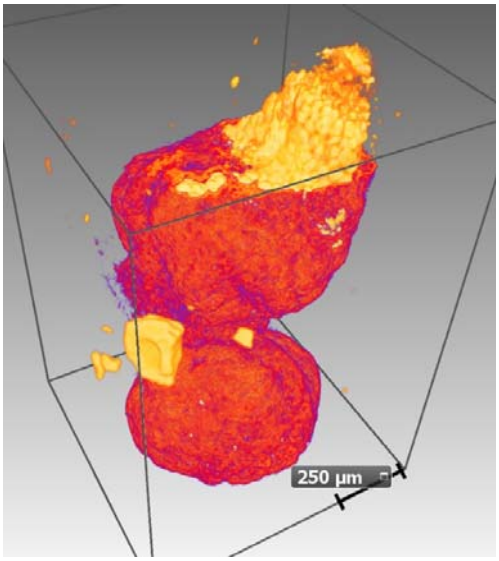


Fig. 4: Bacteria (yellow) infected plant cells (red) – µ-CT image. (Sample: Dr. Rodriguez / group Prof. Ott, plant cell-biology). Image© R.&Y. Thomann

References

[1] M. I. Sierra-Trillo, R. Thomann, I. Krossing, R. Hanselmann, R. Mülhaupt, Y. Thomann (2022): Laser Ablation on Isostatic Graphite-A New Way to Create Exfoliated Graphite. *Materials* **15**(16):5474. https://doi.org/10.3390/ma15165474

[2] A. Egorov,B. Riedel,J. Vinke, H. Schmal, R. Thomann, Y. Thomann, M. Seidenstuecker (2022): The Mineralization of Various 3D-Printed PCL Composites. *J. Funct. Biomater* **13**(4): 238 https://doi.org/10.3390/jfb13040238

[3] J.-C. Bürger, S. Gutsch, Y. Thomann, R. Thomann, B. Christian, O. Ambacher, M. Zacharias (2021): Analysis of the Growth of Laterally Aligned SnO2 Nanowires by Thermodynamic Considerations and Experiments. *Cryst. Growth Des*, **21**(1): 191–199. https://doi.org/10.1021/acs.cgd.0c00983

[4] A. R. Delgado, T. Berestok, K. Shchyrba, A. Fischer, U. A. Würfel (2022): New Figure of Merit for Solar Charging Systems: Case Study for Monolithically Integrated Photosupercapacitors Composed of a Large-Area Organic Solar Cell and a Carbon Double-Layer Capacitor. *Sol. RRL* **6**(10): 2200614. https://doi.org/10.1002/solr.202200614

[5] T. Berestok, C. Diestel, N. Ortlieb, S. W. Glunz, A. Fischer (2022) A Monolithic Silicon-Mesoporous Carbon Photosupercapacitor with High Overall Photoconversion Efficiency. *Adv. Mater. Technol* **7**(11): 2200237. https://doi.org/10.1002/admt.202200237

Functional Processing

Manufacturing technique for bioinspired materials with focus on nanolithography, film technology, and generative processes

- Scientific head: Prof. Dr. Claas Müller[1,2]
- Responsible manager: Dr. Jing Becker[1]

[1]FIT Core Facility "Functional Processing",
[2]IMTEK Department of Microsystem Engineering, Laboratory for Process Technology

Short description of research goals: Manufacturing technique for bioinspired materials with focus on nanolithography, macromolecular foil technology, and 3D-printing technology

In order to support the research projects running in FIT, a powerful technology department, Core Facility "Functional Processing", is established for functional design and efficient manufacturing of (micro-) systems and adaptive bioinspired materials.

The Core Facility "Functional Processing" concentrates particularly on the fabrication of nano- and micro-structures on macromolecular foils. Besides UV-NIL (UV-nanoimprint-lithography) as well as HE-NIL (hot-embossing-nanoimprint-lithography) technologies, various novel manufacturing technologies, such as roll lamination, thin film deposition, surface modification, aerosol jet printing technology, electrophoretic deposition, as well as screen printing technology are developed for special applications on polymer foils.

The equipment installed in the Core Facility "Functional Processing" is divided into two different categories according to the operation complexity. The category 1 includes the Cryomill system for material grinding with its integrated liquid nitrogen cooling system, the Stork roll laminator and the electrophoretic deposition system (EPD) from Permatecs. For this equipment category, after the application from the users and the evaluation by Core Facility "Functional Processing" group, the applicants would receive a clearly defined training course offered by the CF 2 stuffs.

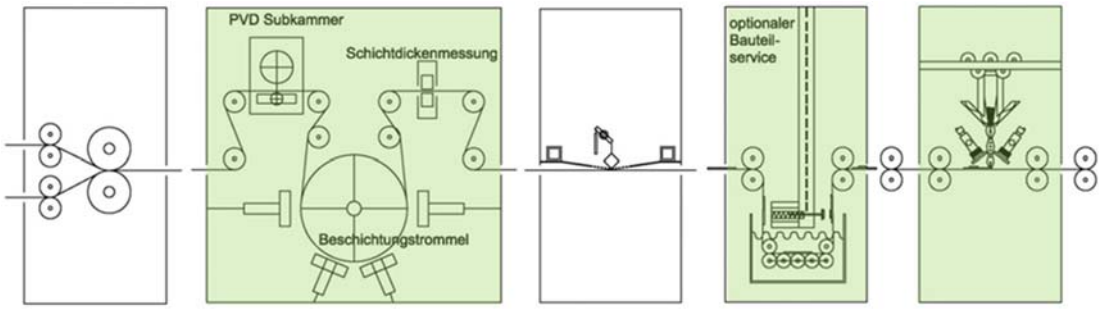


Fig. 1: Arrangement of the process modules in the technology platform 2 (from left): roll laminator, PVD & PECVD system, screen printer, electrophoretic deposition system and aerosol jet printer. © Core Facility 2, FIT, Freiburg

Following the training activities, the applicants will be issued a permit to work on the system. For the other system in CF 2, due to the operation complexity and the maintenance requirements, the users outside the CF 2 group are not allowed to perform alone on the systems. The equipment in this category could only be operated by the CF 2 stuffs.

In year 2022, Core Facility “Functional Processing” has cooperated with research group Speck in Fit on the topic of “A Soft Biomimetic Actuator Inspired by the Self-Sealing Motion of Succulent Plants”. It belongs to the livMatS booster project in the project area C (Longevity and Demonstrators). The goal of this booster project is to develop a biomimetic bending actuator for soft robots inspired by the self-sealing motion of the succulent leaves of Delosperma cooperi. By utilizing the shape memory effect of the SMP thin films, process-induced stress was easily built up into the polymer-based soft multilayer systems. Similar to the plant leaf, the multi-layer SMP/elastomer material system can bend after an external damage. At the end of this booster project, the self-sealing functionality was successfully approved and a paper with the title “Learning from self-sealing deformations of plant leaves: The biomimetic multilayer actuator” was successfully published as a research article in the journal of Advanced Intelligent Systems with an impact factor of 7.298 (Becker et al. 2022). Besides of that, CF2 has also cooperated successfully with researchers from Laboratory for Micro and Materials Mechanics on the generation of mold structures for casting processes.

In year 2022, two project applications have been submitted. These planned research projects are listed below:

1. *liv*MatS Booster Project “Bio-inspired Humidity-Driven Bending Actuators” (accepted)

In this project, biologist of the Plant Biomechanics Group of the Botanic Garden Freiburg and engineers from the Technical Faculty (Core facility 2 in FIT) aim to develop a bio-inspired relative humidity-driven bending actuator inspired by the self-sealing motion of the succulent leaves of Delosperma cooperi after the injury. In this booster project, we aim to develop a bio-inspired smart bilayer system with reversible and programmable actuation functionalities, which is activated by the variation of relative humidity (hydraulic movement) in the surrounding environment. Two different types of materials with different water absorption properties will be selected in this project, e.g. Lliquid Crystalline Polymer (LCP) and other kinds of polymer materials with low to non-water absorbing capability. Due to the different moisture absorption properties of the two monolayers, the humidity induced bending curvature of the actuator system could be designed by careful selection of the polymer materials, the layer thickness, the preparation method and the relatively humidity value.

2. DFG research project “µBlue- Micro fuel cell accumulators and charging concepts for environmentally friendly energy storage systems” (submitted)

The concrete goal of the project is the development of a self-sufficient micro fuel cell accumulator (µBZA) including optimized charging

and operating electronics. This µBZA is intended as a long-term vision in conjunction with an energy harvester to reliably supply autonomous sensor and actuator systems with energy. The centerpiece is a µBZA with integrated hydrogen storage as an environmentally friendly energy converter. The proton-conducting membrane of the µBZA is applied directly to the hydrogen storage unit, which makes active components such as pumps or pressure regulators superfluous. With the hydrogen stored in the storage tank and the oxygen from the ambient air, the stored chemical energy is directly converted into electrical energy. The only waste products are heat and water, which can be reused to recharge the storage.

To achieve the largest possible electrochemically active surface area, the interface between the PEM and the catalyst layer must be maximized. This will be achieved by well-defined nano- or micro-patterns patterned by nanoimprint lithography. This nanostructured interface increases the "three-phase region" between reactant, catalyst and electrolyte. In this case, the performance of µBZA should be significantly improved compared to conventional fuel cells with a "flat" membrane. In this case, it would be possible to adapt the output power of the µBZA to the performance data required for an application through targeted nanostructuring of the PEM-catalyst interface.

By extending a micro fuel cell with an electrolyze and charging electronics, the primary element "fuel cell" becomes a secondary element "fuel cell accumulator". The µBZA system does not require any environmentally harmful materials and at the same time has higher energy densities than commercial miniaturized battery systems.

Modelling and Simulation of Materials Systems

- Scientific head: Prof. Dr. Michael Moseler[1,2,3]
- Responsible manager: PD Dr. Michael Walter[2,1,3]

[1]Fraunhofer IWM, MikroTribologie Centrum µTC, Karlsruhe; 2FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies [3]Cluster of Excellence *liv*MatS @ FIT, [4]Institute of Physics, University of Freiburg

Short description of research goals: Concept Development, Modeling and Simulation of Interactive Materials Systems.

Understanding of the complexity of materials systems is based on simplification in order to be able to grasp the most important aspects of the phenomena under observation. We create a simplified model of the systems from which we derive our expectations. Generally, models are based on and formulated in mathematical equations. These may be derived from surprisingly few basic relations like the Maxwell- or the Schrödinger equations. The complexity comes through the vast number of particles involved in real life materials.

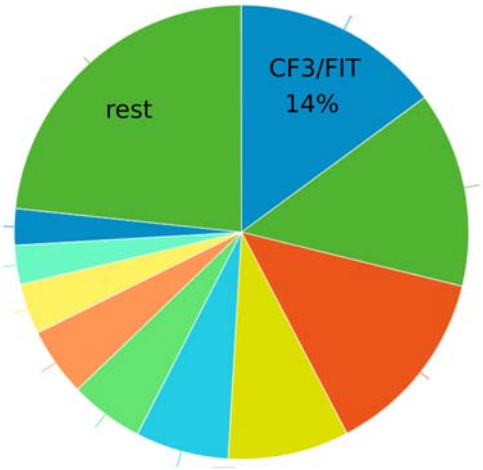


Fig. 1: Partition of computational time used on the full NEMO-cluster in the year 2022 for the 10 heaviest projects. The fraction used by FIT/CF3 is highlighted. © RZ University of Freiburg

As there are are only a few problems that can be solved analytically, numerical treatment of the problems is in order. Here, the ever increasing available computational power becomes beneficial. The funding granted by the Landesstiftung and the German Research Foundation was therfore used in 2017 for an extension of the NEMO-cluster located at the Rechenzentrum of the University of Freiburg. The cluster provides 18.000 cores in total and is accessible by research groups within Baden-Württemberg. The FIT participates in the within the “shareholder” principle providing preerential access, where the granted funding allowed to contribute to 5.6% of the hardware. The synergy obtained by this strategy was a large gain in computational resources for FIT. The last year’s use of computational resources added up to 14% of the full capacity of NEMO making FIT the top user of the cluster (Fig. 1).

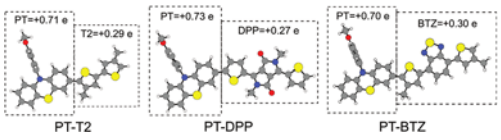


Fig. 2: Relaxed charge-neutral structural models used in DFT calculations (C: grey, N: blue, O: red, S: yellow, H: white) and Bader charge analysis of the oxidized state (cation) from Ref [1] (© 2022 The Authors. Macromolecular Rapid Communications published by Wiley-VCH GmbH)

The Walter research group is mainly concerned about properties of materials on the molecular scale. These nevertheless also determine macroscopic effects as in mechanochemistry of polymers for example. Here, the calculations provide insights about molecular level phenomena that can not be achieved by experimental means alone [1,2]. The studies within the CF3 research group resulted in a total of 8 peer reviewed publications in the year 2022. Further investigations are reported in the Highlights.

An example of a successful FIT based collaboration are the studies of phenothiazine-based donor-acceptor polymers [3]. Here, the simulation reveals redox-potentials and optical spectra that can by directly compared to experimental measurement in order to verify the underlying model assumptions. The calculations also predict the charge distribution within the molecule (Fig. 2), a quantity that is usually not available by experimental means alone. This can clarify structure-property relationships determining macroscopic function.

On a more basic level of interest for experimental groups, modeling of meso- and macroscopic properties are possible with finite element methods. These allow solving (coupled) differential equations that determine materials and their composites or even complex experimental setups. In this respect the software COMSOL, available through the technical faculty, is an easy to use and versatile tool to model may different general-purpose simulation software based on advanced numerical methods. It allows for fully coupled multiphysics, but also single-physics modeling. An introductory course on the basic usage of this software was provided and will be repeated as introduction to the new LivMatS PhD students in 2023.

References:

[1] Raisch, M.; Maftuhin, W.; Walter, M; Sommer, M. (2021) A Mechanochromic Donor-Acceptor Torsional Spring. Nature Comm., 12, 4243

[2] Hertel, R.; Maftuhin, W.; Walter, M.; Sommer, M. (2022) Conformer Ring Flip Enhances Mechanochromic Performance of ansa-Donor-Acceptor-Donor Mechanochromic Torsional Springs. J. Am. Chem. Soc. 144, 21897-21907

[3] Wessling, R.; Delgado Andrés, R.; Morhenn, I.; Acker, P.; Maftuhin, W.; Walter, M.; Würfel, U.; Esser, B. (2022) Phenothiazine-Based Donor–Acceptor Polymers as Multifunctional Materials for Charge Storage and Solar Energy Conversion. Macromol. Rapid Commun., 2200699

MANAGEMENT

Prof. Dr. Jürgen Rühe
(Managing Director)
IMTEK
Department of Microsystems Engineering
Chemistry and Physics of Interfaces

Prof. Dr. Thomas Speck
(Deputy Managing Director)
Plant Biomechanics Group
Botanic Garden
Faculty of Biology

Dr. Stefanie Meisen
(Administrative Director), FIT

Dr. Olga Speck
(Scientific Coordinator), FIT

DIRECTORATE

The Board of Directors of the FIT consists of five full-time professors from the participating faculties of the University of Freiburg that must also be members of the FIT. These professors are appointed by the Rectorate for a term of three years on the recommendation of the general meeting. The Directorate elects the Managing Director and the Rectorate appoints him for a term of three years. The Board of Directors is responsible for managing the business and decides on all matters that are not assigned to another body of the university. It coordinates the tasks to be performed within the FIT and draws up an annual research and financial plan. The members of the Directorate also include the respective Managing Director of the FMF and a representative of the young scientists. In 2022, members of the Directorate were:

Prof. Dr. Jürgen Rühe
(Managing director)
Faculty of Engineering

Prof. Dr. Thomas Speck
(Deputy managing director)
Faculty of Biology

Prof. Dr. Anna Fischer
Faculty of Chemistry and Pharmacy

Prof. Dr. Peter Woias
Faculty of Engineering

Prof. Dr. Bastian E. Rapp
(Managing director of the FMF)
Faculty of Engineering

Dr. Severin Vierrath / Dr. Can Dincer
(Representative of young scientists)
Faculty of Engineering

MEMBERS

Laboratories with the corresponding infrastructure and office space are made available to members for a limited period of time. The members have access to the three Core Facilities. In 2022, the members included (in alphabetical order):

Dr. Maria Asplund (Faculty of Engineering)

Prof. Dr. Frank Balle (Faculty of Engineering, until 19.07.2022)

Dr. Céline Calvino (*liv*MatS)

Dr. Can Dincer (Faculty of Engineering)

Prof. Dr. Christoph Eberl (Faculty of Engineering)

apl. Prof. Dr. Christian Elsässer (Faculty of Mathematics and Physics)

Prof. Dr. Birgit Esser (Faculty of Chemistry and Pharmacy, until 21.02.2022)

Prof. Dr. Anna Fischer (Faculty of Chemistry and Pharmacy)

Prof. Dr. Stefan Glunz (Faculty of Engineering)

Dr. Frank Goldschmidtböing (Faculty of Engineering)

Prof. Dr. Rainer Grießhammer (Faculty of Environment and Natural Resources)

Dr. Dorothea Helmer (Faculty of Engineering)

Prof. Dr. Lore Hühn (Faculty of Humanities)

Prof. Dr. Thorsten Hugel (Faculty of Chemistry and Pharmacy)

Prof. Dr. Henning Jacob Jessen (Faculty of Chemistry and Pharmacy)

Prof. Dr. Andrea Kiesel (Faculty of Economics and Behavioral Sciences)

Dr. Peter Koltay (Faculty of Engineering)

Prof. Dr. Ingo Krossing (Faculty of Chemistry and Pharmacy)

Dr. Tom Masselter (Faculty of Biology)

Prof. Dr. Michael Moseler (Faculty of Mathematics and Physics)

Prof. Dr. Claas Müller (Faculty of Engineering)

Dr. Anayancy Osorio (Faculty of Engineering)

Dr. Charalampos Pappas (*liv*MatS)

Prof. Dr. Lars Pastewka (Faculty of Engineering)

Dr. Uwe Pelz (Faculty of Engineering)

Dr. Thomas Pfohl (Faculty of Mathematics and Physics)

Prof. Dr. Bastian E. Rapp (Faculty of Engineering)

Prof. Dr. Günter Reiter (Faculty of Mathematics and Physics)

Prof. Dr. Ralf Reski (Faculty of Biology)

Prof. Dr. Jürgen Rühe (Faculty of Engineering)

Dr. Viacheslav Slesarenko (*liv*MatS)

Dr. Olga Speck (Faculty of Biology)

Prof. Dr. Thomas Speck (Faculty of Biology)

Dr. Severin Vierrath (Faculty of Engineering)

PD Dr. Michael Walter (Faculty of Mathematics and Physics)

Prof. Dr. Peter Woias (Faculty of Engineering)

Dr. Uli Würfel (Faculty of Mathematics and Physics)

Prof. Dr. Roland Zengerle (Faculty of Engineering)

Scientific Advisory Board

The Scientific Advisory Board accompanies the scientific work of the FIT and shall provide the directorate with suggestions for its further development. Members of the Scientific Advisory Board are external university professors whose research focus lies in the field of activity of the FIT. They are appointed by the rectorate for a period of five years. The following professors belonged to the Scientific Advisory Board:

Spokesperson: Dr. Karine Anselme (Institut de Science des Materiaux de Mulhouse (IS2M), France)

Deputy spokesperson: Prof. Dr. Christoph Weder (Adolphe Merkle Institute, Fribourg, Switzerland)

Prof. Dr. Eduard Arzt (Saarland University and Leibniz Institute for New Materials, Germany)

Prof. Dr. Clothilde Boulanger (Université de Lorraine, France)

Prof. Dr. Ingo Burgert (ETH Zurich, Switzerland)

Prof. Dr. Peter Fratzl (Max Planck Institute of Colloids and Interfaces, Potsdam, Germany)

Prof. Dr. Oskar Paris (University of Leoben, Austria)

Prof. Dr. Eric Yeatman, Imperial College London, UK)

Integrative Board

The Integrative Board is set up as a university-internal advisory body and monitors the development of the FIT. It works towards the reconciliation of interests of the faculties and institutions involved in FIT. In 2022 the following persons were members of the Integrative Board, with the deans always changing to the winter semester.

Prof. Dr. Jürgen Rühe (Managing Director of FIT)

Prof. Dr. Thomas Speck (Deputy Managing Director of FIT)

Prof. Dr. Heiner Schanz (Dean of the Faculty of Environmental and Natural Resources)

Prof. Dr. Sonja-Verena Albers (Dean of the Faculty of Biology)

Prof. Dr. Michael Thoss (Dean of the Faculty of Mathematics and Physics)

Prof. Dr. Andreas Bechthold (Dean of the Faculty of Chemistry and Pharmacy)

Prof. Dr. Roland Zengerle (Dean of the Faculty of Engineering)

Prof. Dr. Lutz Hein (Dean of the Faculty of Medicine)

Prof. Dr. Bastian Rapp (Management Director of the Freiburg Materials Center)

Dr. Frank Krüger (Head of Freiburg Research Services)

Dr. Karine Anselme (Spokesperson of the Scientific Advisory Board)

Dr. Stefanie Meisen (Administrative Management of FIT)

Figures and Finances

The FIT has once again met the challenges within its framework and was able to keep both the number of projects and the available funds constant. In the 32 projects, 83% was spent on personnel. This meant that a total of 335 staff were active, of which 33 were postdocs, 120 were doctoral students, 92 were Master's students and 10 were Bachelor's students.

In addition to the expenditure on personnel, 9% of the budget was spent on material resources and 8% on new investments. In order to be able to understand the figures accordingly, you can take further details from the following graphs and tables.

The Cluster of Excellence *liv*MatS, which is associated with us as a project group and is funded as part of the Excellence Strategy, started its fourth funding year in 2022. The long-term projects, of a project group at FIT, were continued and further projects could be taken up and carried out in 2022. Within the framework of these projects, a total of 3,618 k€ was spent on personnel costs, 1,252 k€ on material costs and 1,014 k€ on investments.

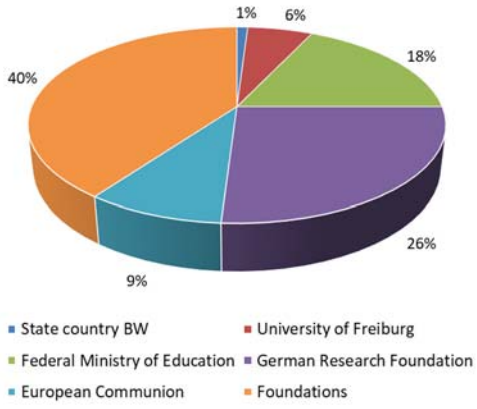


Fig. 1: Percentages participation of the FIT-budget 2022

Tab. 1: Budget from 2019 until today in €

	2019	2020	2021	2022
DFG	1.062.597	828.882	792.305	791.231
Land	0	98.857	112.471	43.164
BMBF	407.970	243.345	552.549	562.775
EU	518.315	576.875	360.206	286.354
Foundations	270.947	777.965	1.714.111	1.218.273
University	82.000	199.446	182.300	196.904
Total	3.012.525	2.725.370	3.713.942	3.098.701

Tab. 2: Project Overview for 2022

Leader of the project	Project	Overall project
Dincer	DFG miPAT	366.549
	DFG miRNAs	369.904
	BMBF MERGE	710.520
Fischer	Vectorstiftung AlkaCell	201.644
	VW-Stiftung In Situ EC-TEM	952.500
Glunz	BMBF PrEsto	498.030
Helmer	DFG Dynamisch schaltbare Sipropyran Oberflächen	234.200
Koltay	MWK DINAMIK	299.987
	DFG 4D-Bioprinting	204.100
Lienkamp	BMBF BioMAMPs	379.680
Pappas	DFG Peptid-Systemchemie	193.000
Osorio	Emmy-Noether-Overhead	7.500
Pelz	DFG MiTEG	321.649
Rapp	EU ERC CaLa	1.999.750
Rühe	DFG Polymer-modifizierte Papiere	211.400
	DFG PAK	165.800
	DFG Dynamisches Verhalten von Wassertropfen	202.500
	DFG KOMMA	246.250
	DFG PAK (Folgeprojekt)	121.500
	DFG Elastokalorisches Kühlen	272.650
	DFG mTOR2	234.161
Rühe, Rapp at all.	Carl-Zeiss IPROM	4.500.000
Speck, T.	EU ERC GrowBot	696.166

Vierrath	Vectorstiftung AlkaCell	259.778
	Vectorstiftung CO2-to-X	1.000.000
	Alexander von Humbold	63.600
	BMBF FC CAT	330.000
	BMBF FC RAT	467.864
Walter	DFG Donor Akzepter	162.950
	DFG HYBRIDS	159.850
	DFG Synthese , in-operando X-ray	169.550
	DFG IRTG Teilprojekt	11.692

Tab. 3: Budgets of project groups from 2019 until 2022 in €

Project group	2019	2020	2021	2022
Asplund	0	0	0	60.771
Dincer	93.407	153.439	286.141	262.021
Fischer	65.373	151.342	116.067	414.418
Glunz	54.468	0	118.617	156.288
Helmer	0	30.104	50.680	111.860
Koltay	0	138.692	166.018	104.179
Lienkamp	507.898	285.240	381.203	120.580
Osorio	0	0	1.919	1.919
Pappas	0	0	0	24.387
Pastewka	0	0	0	48.029
Pelz	0	61.853	77.258	86.259
Rapp	39.077	100.530	22.606	355.767
Rühe	234.350	550.142	1.417.754	477.998
Speck, T.	126.483	98.011	78.254	80.969
Vierrath	31.703	339.089	328.926	358.409
Walter	84.068	66.759	109.159	192.865
Zapp	0	0	0	46.997

HIGHLIGHTS

FUTURE FIELD "ADAPTIVE AND ACTIVE POLYMER MATERIALS"

A sustainable approach towards aqueous phase peptide synthesis

Kun Dai, Mahesh Pol and
Charalampos G. Pappas

Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2193/1 – 390951807

Biological peptide bond formation is activated in water by Adenosine Triphosphate (ATP), where sequence control and termination mechanisms are achieved by complex biomolecular machinery [1], giving rise to aqueous polyamides. Inspired by such dynamics involving interactions within multicomponent systems, systems chemistry focusses on mechanisms and pathways that enable coupling of chemical reactions with self-assembly. These approaches often involve chemical reaction networks and the use of activated precursors to access kinetically trapped structures and systems that function only by constant supply of energy. In these fully synthetic systems, phase changes give rise to supramolecular reconfiguration of different species, enabling self-selection of assemblies, template-driven synthesis and chemically fuelled nanostructures [2]. The chemical information into these systems is often installed within short peptide sequences, which represent simplified versions of known biological structures, involving the construction of helices and β-sheets. Such structural conformations often emerge from minimal amino acid repeats, where aromatic and aliphatic dyads have been associated with gelation, while longer repeats of hydrophilic and charged residues are nowadays gaining significant attention towards phase separation [3]. The chemical information of the repeated residue, the length of the repeat and the nature of bordering patterns dictates a balance between ordered and disordered domains. Despite great progress on using native chemical ligation strategies focusing on cysteine residues, the challenges associated with the solubility of amino acid precursors in water and the unfavourable thermodynamics of peptide condensation, prevents us from exploring directly the effect of sequence, pathway and self-assembly in oligomerisation processes.

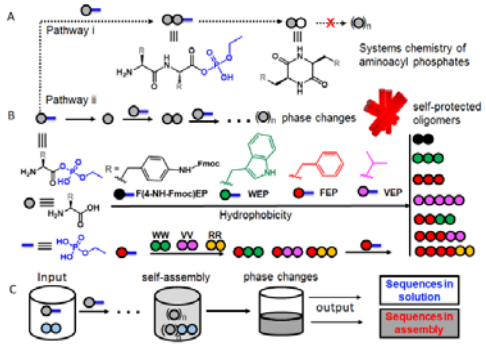


Fig. 1: Systems chemistry of aminoacyl phosphates: (a) Pathway-dependent oligomerisation. (b) Chemical structure of aminoacyl phosphates involved in spontaneous phase changes and (c) Continuous peptide synthesis in water, emerging from self-assembling events. (@Pappas Research Group)

Herein, we utilize aminoacyl phosphates - soluble activated amino acid precursors, which contain enough chemical information to trigger phase changes during spontaneous peptide oligomerisation. This strategy leads to the formation of a pool of oligomers, where aqueous phase peptide synthesis occurs, in which short oligomers are prevalent in the solution phase, while more hydrophobic residues are self-selected in the aggregated phase. We managed to control the pathway of reactive intermediates through pH changes, leading to continuous sequence elongation, by furthermore reducing diketopiperazine formation - a common issue on protecting-group-free synthesis. By continuous addition of activated monomers, oligomers of different length and composition were self-protected, capable of forming highly ordered supramolecular structures. The chemical nature and the length of the amino acid repeat is directly related to the hydrophobicity of the monomers, which in turn affects selectivity and the distribution in different phases. Overall, these approaches could be

potentially automated, through the fabrication of a microreactor, which encapsulates automatically injected amino acids inside droplets containing the phosphate precursors, leading to programmable aqueous peptide synthesis coupled to material screening.

References

[1]. Hendricks, M. P.; Sato, K.; Palmer, L. C.; Stupp, S. I., Supramolecular Assembly of Peptide Amphiphiles. *Acc. Chem. Res.* 2017, 50 (10), 2440-2448.

[2]. Boekhoven, J.; Hendriksen, W. E.; Koper, G. J.; Eelkema, R.; van Esch, J. H., Transient assembly of active materials fuelled by a chemical reaction. *Science* 2015, 349 (6252), 1075-9.

[3]. Chen, C.; Tan, J.; Hsieh, M.-C.; Pan, T.; Goodwin, J. T.; Mehta, A. K.; Grover, M. A.; Lynn, D. G., Design of multi-phase dynamic chemical networks. *Nat. Chem.* 2017, 9 (8), 799-804.

Transition between wetting states using physical gels with adjustable softness

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[1]Laboratory of Process Technology (Neptun Lab), Department of Microsystems Engineering; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [3] Freiburg Materials Research Center (FMF)

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within the priority program 2171, Dynamic wetting of flexible, adaptive, and switchable surfaces, project ID: 422798085

Surface softness has a major effect on droplet state and three-phase contact line (3PCL) in static and dynamic droplet analysis. When a droplet is placed on a stiff surface, no deformation is observed in the substrate. However, on a softer substrate, the droplet can pull the surface upwards at the 3PCL (Fig. 1). This deformation at the 3PCL is referred to as a wetting ridge. On very soft substrates where elasticity is negligible, the droplet forms a liquid lens shape and deforms the whole interface between the droplet and the substrate.

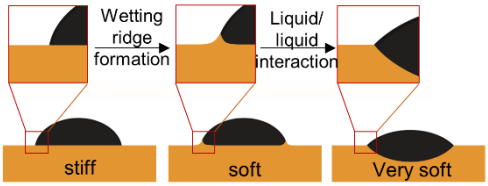

Fig. 1: Schematic representation of wetting states depending on the softness. The softer the substrate, a droplet caused larger substrate deformations at the contact line. (© HelmerLAB, IMTEK)

For the study of soft wetting and for droplet manipulation, reversibly switchable surfaces that can be switched in terms of their stiffness are of high interest. Different materials such as silicone gels [1], polymer melts [2], and polymer brushes [3] have been employed for soft wetting studies. However, their softness cannot be altered later on demand and softness patterns remain static. Here, we introduce a physical gel as a soft substrate whose softness can be tuned by light to investigate the effect of on-demand softness changes at 3PCL.

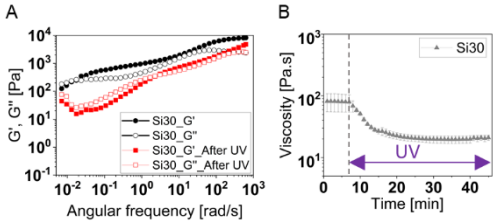

Fig. 2: Effect of UV exposure on rheological behavior of the photoswitchable gel. A) Dynamic behavior of the gel before (black) and after (red) exposed to UV. B) Decrease in gel viscosity as the UV exposure started at t = 7 min. (© HelmerLAB, IMTEK)

We utilized spiropyran-containing photorheological fluids [4] which show a significant decrease in viscosity upon UV irradiation. However, they suffer from a liquid-like and time-dependent rheological behavior, and the common solvents for their fabrication such as cyclohexane or n-decane are highly volatile. To engineer them for soft wetting studies where time-independent stable soft materials are required, 30 wt.% of silica nanoparticles with the size of 200-300 nm was added to the samples (referred as Si30 in this report) and the solvent ws replaced with isopropyl palmitate. Upon introduction of the particles, the photorespon-

sive properties were preserved, so that the behavior switched from a solid-like dominant to liquid-like dominant behavior with lower modulus and lower viscosity after UV exposure (Fig. 2)

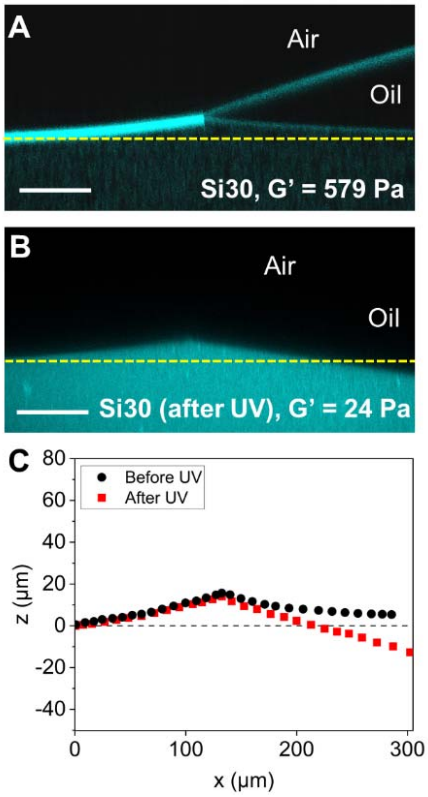

Fig. 3: Transition of wetting state from soft wetting to liquid/liquid interaction as the UV irradiation softens the substrate. Confocal microscopy images in xz plane exhibit: A) wetting ridge formation at 3PCL before UV exposure, B) the deformation of the interface of the droplet and the substrate as UV light softened the substrate. C) Surface profiles of wetting ridges in A and B. (© HelmerLAB, IMTEK)

The modified physical gels were coated as a thin film (800 µm) on a glass slide and a 2 µl fluorinated oil droplet was placed on top of the surface. The wetting ridge at the 3PCL was visualized using confocal microscopy in a xz plane. Samples with 30wt% of silica nanoparticles and modulus of 579 ± 67 Pa formed a wetting ridge of about 15 µm height (Fig. 3.A) which is representative of a soft wetting state. Using the UV light, the physical gel became softer, i.e. with less elasticity and a modulus of 24 Pa. Hence, the droplet state started to change towards the liquid/liquid interaction (Fig. 3.B) and the interface of the droplet and substrate was deformed. The surface outlines were extracted and plotted to elucidate the change in contact lines before and after UV irradiation (Fig. 3.C).

The UV-softening of the gel has a very high resolution: the switching of the gel could be induced using a maskless lithography system with a resolution of <500 µm (Fig 4).

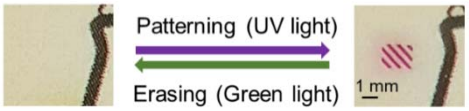

Fig. 4: High resolution and reversibility of the switch could be used for creating patterns (magenta) with high resolution using a maskless lithography system. Switching is reversible and patterns can be consecutively erased with green light. (© HelmerLAB, IMTEK)

This high resolution switch can be used for droplet manipulation, as a softness gradient induces the movement of droplets to softer area (durotaxis) [5] By softening the substrate on one side of the droplet, the 3PCL moved which resulted in the asymmetric spreading of the droplet (Fig. 5).

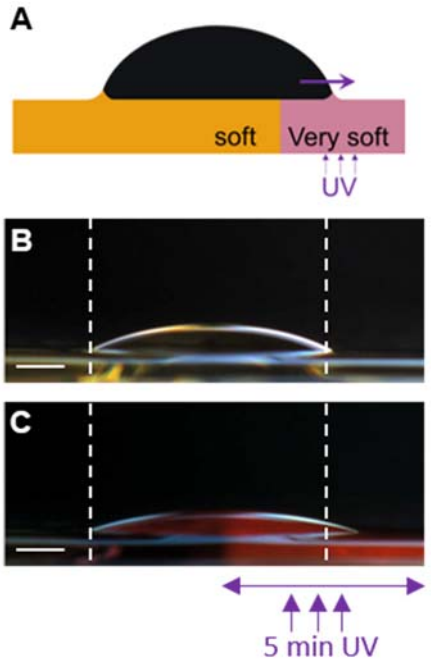

Fig. 5: Droplet manipulation employing the high resolution of the UV-softening of the substrate. A) schematic representation of the experiment showing durotaxis of the droplet towards softer areas, B) a 2 µl fluorinated oil droplet on the gel, C) the droplet moves towards the UV-softened area. (© HelmerLAB, IMTEK)

In this work, we have successfully engineered a physical gel with tunable softness to create

on-demand softness changes. The gel was employed to present an on-demand transition between wetting states depending on the softness. The softness change features a color change to magenta, which was used to show the high resolution of the switch. Droplet durotaxis was shown by using the high resolution switching to manipulate the droplet to move to areas of the substrate that were softened by UV light.

References

[1] M. Sokuler, G.K. Auernhammer, M. Roth, C. Liu, E. Bonacurrso, H.-J. Butt, Langmuir 2010, 26, 1544.

[2] K. Chaudhuri, J.T. Pham, Soft Matter 2022, 18, 3698.

[3] S. Schubotz, C. Honnigfort, S. Nazari, A. Fery, J.-U. Sommer, P. Uhlmann, B. Braunschweig, G.K. Auernhammer, Advances in Colloid and Interface Science 2021, 294, 102442.

[4] H.-Y. Lee, K.K. Diehn, K. Sun, T. Chen, S.R. Raghavan, J. Am. Chem. Soc. 2011, 133, 8461.

[5] R.W. Style, Y. Che, S.J. Park, B.M. Weon, J.H. Je, C. Hyland, G.K. German, M.P. Power, L.A. Wilen, J.S. Wettlaufer, E.R. Dufresne, Proceedings of the National Academy of Sciences of the United States of America 2013, 110, 12541.

Development of a baseline bioinspired macroscopic gripper system within livMatS

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Macroscopic devices are well suited to be technological demonstrators for public outreach and science communication of novel bioinspired materials systems, which are being developed in the *liv*MatS cluster. Grippers, on a familiar macroscopic scale, are particularly suitable for this purpose due to their ubiquity in everyday life and accordingly their proximity to real-life applications. In the "Demonstrator" research area of the *liv*MatS Cluster, we are researching such a gripper inspired by elastic movements found in animals and plants.

In technology and nature, grippers of any kind are vitally important for manipulating and interacting with the environment, and are accordingly found quite frequently in both domains. With hands, claws, tentacles, suckers, tongues, prehensile tails or proboscises, objects can be grasped, held, moved or even modified. Hands even give some animals, and especially humans, the ability to create specialized tools from inanimate objects. A culmination of such tools are machines, such as industrial robots, which often far surpass their biological counterparts in terms of the specific task for which they were designed. However, due to this specialization, they can often only be used in a narrow (industrial) application domain with predictable circumstances and sufficient safety measures, and are even completely unsuitable for some tasks. Such tasks can be manipulating objects with varying properties or in environments with rapidly changing conditions, such as in the interaction with living beings (e.g. human-machine interaction) or fragile objects.

It is in this variability and adaptability that nature's grippers are far superior to technical solutions, which are usually made of solid and predictable but less flexible materials. The human hand, for example, can grasp almost any conceivable object (in the right size and temperature range) and can adapt to its properties, such as shape, weight or fragility, and grasp it with appropriate force. Rooted in the high selection pressure that acts on motile organisms, this universality is achieved while requiring little energy compared to state-of-the-art pneumatic soft robotic solutions. For instance, like animals themselves, prehensile organs consist not only of muscles and often bones, but also of a variety of other tissues, such as tendons, ligaments and fascia. Through their passive elastic properties, these tissues not only influence movement, but are also designed to support and modulate it.

Often, the influence of passive tissues allow living beings to achieve peak performances that would otherwise not be possible through purely muscular strength. Popular examples

have so far mostly been described in relation to locomotion. Insects use the resonance properties of their thorax to beat their wings faster than the frequency of the electrical stimulus [1], and kangaroos only achieve energy efficient jumping through the storage of energy in their pre-stretched jump tendons [2]. Even humans are only able to run enormous distances in a single stretch because of the very low energy consumption of the upright gait, which it partly reaches due to the elastic properties of the myofascial system [3]. Similar influences of passive components, albeit less spectacular, can also be found in prehensile organs.

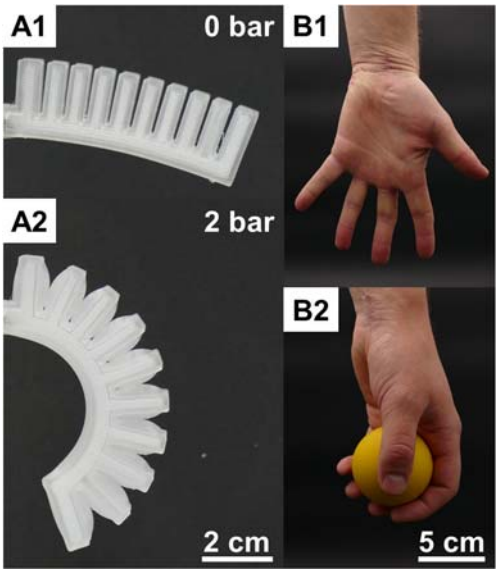

Fig. 1: Comparison of a classically designed soft robotic pneumatic network (PneuNet) bending actuator (A) with the human hand (B). A1: The actuator is extended without pneumatic actuation and only bends while energy input is supplied by pressurized air (A2). B1: Muscular contraction extends fingers and opens the hand. B2: Releasing the contraction induces a myofascial relaxation, which partly closes the hand and generates a movement, which is sufficient to grasp, and hold light objects such as a lacrosse ball (mass ≈ 140 g). (© Plant Biomechanics Group)

When relaxed, muscles assume a resting state—a length in the middle range of their movement amplitude. That they do not stretch out completely is due to the strain resistance of the musculature itself transverse to the longitudinal axis as well as the strain resistance of passive tissues connected in parallel [4]. The fingers assuming, for example, due to this relaxation a curved posture at rest and the entire hand thus assuming a concave posture that supports grasping (Fig. 1). The active contraction of the extensor muscles of the hand not only leads to the extension of the fingers, but also simultaneously to a pre-stretching of counteracting passive components of this materials system. Thus, the relaxation of the musculature already generates a force, which alone can be enough to grasp and hold objects [5]. This force is already sufficient to grip light and fragile objects, while active contraction of the flexor muscles is only necessary for a more firm grip on heavier objects.

In the demonstrator research area, we are currently researching novel gripper systems that, inspired by such elastic components of biological gripping organs, have an improved ability to grip a wide variety of objects. Applying the relaxation principle enables energy-free grasping, which means no additional energy input is needed for grasping and holding, but rather is only needed for releasing the grip. Furthermore, reducing energy requirements should make it possible to integrate *liv*MatS' energy-harvesting systems, thus contributing to the goal of obtaining autonomously functioning systems. The *liv*MatS multi-material 3D printer was developed for rapid prototyping of such pneumatic actuators from flexible filament [6, 7]. In an application-related approach, we compared the FDM printer with another state-of-the-art printing process, photopolymer material jetting [8]. This comparison was made using a pneumatic comparative bending actuator designed for this purpose and revealed new insights into the advantages and disadvantages of both printing processes. The results revealed a high tensile strength of the FDM material and a resulting robustness and reliability of the actuators. These results helped us decide to use this printing process to develop and test the macroscopic gripper with passive components.

References

[1] Machin, K., & Pringle, J. (1959). The physiology of insect fibrillar muscle. II. Mechanical properties of a beetle flight muscle. Proceedings of the Royal Society of London. Series B, Biological Sciences, 151(943), 204–225.

[2] Dawson, T. & Taylor, C. (1973). Energetic cost of locomotion in kangaroos. Nature, 246, 313-314

[3] Roberts, T., J. & Azizi, E. (2011). Flexible mechanisms: the diverse roles of biological

springs in vertebrate movement. The Journal of Experimental Biology, 214, 353-361

[4] Wiemann, K., Klee, A., & Startmann, M. (1998). Filamentäre Quellen der Muskel-Ruhespannung und die Behandlung muskulärer Dysbalancen. Deutsche Zeitschrift für Sportmedizin, 49(4), 111-118.

[5] Brand, P., W. (1993). Biomechanics of balance in the hand. Journal of Hand Therapy, 6(4), 247-251,

[6] Conrad, S., Speck, T. & Tauber, F. (2020). Multi-material 3D-printer for rapid prototyping of bioinspired soft robotic elements. In: V. Vouloutsi, A. Mura, F. Tauber, T. Speck, T.J. Prescott & P.F. Verschure (eds.), Biomimetic and Biohybrid Systems. Living Machines 2020, 46 – 54. Lecture Notes in Computer Science LNAI 12413. Springer Nature, Cham.

[7] Conrad, S., Speck, T. & Tauber, F. (2021). Tool changing 3D printer for rapid prototyping of advanced soft robotic elements. Bioinspiration & Biomimetics, 16, 055010

[8] Kappel, P., Kramp, C., Speck, T., Tauber, F. (2022). Application-oriented comparison of two 3D printing processes for the manufacture of pneumatic bending actuators for bioinspired macroscopic soft gripper systems. In: In: Hunt, A., Vouloutsi, V., Moses, K., Quinn, R., Mura, A., Prescott, T.J. & Verschure, P.F. (eds.), Biomimetic and Biohybrid Systems. Living Machines 2022. 54 – 67. Lecture Notes in Computer Science LNAI 13548, Springer Nature, Cham.

Swelling-induced instabilities of membranes for microfluidic applications

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"The blob" – *Physarum polycephalum* – is an impressive example of a single-celled system composed of a microchannel network, capable of solving complex problems, such as moving through a maze, minimizing distances in its network between food sources and responding to external triggers. The fluid flows in its network are critical for transporting information from one part of "the blob" to another.[1] To replicate this intelligent microchannel network, mechanisms must be created for the network to interact with fluids and its environment.

One possible approach for introducing interactions in fluid networks is the mechanical deformation of soft elastic elements by buckling. To investigate the controlled shape-dependent deformation of soft elements, we designed patterned microstructures using polydimethylsiloxane (PDMS), consisting of several parallel membranes embedded in microchannels (Figure 1). The membranes have a length of $a = 10\,\mathrm{mm}$, a width of $b = 100\,\mu\mathrm{m}$ and a height $h = 10$ or $20\,\mu\mathrm{m}$. All micrographs of the membranes in Figure 1 were taken on the xy-plane and the focal plane was set to $z = b$.

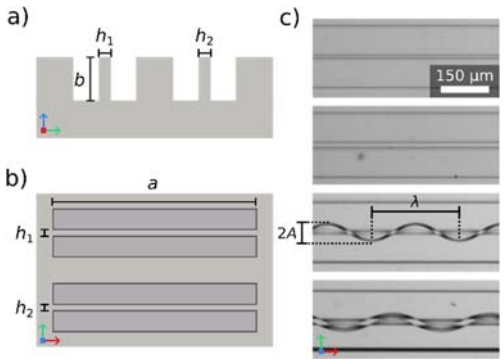

Fig. 1: a) Schematic side view of the lamellar microstructure. b) Schematic top view on the xy-plane of the lamellar micro-structure. c) Micrographs of the xy-plane of the membrane with $b = 100\,\mu\mathrm{m}$. Top to bottom: dry membrane with $h = 10\,\mu\mathrm{m}$ and $h = 20\,\mu\mathrm{m}$, membranes immersed in isopropanol with $h = 10\,\mu\mathrm{m}$ and $h = 20\,\mu\mathrm{m}$. © Pfohl Group

When a straight, unbent membrane comes into contact with binary isopropanol-water mixtures, the membrane material PDMS swells as a function of the volume fraction of isopropanol ϕ_{iso}. The boundary conditions of the membrane at its lower edge prevent lateral movements, but allow out-of-plane deformations. Moreover, lateral stress rises along the xz-plane. As the swelling increases, the lateral stress increases, and for a certain volume fraction of isopropanol ϕ_{iso} the bending stiffness of the membrane is lower than the stretching stiffness, resulting in energy minimization by buckling of the membrane.[2,3]

The dependence of the amplitude A on the aspect ratio b/h of the buckled membrane is shown in Figure 2: as b/h increases, A slightly

increases. Another way to increase A of the buckled membranes is to change the swelling ratio of PDMS; a decreasing of A is found while lowering ϕ_{iso} of the aqueous isopropanol mixture.

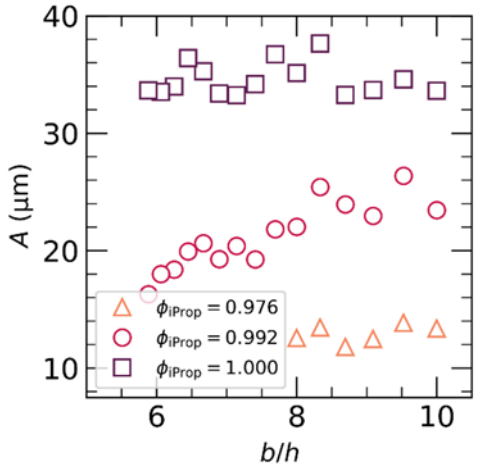

Fig. 2: Amplitude A of membranes structures of different b/h, exposed to ϕ_{iso} fractions of 1.000, 0.992 and 0.976. For $\phi_{\mathrm{iso}} = 0.976$ no buckling pattern was observed for $b/h < 8$. © Pfohl Group

The dependence of the wavelength λ of the buckles on h/b at different ϕ_{iso} are shown in Figure 3. In contrast to A, λ of the buckled membranes are almost independent of b/h. Furthermore, it is stable against changes in ϕ_{iso} as λ mainly determined by its width b.[2]

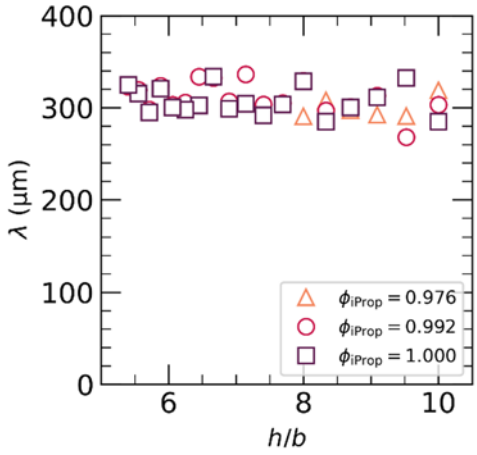

Fig. 3: Wavelength λ of membrane structures of different b/h exposed to solutions of $\phi_{\mathrm{iso}} = 1.000$, 0.992 and 0.976. For $\phi_{\mathrm{iso}} = 0.976$ no buckling pattern was observed for $b/h < 8$. © Pfohl Group

The stress (normalized by the Young's modulus) at which a membrane buckles depends on the geometry of the membrane and is mainly determined by b/h.[3] To analyze the b/h-dependency, we designed a membrane of $a = 10\ \mathrm{mm}$, $b = 100\ \mu\mathrm{m}$ and h, which has a gradual linear change from $h_{\mathrm{max}} = 50\ \mu\mathrm{m}$ to $h_{\mathrm{min}} = 8\ \mu\mathrm{m}$ along the length a (Figure 4). An initially straight and perpendicular to the substrate standing membrane shows deflections after immersing in isopropanol ($\phi_{\mathrm{iso}} = 1.000$). The onset of buckling can be observed at a position with $b/h \approx 3.4$. At positions of $b/h > 3.4$, buckles become more pronounced and the amplitude A is increasing with increasing b/h (Figure 4b).

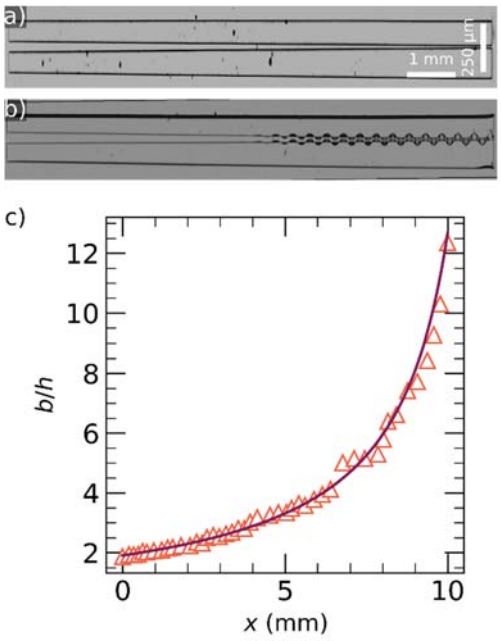

Fig. 4: a) Membrane with position-dependent b/h in contact with air (micrograph is stretched by a factor of 4 in height – see scale bars). b) Membrane with position dependent b/h immersed in isopropanol (micrograph is stretched by a factor of 4 in height – see scale bars). c) b/h of the membrane with h linearly decreasing from $h_{\mathrm{max}} = 50\ \mu\mathrm{m}$ at $x = 0$ to $h_{\mathrm{min}} = 8\ \mu\mathrm{m}$ at $x = 10\ \mathrm{mm}$. © Pfohl Group

Using the relationship between the swelling properties of the solvent and the membrane dimensions determined by b/h, controlled buckling of membranes can be generated in order to build microresistors, which can spatially and temporally change the hydrodynamic properties within fluidic networks.[4] In addition, the selective buckling of specific elements in fluidic networks allows for the incorporation of logical elements for material and information transport in microfluidic chips.

References

[1] Alim K., Amselem G., Peaudecerf F., Brenner M. P. & Pringle A. (2013). Mechanism of signal propagation in Physarum polycephalum. Proceedings of the National Academy of Sciences of the United States of America, 110, 13306–13311.

[2] Jiang R., Xiao J. & Song J. (2017). Buckling of thin gel strip under swelling. Theoretical and Applied Mechanics Letter 7, 134-137.

[3] Timoshenko S. P. & Gere J. M. (1961). Theory of Elastic Stability. 2nd Edition, Dover Publications (348-428).

[4] Stamp C. H., Solomon B., Lang F., Mitropoulos E. & Pfohl T. (2023) Tuning the hydraulic resistance by swelling-induced buckling of membranes in high-aspect-ratio microfluidic devices, under review.

Future Field "Biomimetic, Biobased and Bioactive Materials Systems"

Artificial Venus flytraps demonstrators outperforming the biological model

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The Cluster of Excellence "Living, adaptive and energy-autonomous Materials Systems (livMatS)" at the University of Freiburg develops novel materials systems displaying dynamic, life-like and non-equilibrium (energy-autonomous) features. In the livMatS research area "Demonstrators" bioinspired demonstrators like an artificial Venus flytrap are envisaged demonstrating the feasibility of the novel materials systems. Natural material systems and their functionality serve as idea generators and "biological models" for bioinspired material systems. Our research aims to translate the functions of animate nature into engineering applications, enabling novel functions such as embodied intelligence and embodied energy. For example, current artificial Venus fly traps (AVF), which represent plant-inspired (soft) robotic systems are based on various plant motion and actuation principles, and adaptation modes, using, for example, the principles of carnivorous snap trap plants for fast movements [1–5].

In this project. through metamaterial design strategies and adaptation of the mechanical metamaterial unit cell design of "Kinetix" unit cells by Ou et al. [6], we created a unit cell based artificial Venus flytrap (UC AVT) [5]. These unit cell systems are produced using the polyjet 3D printer available at the FIT. The basic structures are rotating polygonal auxetic structures simplified as four-bar connections of rigid plates and elastic or rotating pin hinges. This allows planar and spatial shape changes by varying the angles and positions of plates and hinges, creating uniformly scaling, shearing, bending or rotating unit cells. Our combination of these different unit cells into one unit cell with two sets of angled rigid plates allows not only bending, but also curved movement of the designed surface. This novel design enables the creation of doubly curved surfaces, which can create a convex or concave shape, like the trap lobe of Venus flytrap (*Dionaea muscipula*) [7]. Connecting two of these surfaces via a basic unit cell creates the UC AVF [5]. Compressing the central unit laterally results in a closure motion of the trap lobes via kinematic coupling of the unit cell walls (Fig.1). Characterizing the UC AVT demonstrators in terms of motion kinematics and actuation forces shows a fast closure within 300 to 600 ms and lobe speeds up to 1.36 m/s depending of the actuation speed and force.

The characterization showed that the force drops abruptly down to 0.5 N when passing the zero degree curvature line (Fig. 1 B). If the closing motion is stopped before the steric hindrance of the geometry occurs, the actuation force required to fully close the UC AVT can be maintained at the first maximum of the curvature inversion. This first peak can thus be considered as the minimum force requirement for a possible actuator, so that it "only" needs to overcome the internal frictional forces of the joints at the beginning of the movement of the joints, which averages at 2 N.

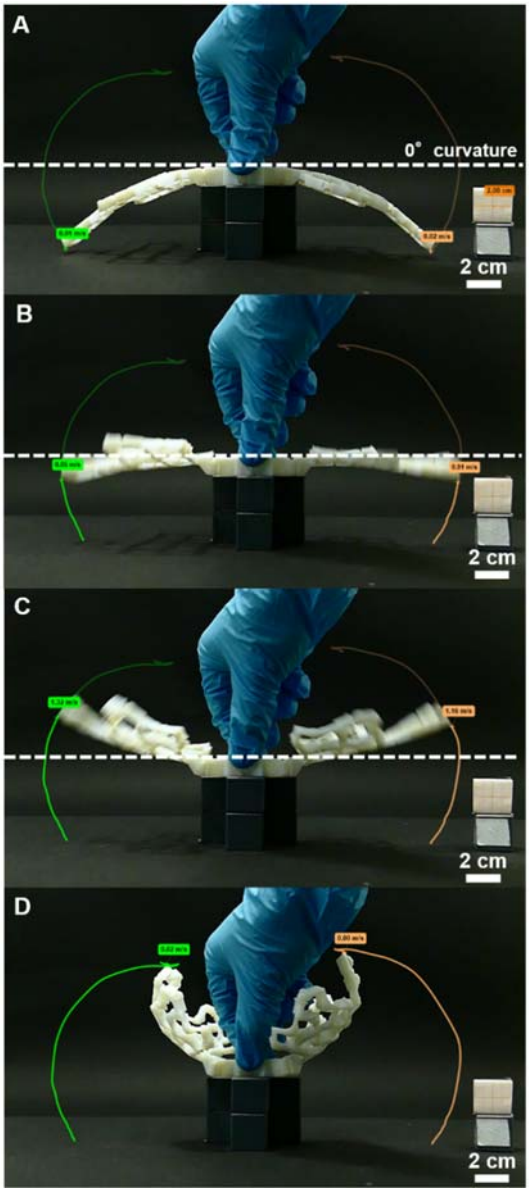

Fig. 1: UC AVT closure motion. Manual actuation of the central unit is followed by closure motion (A-D). Due to kinematic coupling of the trap lobe to the central unit, is their curvature inverted from concave (A) to convex (D). The UC AVT closes within 300 to 600 ms with lobe tip speeds of up to 1.32 m/s (C). © Plant Biomechanics Group Freiburg

The analysis of the force-displacement measurements shows that an internal force maximum - due to the internal joint resistance and friction - must first be overcome in order to initially set the trap halves in motion and reach the horizontal alignment of the 0° curvature. After passing the 0° curvature point, a local force minimum occurs when the closing movement starts, followed by a force increase during further closing and reaching its maximum when the steric hindrance due to the geometry occurs.

In the livMatS UC AVT, the basic snap-trap geometry of the plants was abstracted to a 3D printed mechanical metamaterial model. Using pin joints and kinematic coupling of the central unit a one dimensional compression motion resulted in a 3D curvature inversion of the trap lobes.

Identifying the force requirements and kinematics allows us to select a suitable actuator for autonomous actuation in the next step. The novel UC AVT enables us to build unit cell based autonomous grippers and support structures for soft machines in the future that perform complex motion sequences. These are regarded as guideline values for future materials systems and AVTs currently under development within *liv*MatS.

References

[1] Esser F, Scherag F D, Poppinga S, Westermeier A, Mylo M D, Kampowski T, Bold G, Rühe J and Speck T 2019 Adaptive Biomimetic Actuator Systems Reacting to Various Stimuli by and Combining Two Biological Snap-Trap Mechanics Biomimetic and Biohybrid Systems: 8th inter-national conference Living machines (Nara; Japan, 2019) ed U Martinez-Hernandez et al (Cham: Springer, Cham) pp 114–21

[2] Esser F J, Auth P and Speck T 2020 Artificial Venus flytraps: a research review and outlook on their importance for novel bioinspired materials systems Front. Robot. AI 7 75

[3] Speck T, Poppinga S, Speck O and Tauber F 2022 Bio-inspired life-like motile materials systems: Changing the boundaries between living and technical systems in the Anthropocene The Anthropocene Review 9 237–56

[4] Tauber F J, Auth P, Teichmann J, Scherag F D and Speck T 2022 Novel Motion Sequences in Plant-Inspired Robotics: Combining Inspirations from Snap-Trapping in Two Plant Species into an Artificial Venus Flytrap Demonstrator Biomimetics (Basel, Switzerland) 7

[5] Tauber F J, Riechert L, Teichmann J, Poovathody N, Jonas U, Schiller S and Speck T 2022 Unit cell based artificial Venus flytrap Living machines Biomimetic and biohybrid systems. 11th inter-national conference. LNCS 13548

[6] Ou J, Ma Z, Peters J, Dai S, Vlavianos N and Ishii H 2018 KinetiX - designing auxetic-inspired deformable material structures Computers & Graphics 75 72–81

[7] Poppinga S, Bauer U, Speck T and Volkov A G 2018 Motile traps Carnivorous plants: physiolo-gy, ecology, and evolution ed A Ellison and L Adamec (Oxford University Press) pp 180–93

Multiplexed biosensor for point-of-care COVID-19 monitoring: CRISPR-powered unamplified RNA diagnostics and protein-based therapeutic drug management

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The general concept of the microfluidic lab-on-a-chip device used within the scope of this project has been validated by previous works of our group, amongst other purposes employing the biosensor for the detection of ß-lactam antibiotics [1], or biomarkers for pediatric medulloblastoma [2]. In this study, the platform was further developed and paired with an optimized CRISPR-powered assay for the detection of SARS-CoV-2 genetic material as well as an existing ß-lactam bioassay. Engineers of the Disposable Microsystems Group from the Faculty of Engineering (PI: Dr. Can Dincer), biologists of the Cluster of Excellence CIBSS – Centre for Integrative Biological Signalling Studies (PI: Prof. Wilfried Weber) and clinicians from the Institute of Virology of the University Medical Center Freiburg (Dr. med. Daniela Huzly) contributed to this project.

With decreasing temperatures and more time spent indoors COVID-19 infections are back on the rise. Considering the recent decisions of four federal states to end isolation requirements for infected individuals as well as the virus constantly evolving and mutating (and thus, escaping detection by commercially available lateral flow devices) rapid and sensitive testing opportunities, ideally targeting viral RNA to keep pace with new variants, again gain major significance for the containment of the disease.

Similar to the current gold standard for RNA detection, rt-qPCR, our bioassay targets short sequences which are characteristic to the SARS-CoV-2 single-strand RNA genome. In contrast, however, our system omits reverse transcription of these snippets into DNA by utilizing the Leptotrichia buccalis CRISPR associated protein 13a (LbuCas13a), that directly binds its RNA target sequences and thereby activates to collaterally cleave RNA strands in its surrounding.

In brief, a sample solution, obtained by oro- or nasopharyngeal swab sampling, is added to a reaction mix containing the effector (LbuCas13a), the reporter RNA (reRNA: 20 uracils labelled with a biotin and a 6-FAM molecule on each end, respectively) CRISPR-RNA (crRNA), designed reverse complementary to the RNA sequence of interest and an RNase inhibitor to prevent unspecific cleavage of reRNA. After incubation at 37°C, the reaction solution is applied to the immobilization area of the microfluidic channel that has been pre-incubated with neutravidin and subsequently blocked with casein to prevent unspecific binding of biomolecules to the surface of the chip. The biotin molecules on the reRNA attach themselves to the immobilized neutravidin and, if still uncleaved, can be read out via the glucose-oxidase (GOx) conjugate on the anti-6-FAM antibody incubated in the last step of the immobilization procedure (Fig. 1). The enzyme is herein used to catalyse the conversion of the substrate (glucose) into the electrochemically active species (hydrogen peroxide) that is then flushed over the electrochemical cell, located directly behind the immobilization area within the microfluidic channel, and separated from the latter by a hydrophobic stopping barrier. The peak in measured current density corresponds to the viral load detected within the sample in an inversely proportional manner.

We were able to reduce the incubation time required for the Cas13a-mediated reporter cleavage to only 5 minutes (compared to our previous work with 3 hours) while still achieving a limit of detection in the femtomolar range

(~10,000 copies/µl) without prior amplification of the genetic material. Taking into account an overall sample-to-result time of approximately 30 minutes, our system positions itself squarely among the top performers in the field [3].

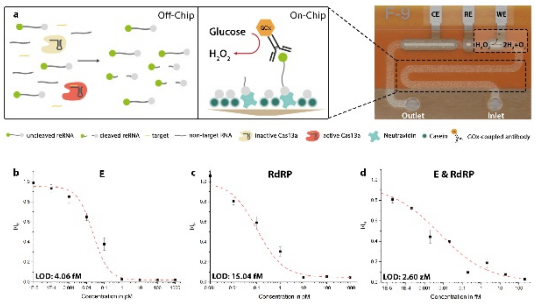

Fig. 1: Working principle of the CRISPR-powered bioassay. LbuCas13a (beige: inactive; red: active) and crRNA form a complex within the reaction mix and if activated by binding to the target RNA (yellow) trans-cleave the reRNAs (labelled with biotin (grey) and 6-FAM molecules (green)). Following application to the biosensor, the reRNA binds to neutravidin (light green) and, if still intact, is detected by a GOx (orange)-conjugated anti-6-FAM antibody that catalyses the conversion of the glucose substrate to hydrogen peroxide. Unspecific adherence of biomolecules is prevented by blocking with casein (dark green) prior to and biotin after introduction of the reaction mix. (b-d) Calibration curves measured with synthetic SARS-CoV-2 E, RdRP, and a combination of both genetic sequences, respectively (crRNA: CRISPR-RNA, reRNA: reporter RNA, 6-FAM: 6-Carboxyfluorescein, GOx: glucose-oxidase, WE: working electrode, RE: reference electrode, CE: counter electrode. N=4, error bars represent ± SD). Adapted with permission from [3] Copyright 2022, Elsevier.

In order to guarantee the meaningfulness of each test result we made use of the multiplexing capacity of the platform by implementing CRISPR-assays for the detection of the envelope (E) gene (a relatively stable genetic region of the virus that is common to members of the SARS-related Betacoronavirus family), the RNA-dependent RNA polymerase (RdRP) gene (a region specific to SARS-CoV-2), a positive and a negative control for the assay on one single chip. We then supplemented these CRISPR-powered assays with a ß-lactam antibiotic detection complete with its own control assay to facilitate simultaneous monitoring of the viral load alongside the blood antibiotic levels of patients that are being treated for a bacterial co-infection (Fig. 2).

To further improve the point-of-care applicability of our system, we performed measurements using a credit card sized near field communication (NFC) potentiostat and a microperistaltic pump, kindly provided by Silicon Craft Technology PLC and Jobst Technologies, respectively.

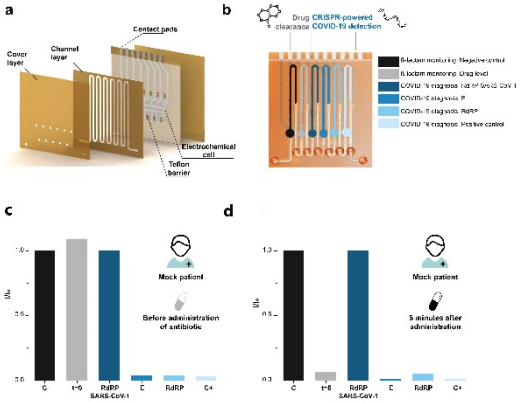

Fig. 2: Design of the multiplexed microfluidic biosensor for 6 targets. (a) Explosion diagram showing the layers that constitute the device. (b) Each of the six immobilization areas is equipped with its own electrochemical cell. The areas marked in blue were used to immobilize the CRISPR-powered SARS-CoV-2 assays while the areas marked in grey and black were incubated with the ß-lactam detection assay. (c, d) Measurement results of two simulated COVID-19 patients undergoing antibiotherapy. Low signals indicate high viral load or antibiotic levels, respectively. Adapted with permission from [3] Copyright 2022, Elsevier.

Although the platform sets itself apart from other methods employing different Cas effectors by omitting nucleic acid amplification, only necessitating non-toxic, shelf-stable and inexpensive reagents and performing within a relatively short sample-to-result time, it is still prone to errors due to several hands-on steps that could introduce RNase contamination. In future work, we aim at reducing these steps as far as possible and elaborate on the point-of-care applicability, cost-effectiveness and ease of setup by further experiments with the miniaturized measurement components.

References

[1] H. C. Ates et al., “Biosensor-Enabled Multiplexed On-Site Therapeutic Drug Monitoring of Antibiotics,” Adv. Mater., 2021, doi: 10.1002/adma.202104555.

[2] R. Bruch et al., “CRISPR/Cas13a-Powered Electrochemical Microfluidic Biosensor for Nucleic Acid Amplification-Free miRNA Diagnostics,” Adv. Mater., vol. 31, no. 51, 2019, doi: 10.1002/adma.201905311.

[3] M. Johnston et al., “Multiplexed biosensor for point-of-care COVID-19 monitoring: CRISPR-powered unamplified RNA diagnostics and protein-based therapeutic drug management,” Mater. Today, 2022, doi: 10.1016/j.mattod.2022.11.001.

Tendril coiling in passion flowers

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www.growbot.eu

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Despite their sessile nature, plants do move a lot, especially climbing plants. Instead of producing a solid, self-supporting stem, these plants climb upwards relying on support structures. Passion flowers for example climb by using tendrils, which are long, filamentary organs that attach to a support either via adhesive discs (e.g. *Passiflora discophora*) or by “grasping” slender supports and coiling around them (e.g. *Passiflora caerulea*). Eventually, the tendrils coil along their length axis and form a spring-like structure.

We investigated the ontogenetic development of tissue anatomy of *P. caerulea* tendrils during coiling [1, 2], to identify the driving principle behind the motion. We found that while in young, straight tendrils, only the primary vessel elements are lignified (fig. 1), during coiling, the tendril’s central cylinder lignifies unilaterally between the vessel elements (fig. 1).

This indicates, that unilateral tissue maturation contributes to the coiling. In mature tendrils, the entire tendril center is lignified.

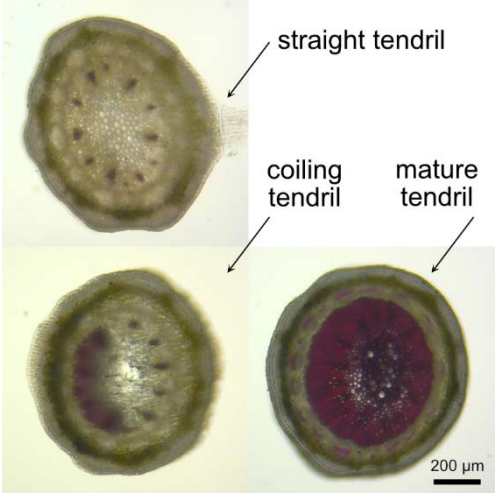

Fig. 1: Ontogenetic development of tendril anatomy. Cross-sections of a straight tendril, a coiling tendril and a coiled mature tendril of P. caerulea. Cross-sections are free hand sections, stained with phloroglucinol-hydrochloric acid, which indicates lignin in red. (© Plant Biomechanics Group)

The coiling movement leads to shortening of the tendril, and thereby generates a tensional force that pulls the plant to its climbing substrate. This force has already been measured before, however only as a momentary snapshot (e.g. [3]) or by accepting interference from self-weight forces. In order to continuously measure the change of tensional force generated by the tendrils during the coiling process, we developed a novel testing setup (fig. 2) [1], consisting of a 2 N 3-axis force sensor, mounted to a metal frame, so that the sensor can be positioned freely in a 2D plane. The sensor is equipped with a small handle that is brought in contact with a climbing plant tendril, which coils around it. The stem at the tendril base is restrained with a clamp, so that the plant’s own weight does not influence the measurement. Tendril coiling is documented by time lapse photography, so that the force can be correlated with the tendril movement. First experiments indicate, that the tendrils of *P. caerulea* generate tensional forces ranging between several millinewtons and more than 100 mN.

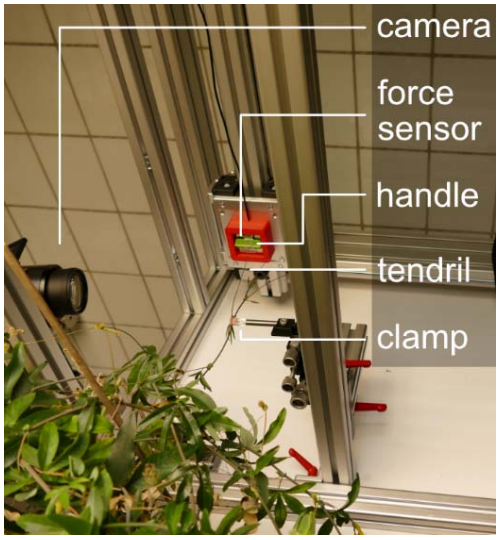

Fig. 2: Coiling force measurement setup. A tendril of *P. caerulea* attaches to a small handle, mounted to a 3-axis force sensor. The force is measured over time during coiling of the tendril axis. The plant stem is restrained in a clamp so as to isolate the measured force from the plants own weight. (© Plant Biomechanics Group)

The conspicuous, spring-like shape of climbing plant tendrils acts as an energy-dissipating element in the climbing plant's attachment system, as we have shown for example by detailed mechanical analysis of individual tendrils of *P. discophora* [4]. The tendrils of *P. discophora* are positioned alternatingly along the plant stem (fig. 3). We complemented our tests on individual tendrils with pull-off tests on stem segments comprising several tendrils, and found that the tendrils are not loaded sequentially one after the other, but are acting as parallel system, so that load and energy-dissipation is distributed between multiple tendrils [2].

Climbing plant movements and attachment strategies such as the ones discussed above will inspire the development of artificial attachment devices and foster the emergence of the new field of plant-inspired soft robots [e.g. 2, 5].

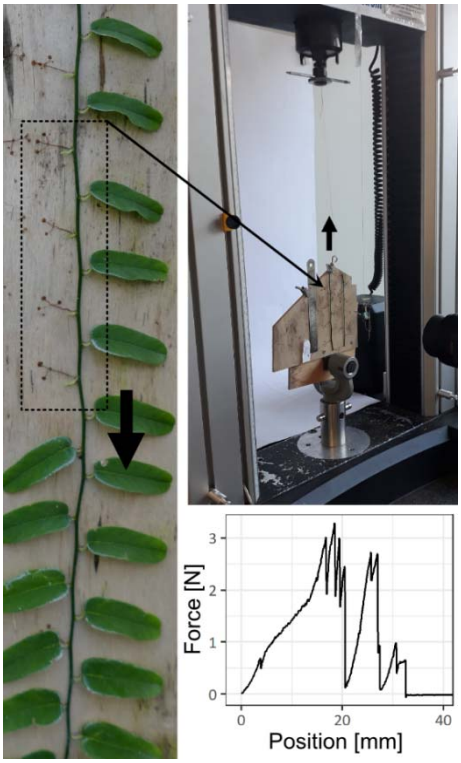

Fig. 3: Pull-off tests of *P. discophora* stem segments, comprising multiple tendrils. Axillary tendrils attach alternatingly on each side of the plant stem (several leaves removed for photography). A segment of the plant stem attached to wooden substrate was excised and mounted in a material testing system. Note that the stem segment is mounted upside down and that the pull-off force was applied towards the stems basis (corresponding to downwards in natura). (© Plant Biomechanics Group)

References

[1] Klimm, F., Speck, T. & Thielen, M. (2022). Force generation in the coiling tendrils of *Passiflora caerulea*. (submitted)

[2] Speck, T., Cheng, T., Klimm, F., Menges, A., Poppinga, S., Speck, O., Tahouni, Y., Tauber, F., Thielen, M. (2022). Plants as inspiration for material-based sensing and actuation in soft robots and machines, MRS Bulletin. (in print)

[3] MacDougal, D. T. (1896). The mechanism of curvature of tendrils. Annals of Botany, os-10(3), 373–402.

[4] Klimm, F., Schmier, S., Bohn, H. F., Kleiser, S., Thielen, M., & Speck, T. (2022). Biomechanics of tendrils and adhesive pads of the climbing passion flower *Passiflora discophora*. Journal of Experimental Botany, 73(4), 1190–1203.

[5] Meder F., Murali Babu, S.P., Mazzolai, B. (2022). A plant tendril-like soft robot that grasps and anchors by exploiting its material arrangement, IEEE Robotics and Automation Letters 7(2) 5191–5197.

Materials transitions and delamination resilience in cones and cone scales of *Pinus jeffreyi* and *Pinus nigra*

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This project aims to implement bio-inspired principles into hygroactive demonstrators for improving their resistance and resilience, and thereby the longevity of hygroactive bending actuators.

In recent years, passive and energy-autonomous façade shading systems have increasingly become a focus in architecture and construction engineering. A cooperation between the Plant Biomechanics Group Freiburg and the Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS) at the University of Freiburg with the Cluster of Excellence Integrative Computional Design and Construction for Architecture (IntCDC) at the University of Stuttgart resulted in 3D-printable, passive hygroactive bending actuators inspired by the hygroscopic movements of pine cone scales [1]. Due to the different hygroscopic expansions of the layers of this multilayer system, these actuators can perform bending movements in multiple directions. Currently, the long-term usability of such actuators is limited due to possible delamination between the different hygroactive and resistance layers, which finally may result in a loss of function.

To contribute to the solution of this problem, analyses were performed on the repetitive motion and mechanical wear of pine cone scales and tissues building them up. In these scales a bending motion is generated by the different longitudinal expansion of their tissues when they are exposed to humidity. The sclereid cells of a scale represent the (main) active layer and the sclerenchyma fibers the restricting layer. The unequal extension in the longitudinal direction of these layers seems to depend on the different angles of the microfibrils in the cells of which these two tissues consist of [2]. While the scales were initially described as a bilayered system, the importance of the brown tissue as an intermediate layer and gradients inside the tissues was recently highlighted [3,4]. With the ability of some tissues (the sclerenchyma fibers) to bend on their own, without the contribution of the other tissues [5], the pine cone scale seems to be much more complex than previously thought. Even in more than 10 million years old fossil conifer cones a hygroscopic bending motion could be observed [6]. This raises the question of how the complex interaction of the different pine cone scale tissues contributes to delamination resistance and resilience to maintain functionality.

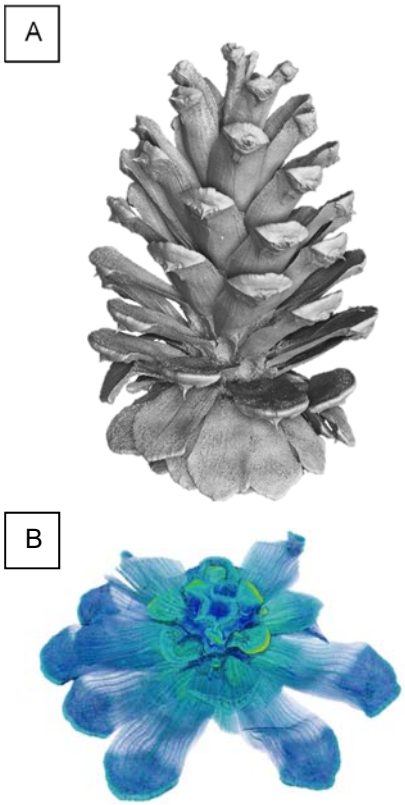

Fig. 1: A) Isosurface rendering of a pine cone from Pinus jeffreyi based on the reconstruction data of a µCT scan. B) Section from the lower third of a pine cone. The colorization represents the density based on the grey values from the µCT reconstruction. Yellow: high density, blue: low density. (© Plant Biomechanics Group)

In order to answer this question, ten pine cones from *Pinus jeffreyi* and *Pinus nigra* (five of each species) were scanned in a µCT (Fig. 1). Additionally, we measured the activation force of selected scales by blocking them in an open position with a force sensor and initiating the closing of the scales by submerging the cones completely in water. In the next step, these cones were placed in a custom-made testing device where they can be repetitively submerged in water and then air-dried. During this repeated opening and closing of the cones, the scale tip displacement during drying is monitored. Thereby changes in the opening range of multiple scales across a cone can be described based on the distance between the cone mounting and the scale tip. After a set time period of frequent repetitions, the samples will be taken out of the device and scanned in the µCT again. Additionally, the blocking force of the same scales is measured once more.

By comparing the reconstructions of the µCT images before and after the period of repeated hydration-induced bending of the scales, we can localize delamination and other damages between and inside the scale tissues (Fig. 2). In order to analyse if and to what extent this damage influences the functionality of the scales, we additionally take the results of the force measurements and the scale tip displacements into account.

Fig. 2: Cross-section of a pine cone scale of *Pinus jeffreyi* (µ-CT scan reconstruction). Red arrow: Visible delamination between the sclerenchyma fibers and the brown tissue. (© Plant Biomechanics Group)

As the project progresses, the analyses of pine cones and their mechanical behavior will deepen the understandind of tissue properties and interaction and allow to abstract principles for delamination resistance and resilience. Together with the results from other biological models that will be analyzed in the future, those principles will then be implemented in hygroactive technical material systems to show how delamination resistance and resilience can be improved in passive, energy-autonomous façade shading systems.

References

[1] Correa, D., Poppinga, S., Mylo, M. D., Westermeier, A. S., Bruchmann, B., Menges, A., & Speck, T. (2020). 4D pine scale: biomimetic 4D printed autonomous scale and flap structures capable of multi-phase movement. Philosophical Transactions of the Royal Society A, 378(2167), 20190445.

[2] Dawson, C., Vincent, J. F., & Rocca, A. M. (1997). How pine cones open. Nature, 390(6661), 668.

[3] Eger, C. J., Horstmann, M., Poppinga, S., Sachse, R., Thierer, R., Nestle, N., ... & Rühe, J. (2022). The structural and mechanical basis for passive-hydraulic pine cone actuation. Advanced Science, 9(20), 2200458.

[4] Quan, H., Pirosa, A., Yang, W., Ritchie, R. O., & Meyers, M. A. (2021). Hydration-induced reversible deformation of the pine cone. Acta Biomaterialia, 128, 370-383.

[5] Zhang, F., Yang, M., Xu, X., Liu, X., Liu, H., Jiang, L., & Wang, S. (2022). Unperceivable motion mimicking hygroscopic geometric reshaping of pine cones. Nature Materials, 21(12), 1357-1365.

[6] Poppinga, S., Nestle, N., Šandor, A., Reible, B., Masselter, T., Bruchmann, B., & Speck, T. (2017). Hygroscopic motions of fossil conifer cones. Scientific reports, 7(1), 40302.

3D printed robotic arm with integrated soft muscle

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Stefan Conrad is a Hermann-Staudinger-Fellow.

The *liv*MatS research area "Demonstrators" researches on and builds technical prototypes like an artificial Venus flytrap [1–5] and autonomous adaptive grippers [6], which highlight the potential of the developed material systems. These bio-inspired demonstrators are

supposed to respond to environmental changes triggered by material embedded decision-making. Unlike classic machines, these devices are not based on rigid metal components but consist of compliant mechanisms and soft elastomers. One popular actuation approach for such soft robots is the use of pneumatic actuators. These muscle-like structures expand or bend via pressurization with air and provide a natural adaptivity which motorized gripper made of “hard” components could never reach.

As a contribution to faster test cycles of varying complex geometries made of novel material combinations, we constructed and programmed an innovative multi-material 3D printing platform [7,8]. This system switches tools during a print allowing the integrated processing of substances with different mechanical properties. As the printheads are independent, there is no interaction and cross contamination. Since each tool is loaded with a specific material, it can be adapted to the individual requirements of this substance. This way the platform potentially covers a wide range of extrudable compounds like polymers, gels and waxes.

To characterize the developed device we previously manufactured multiple kinds of soft actuators [6-9]. By pushing the system to its limits, we were able to optimize the print parameters and object geometries. Thanks to the adapted tools, the platform handles the most flexible TPU filaments available and creates airtight walls and membranes of just 0.5 mm thickness. The system is able to bridge gaps of up to 10 mm, which enables creation of hollow structures without the need of support material. The resulting actuators are highly deformable and expand or bend under changing pressure as demanded by design. Loaded with weight, they proved their ability to grab and lift objects [6-8].

Based on this experience we were able to go a step further and to 3D print a robotic arm with an integrated soft pneumatic muscle [9]. The arm itself is made of two rigid PLA struts representing upper arm and forearm (Fig. 1 A). A compliant hinge and the soft TPU actuator connect both pieces. As the bending arm requires the actuator to change its angle, both sides provide an attachment joint that allows the actuator to rotate freely (Fig. 1 B). The arm is manufactured in one simultaneous printing process involving about 180 tool changes. To ensure a consistent flow rate after each switch the printer builds a prime tower next to the arm that is printed first on each layer. This strategy ensures a reliable airtight print quality for the thin actuator walls. With 20 mm height, the arm is 5 mm taller than the muscle. To locate it symmetrically the actuator is supported by a PLA platform of 2.5 mm that is easily removed after printing due to the poor chemical bonding between both materials.

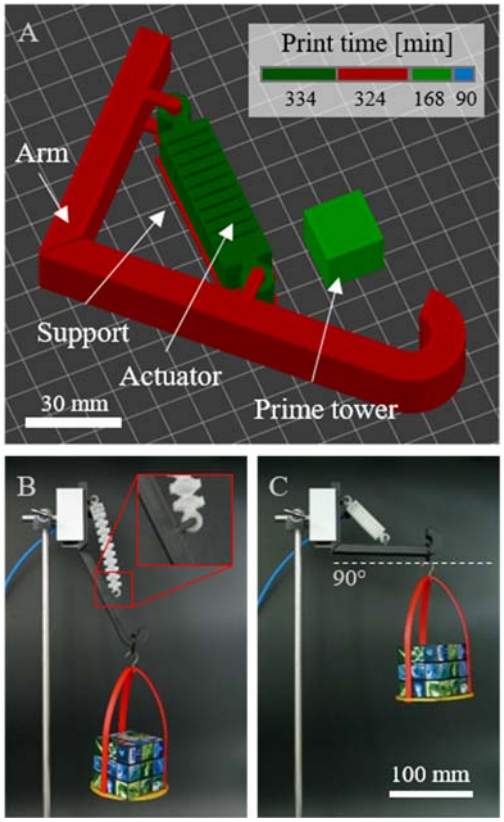

Fig. 1: Multi-material FDM 3D printed soft robotic arm (SRA). **A:** Sliced SRA made of PLA (red) and TPU (green) (PrusaSlicer 2.4.0). Print time color marked (Tool changes in blue). **B:** SRA overstretched state (+1.0 bar). **C:** SRA in actuated state (-0.996 bar). [9]

In characterizing experiments the arm was connected to a vacuum pump and loaded with weight. The arm was able to lift a mass of up to 270 g when evacuated (Fig. 1 C) and overstretched at 1 bar pressure (Fig. 1 B). A detailed analysis of the fabrication process additionally revealed that tool changes and prime tower consumed only 28 % of the print time.

That is a promising result for a procedure, which involves elaborate mechanical movement.

Based on the developed design and print parameters we are now able to investigate the integrated manufacturing of more complex objects. A simultaneous print of rigid hinge connected structures actuated by multiple soft robotic muscles would be a great advantage for the rapid prototyping within *liv*MatS. Especially the research on the adaptive gripper systems [6] will profit from the possibility to 3D print airtight flexible demonstrators with no need for manual support removal. A second focus will be on our continuous development of completely soft pneumatic logic gates that have the potential not only to control the adaptive behavior of the gripper but also to contribute to the aspired artificial Venus flytrap and to drive upcoming demonstrator projects for more autonomous machines. Such electronics-free demonstrators are an important step towards the material embedded intelligence *liv*MatS is aiming for.

References

[1] Ellison AM, Adamec L (2019) Carnivorous plants: Physiology, ecology, and evolution. Oxford University Press, Oxford, United Kingdom.

[2] Esser F, Scherag FD, Poppinga S, Westermeier A, Mylo MD, Kampowski T, Bold G, Rühe J, Speck T (2019) Adaptive Biomimetic Actuator Systems Reacting to Various Stimuli by and Combining Two Biological Snap-Trap Mechanics. Springer, Cham, pp. 114–121.

[3] Poppinga S, Joyeux M (2011) Different mechanics of snap-trapping in the two closely related carnivorous plants Dionaea muscipula and Aldrovanda vesiculosa. Physical review. E, Statistical, nonlinear, and soft matter physics 84(4 Pt 1):41928.

[4] Sachse R, Westermeier A, Mylo M, Nadasdi J, Bischoff M, Speck T, Poppinga S (2020) Snapping mechanics of the Venus flytrap (Dionaea muscipula). Proceedings of the National Academy of Sciences of the United States of America 117(27):16035–42.

[5] Westermeier AS, Sachse R, Poppinga S, Vögele P, Adamec L, Speck T, Bischoff M (2018) How the carnivorous waterwheel plant (Aldrovanda vesiculosa) snaps. Proceedings. Biological sciences 285(1878).

[6] Kappel P, Kramp C, Speck T, Tauber FJ (2022) Application-Oriented Comparison of Two 3D Printing Processes for the Manufacture of Pneumatic Bending Actuators for Bioinspired Macroscopic Soft Gripper Systems. Springer, Cham, pp. 54–67.

[7] Conrad S, Speck T, Tauber F (2020) Multi-material 3D-Printer for Rapid Prototyping of Bio-Inspired Soft Robotic Elements. Springer, Cham, pp. 46–54.

[8] Conrad S, Speck T, Tauber FJ (2021) Tool changing 3D printer for rapid prototyping of advanced soft robotic elements. Bioinspir. Biomim. 16(5):55010.

[9] Conrad S, Speck T, Tauber FJ (2022) Multi-material FDM 3D Printed Arm with Integrated Pneumatic Actuator. Springer, Cham, pp. 27–31.

Transition zones between rod-shaped and planar elements: A technical challenge solved by plants?

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In the context of longevity of biological and technical materials systems, damage control in terms of damage prevention and damage repair is a crucial concept [1]. Damage resulting from discontinuities in geometric and/or mechanical properties can be compensated by gradual transitions. Suitable biological models for a later transfer into technical applications are plant leaves with a rod-shaped and U-shaped petiole and a planar lamina connected by a damage-resisitant and smooth transition zone. During biological evolution a variety of concepts evolved, that guarantee the structural and mechanical integrity of all leaf parts.

In a comparative study, we investigated morphology, anatomy and biomechanics of plant leaves with different body plans and spatial configuration in terms of damage resistance to bending and torsional loads. In foliage leaves rod-shaped petioles and planar laminae are connected by various types of transition

zones. In order to study similarities and dissimilarities, we selected four leaf models (Fig. 1) that differ in the spatial configuration of petiole and lamina (3D-configuration: peltate leaves and 2D-configuration: stem connected to the basal region of the lamina) and in the 3D-arrangement of the involved tissues (body plan of monocotyledons and dicotyledons) [2-4].

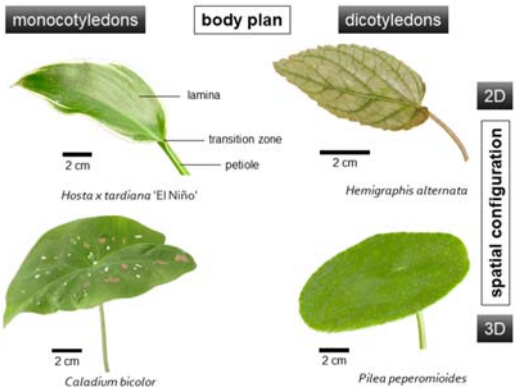

Fig. 1: Selected foliage leaves with various body plans (monocotyledons and dicotyledons) and stapial configurations of the petiole and lamina (2D-configuration: stem connected to the basal region of the lamina and 3D-configuration: peltate leaves). © Plant Biomechanics Group

The investigations include a quantitative analysis of the internal tissue arrangements using serial thin-sections and µCT scans and a quantitative description of size, cross-sectional geometry and shape of the transition zones. We found that the gradients of all these variables overlap and integrate with each other, where some features depend more on the body plan and others more on the spatial configuration.

Since the flexural rigidity and torsional rigidity are composed of geometric properties (axial and polar second moment of area) and mechanical properties (bending elastic modulus and torsional modulus), all necessary variables for a later mechanical application are taken into consideration. Furthermore, the dimensionless twist-to-bend ratio allows a comparison between the studied plant leaves and technical objects [5]. The twist-to-bend ratios of the selected petioles ranged from 12 to 39 [3].

In addition, we subjected peltate leaves of the Ufo plant (*Pilea peperomioides*) to mechanical stimuli (wind, touch, wind and touch) for six weeks. We determined the twist-to-bend ratios of both the petioles and the transition zones between the rod-shaped petiole and the planar lamina. The petioles of the control group and of all treatment groups were stiffer in bending than in torsion. In contrast, the transition zones of all groups revealed that they are stiffer in torsion than in bending, reflected by a twist-to-bend ratio of less than 1.0. Although we did not find significant thigmomorphogenetic changes in geometric and mechanical properties, the twist-to-bend ratio increased for all mechanically stimulated petioles and transition zones (with the exception of the wind-stimulated group). Based on these twist-to-bend ratios, we hypothesise that bending loads are accommodated by the petiole, while torsional loads are shared between the transition zone and the petiole [4].

Overall, the insights gained from the study of the four transition zones of the selected leaves can be considered a template for the design and optimisation of more resilient and diverse technical transition zones between rod-shaped and planar structures.

References

[1] O. Speck, M. Langer, M.D. Mylo (2022): Plant-inspired damage control—An inspiration for sustainable solutions in the Anthropocene. The Anthropocene Review 9(2): 220-236.

[2] M. Langer, T. Speck, O. Speck (2021): Petiole-lamina transition zone: A functionally crucial but often overlooked leaf trait. Plants 10(4): 774 doi: 10.3390/plants10040774

[3] M. Langer, M. Kelbel, T. Speck, C. Müller, O. Speck (2021): Twist-to-bend ratios and safety factors of petioles having various geometries, shapes and sizes. — Frontiers in Plant Science 12: 2586. doi: 10.3389/fpls.2021.765605

[4] M. Langer, E. Hegge, T. Speck, O. Speck (2022): Acclimations to wind loads and/or contact stimuli? A biomechanical study of peltate leaves of Pilea peperomioides. – J. Exp. Bot. 73(4): 1236-1252. doi: https://doi.org/10.1093/jxb/erab541

[5] S. Wolff-Vorbeck, O. Speck, M. Langer, T. Speck, P.W. Dondl (2022): Charting the twist-to-bend ratio of plant axes. – J. R. Soc. Interface 19: 20220131. doi: 10.1098/rsif.2022.0131

The European mistletoe and its connection to the host: a morphological, anatomical and biomechanical analysis of a damage-resistant interface

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The evergreen European mistletoe (*Viscum album*) is one of the most striking and frequently found plant parasites in Central Europe (Figure 1A). As a hemi-parasite, it is photosynthetically active, i.e. it produces its own glucose, but it draws water and solved nutrients from its host, which most plants uptake via roots. For this purpose, parasites grow the so-called "haustorium", a transformed organ with which they establish a mechanical and physiological connection with their host [1]. Once this connection is established, mistletoe and host grow together, and mistletoe can live for over 20 years and grow more than 2 meters tall. Despite the resulting additional mechanical loads on the tree, mechanical failure of the interface has not been observed in nature. The aim of our project was the functional morphological and mechanical analysis of this damage-resistant connection of soft mistletoe tissue (parenchymatic cells) with much stiffer wood tissue (lignified cells). The gained understanding of this plant role model can contribute as a biological basis to Area C of the Cluster of Excellence *liv*MatS for the development of bioinspired multi-materials systems with a high longevity potential.

A total of 130 mistletoe samples (ranging from 3 to 21 years of age) were harvested from a yellow buckeye tree (*Aesculus flava*) from the Botanic Garden Freiburg and measured morphometrically, with special regard to the hypertrophic attachment site. Three selected samples of different age groups (young, middle-aged, old) were chosen for morphological examination by X-ray microtomography (µ-CT) and additional samples were analyzed microscopically at the cellular level using stained thin sections. Seventy samples were tested under uniaxial tensile loading to obtain mechanical properties of the interface (Figure 1C&D). The resulting fracture areas were quantified using digital microscopy (in cooperation with the group of Frank Balle, INATECH Freiburg). A group of plain wood samples from the same tree and with the same fiber orientation were tested as control samples.

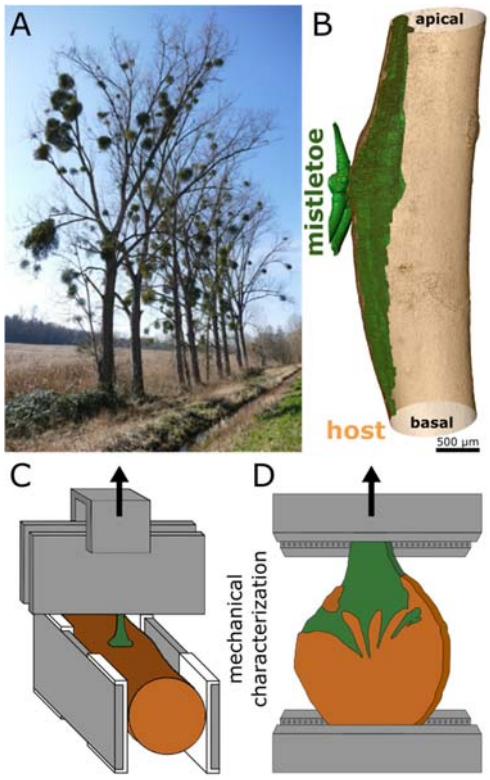

Fig. 1: A: Trees parasitized by several dozen mistletoes captured during winter time in southern Germany. B: Segmented µ-CT scan of a young mistletoe (colored green) inside a host branch (colored transparent brown). Mechanical test setup of a uniaxial tensile test on intact (C) and sliced (D) mistletoe-host samples. ©Plant Biomechanics Group Freiburg.

The maximum increase in thickness of the host branch as a result of mistletoe ingrowth was found to be about 50%, occurring already at early stages of mistletoe development and remaining approximately constant during further growth. Tissue segmentation based on the µ-CT scan of the young mistletoe sample (4 years old) showed that the haustorium is

composed by a large number of small, redundant sinkers that maximize the contact area with the host and thus the possible water uptake. In addition, mistletoe tissue was shown to have grown several centimeters along the host branch already at this young stage (Figure 1B). The comparisons with the µ-CT scans of the older samples showed that the individual sinkers gradually merge, presumably to withstand the internal growth stresses of the host, and form a single, large and wedge-shaped sinker in older mistletoes. Microscopic analyses showed that a clear cellular separation is evident between the two species at all age stages of the mistletoe. At the interface between mistletoe and host, there is no abrupt transition between non-lignified and lignified tissue, but a lignification gradient towards the inside of the sinkers became apparent. Along the dividing line, misaligned woody fibers were visible (e.g. arranged in swirls), presumably as a result of internal growth stresses and competition between the species [2].

The mechanical properties of the mistletoe-host samples were, as anticipated, lower than those of the plain wood samples. However, due to an increased roughness of the fracture surfaces and the successive failure of individual sinkers (visible through pre- and post-failure events of the force-displacement curves), the resulting failure energy of the mistletoe samples increased and was only about 80% lower than that of the plain wood samples. Analysis using digital image correlation technique showed that local strains of more than 30% are necessary to initiate fissures, which then mostly propagate along the interface or slightly offset into the interior of the mistletoe sinker. Furthermore, correlation analyses with mistletoe age revealed that both tensile strength and failure energy are age-independent. This enables a damage-resistant, mechanical and physiological anchorage of the mistletoe in the host over the span of more than two decades [3].

Our results provide exciting insights into how the longevity of interfaces between two composite materials with different mechanical properties could be increased by a geometrical materials arrangement and the use of gradient structures along the interface.

References

[1] Teixeira-Costa, L. (2021). A living bridge between two enemies: haustorium structure and evolution across parasitic flowering plants. *Brazilian Journal of Botany*, *44*(1), 165-178.

[2] Mylo, M. D., Hofmann, M., Delp, A., Scholz, R., Walther, F., Speck, T., & Speck, O. (2021). Advances on the visualization of the internal structures of the European mistletoe: 3D reconstruction using microtomography. *Frontiers in Plant Science*, *12*, 715711.

[3] Mylo, M. D., Hofmann, M., Balle, F., Beisel, S., Speck, T., & Speck, O. (2022). Biomechanics of the parasite–host interaction of the European mistletoe. *Journal of Experimental Botany*, *73*(4), 1204-1221.

Leaf unfolding: Approaches to investigate biomechanical properties of the leaf lamina

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Leaf unfolding is present throughout the plant kingdom: be it leaves of trees unfolding from a bud [1], grasses with their long and slender unfurling leaf blade [2], or floating waterlilies unfolding on the water surface [3]. This diversity makes leaves promising biological models for bioinspired packaging and unpackaging systems [1].

The assessment of leaves' structural and biomechanical properties is crucial for implementing their unfolding principles into technology. We therefore perform biomechanical analyses (1) during natural leaf unfolding, (2) during artificially induced leaf unfolding in a tensile testing machine, and (3) on isolated leaf areas. *Syngonium podophyllum* (Araceae) serves as a first model species for these three approaches of biomechanical analyses.

(1) Forces that arise during natural leaf unfolding will be quantified via a load cell (Fig. 1). The folded lamina is positioned next to the

force sensor and the stalk is fixed in order to maintain the leaf in a firm position while unfolding.

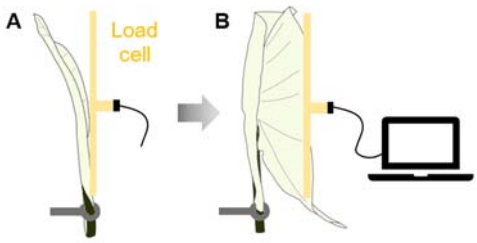

Fig. 1: Illustraion of force measurement during natural leaf unfolding in *Syngonium podophyllum*. (A) Leaf fully folded. (B) One leaf half unfolded. (© Plant Biomechanics Group)

(2) For mechanical "artificial" leaf unfolding, an inflatable and dilatable catheter will be inserted into the folded leaf. Catheter inflation will cause the lamina to unfold whereupon the required force to do so will be determined. Comparing natural and mechanical leaf unfolding will allow to quantify lamina response in each experiment and thus to assess its properties.

(3) In a micro-tensile testing machine isolated leaf areas and leaf veins will be tested in tension (Fig. 2).

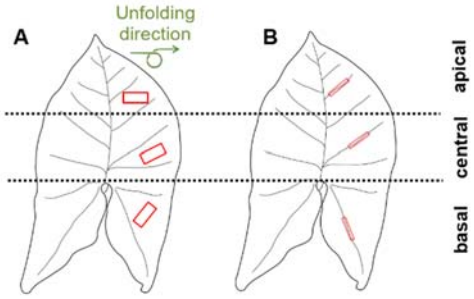

Fig. 2: Illustraion of leaf preparation for tensile experiments on isolated leaf areas. (A) Sample preparation parallel to unfolding, as well as parallel and perpendicular to leaf venation. All three sample orientations will be performed in ervery leaf area (apical, central and basal). (B) Vein sample preparation in the three different leaf areas. (© Plant Biomechanics Group)

With these three approaches, we aim to establish reliable and reproducible methods for biomechanical analyses during leaf unfolding. This will allow comparison of different leaf species, independent of their unfolding principle, their habitat or environmental conditions. Once a better understanding of leaf unfolding is achieved, a step towards technical implementation can be made.

References

[1] Kobayashi, H., Kresling, B. & Vincent, J.F.V. (1998). The geometry of unfolding tree leaves. Proc. Royal Soc. B, 265, 147–154.

[2] Amidei, T.P. (1932). The anatomy of the leaf of Panicum palmifolium. Bull. Torrey Bot. Club, 59, 491–499.

[3] Wu, P., Zhang, L., Zhang, K., Yin, Y., Liu, A., Zhu, Y., Fu, Y., Sun, F., Zhao, S., Feng, K., Xu, X., Chen, X., Cheng, F. & Li, L. (2022). The adaptive evolution of Euryale ferox to the aquatic environment through paleo-hexaploidization. Plant J., 110, 627–645.

4D-Bioprinting of vascularized bone tissue and evaluation of blood vessel and bone formation in an orthotopic bone defect model

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Project funding: German Research Foundation (DFG FKZ KO 3910/1-2)

In recent years, 3D-bioprinting of artificial tissues has become an important field of research. This involves the use of living material in the form of a cell suspension or cell-laden hydrogels known as a bioinks. As the architecture and required precision of the bioprinted tissues increase, the complexity of the used bioinks and the number of printing technologies increases. The process parameters and the material properties of the bioinks need to be finely adjusted to achieve cell biological functionality and printing accuracy of the 3D-printed artificial tissue [1].

In the last report, a hybrid bioprinting process using polycaprolactone (PCL) as a supporting scaffold was presented, which could be published in the meantime [2]. In analogy, an extrusion-based hybrid bioprinting process was developed based on a more physiological cal-

cium phosphate cement (CPC). By varying geometric printing parameters, the influence on the mechanical properties of CPC scaffolds was investigated with the aim of producing tunable scaffolds that approximate the mechanical requirements of the native microenvironment of bone tissue. The morphological and mechanical investigations of single filaments of CPC provided a basis for better evaluating the results of the scaffolds. In addition to the tensile strength of single filaments, the influences of the type of dosing needle, as well as the extrusion value on the morphology of the print results were investigated. Both, the printing width of the filaments and the printing accuracy in dependence on the extrusion values were evaluated. The results obtained enabled CPC scaffolds of different configurations to be designed, printed and also assessed based on their morphological and mechanical properties. The influence of different geometric and printing parameters, such as printing design, extrusion value and filling degree of the scaffolds, was investigated (Figure 1).

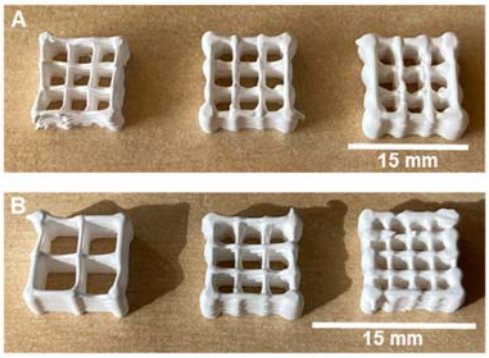

Fig. 1: Representative CPC constructs after extrusion printing varying different printing parameters such as filament width (A) or the number of filaments per layer (B). (© Laboratory of MEMS applications)

Therefore, the individual parameters were analyzed and evaluated in context to determine their influence on the fabrication of constructs that are as mechanically and dimensionally stable as possible. As a result, the parameters for a scaffold with the highest mechanical stability and printing accuracy and lowest number of breaks are an alternating printing design (scaffold type 1), a filling degree of the scaffold of 26 % and an extrusion value of 0.04 mm, resulting in a filament width of 352 µm (Figure 2).

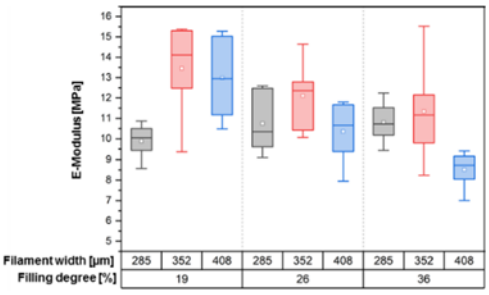

Fig. 2: Elastic moduli of CPC constructs for a scaffold type 1 with different filament widths and different filling degree. n=6. (© Laboratory of MEMS applications)

Based on the results of the 18 different scaffold variations, a weighting of the individual parameters could be applied according to their influence on the mechanical properties of the scaffolds. By this, the extrusion value has the highest and the filling degree of the scaffold the lowest influence. Thus, it could not only be confirmed that the geometry of the scaffolds has a significant influence on the mechanical properties of the structures [3] but also the extent of the influence of the individual parameters could be described in more detail. The resulting CPC scaffolds yielded Young's moduli of up to 15.5 MPa and are thus within the range of mechanical properties of bone. The developed hybrid 3D-bioprinting method also confirmed the influence of hydrogel on the mechanical properties of CPC scaffolds [4], and also showed the influence of the proportion of hydrogel in a hybrid scaffold. Despite a reduction in the compressive strength of the CPC scaffolds due to the hydrogel, the hybrid scaffolds yielded Young's moduli that were within the Young's modulus ranges of bone. With the developed hybrid 3D-bioprinting method, it was also possible to both print and subsequently culture cells. The influence of a direct contact with CPC on the cells was investigated and the importance of the distance of the bioink to the CPC could be shown (Figure 3).

Finally, by designing a prototype for an orthotopically implantable bone replacement construct, the flexibility and adaptability of the 3D-bioprinting process, as well as the CPC scaffolds, could be demonstrated. This work was carried out by Mark Cedric Kelbel in the course of his master's thesis. The knowledge gained here is an important step towards enabling a variety of implementation options of specific

tailored anatomical models for bone regeneration and thus the fabrication of individualized implants that meet the necessary requirements of a graft.

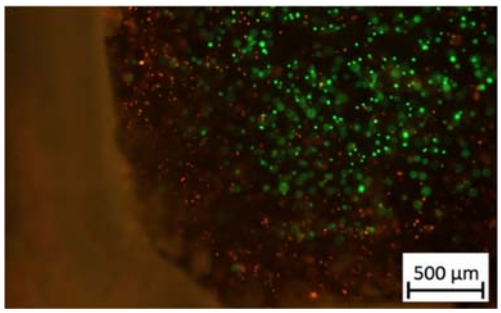

Fig. 3: Live/Dead staining of CPC/hydrogel hybrid constructs featuring immortalized mesenchymal stem cells (iMSCs). Red dots indicate dying cells in proximity of the CPC scaffold (yellow) and green dots living cells at a greater distance. (© Laboratory of MEMS applications)

References

[1] Ozbolat, I.T., Yu, Y., (2013). Bioprinting toward organ fabrication: challenges and future trends. IEEE Trans Biomed Eng, 60(3), 691-699.

[2] Koch, F., Thaden, O., Conrad, S., Tröndle, K., Finkenzeller, G., Zengerle, R., Zimmermann, S. and Koltay, P. (2022) Mechanical properties of polycaprolactone (PCL) scaffolds for hybrid 3D-bioprinting with alginate-gelatin hydrogel. Journal of the Mechanical Behavior of Biomedical Materials. 130:105219, https://doi.org/10.1016/j.jmbbm.2022.105219.

[3] Kilian, D., Sembdner, P., Bretschneider, H., et al. (2021): 3D printing of patient-specific implants for osteochondral defects: workflow for an MRI-guided zonal design. Bio-Design and Manufacturing, 4 (4), 818–832. https://doi.org/10.1007/s42242-021-00153-4

[4] Ahlfeld, T., Doberenz, F., Kilian, D., et al. (2018): Bioprinting of mineralized constructs utilizing multichannel plotting of a self-setting calcium phosphate cement and a cell-laden bioink Biofabrication, 10 (4), 045002. https://doi.org/10.1088/1758-5090/aad36d

Future Field "(Micro)Systems for Energy Conversion, Storage and Energy-Autonomy"

Investigation of high surface area PtCo/C intermetallic catalysts for improved PEM fuel cell performance

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Parts of the following article have already been incorporated into a manuscript preprint available on chemrxiv.com.[1] For further in-depth information about this study, we kindly refer to this preprint.

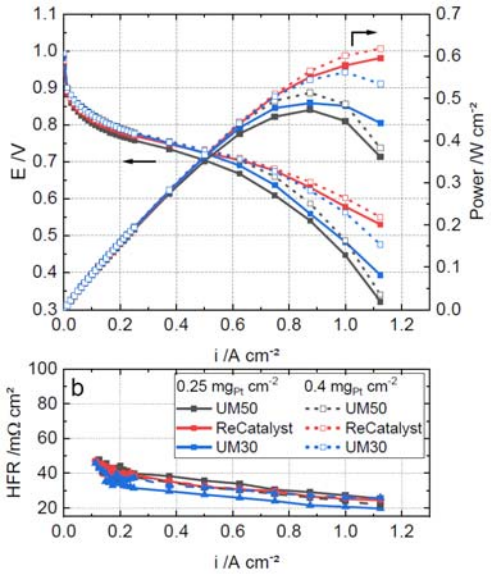

Fig.1: Polarization curves (a) and the high-frequency resistances (b) of the MEAs with UM50, ReCatalyst and UM30 at 0.25 mg_{Pt} cm^{-2} loading and 0.4 mg_{Pt} cm^{-2} loading under H_2/air, 80 °C, 96 % RH and ambient pressure. (© Electrochemical Energy Systems Group)

Due to their high power density, low operating temperature and quick refuelling times, proton exchange membrane fuel cells (PEMFCs) present themselves as a promising and environmentally friendly technology for power source applications in the automotive heavy duty and energy industries.[2] The high cost of PEMFCs, with the typical platinum-based electrocatalyst accounting for a sizable amount of the price, is a significant impediment to large-scale commercialization. In search of possibilities to reduce the precious metal content, Pt*M*/C alloy catalysts (*M* e.g. Co, Fe, Ni) have demonstrated increased activity for the desired oxygen reduction reaction (ORR), resulting in a significant performance improvement when compared to pure Pt/C based systems.[3]

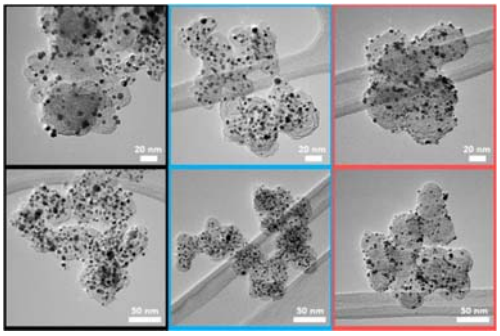

Fig. 2: Representive TEM micrographs of the three catalysts UM50 (black), UM30 (blue) and ReCatalyst (red). Scale bars represent 20 nm (top) and 50 nm (bottom). (© Electrochemical Energy Systems Group)

To gain a deeper fundamental understanding of this performance increase, and to facilitate the development and optimization of suitable electrocatalysts, two state-of-the-art commercial PtCo/C catalysts and a promising novel electrocatalyst based on a double passivation galvanic displacement method (provided by the collaborating research group led by Dr. Matija Gatalo and Dr. Nejc Hodnik from the National Institute of Chemistry, Ljubljana, Slovenia, and denoted as ReCatalyst) were intensively studied. In that regard, electrochemical performance in the cathodes of membrane-electrode-assemblies (MEAs) was used to derive electrochemical parameters and compared to morphological aspects of the catalysts obtained by statistical transmission electron microscopy (TEM).[4] The commercial PtCo/C catalysts were purchased from Umicore N.V. and are denoted UM50 for Elyst Pt50 0690 and UM30 for Elyst Pt30 0690.

Polarization curves (H_2/air, 80 °C, 96 % RH, ambient pressure) of the electrocatalysts employed in MEAs reveal that although all samples exhibit significant ORR activity, especially the novel ReCatalyst shows superior performance at high current densities for both tested cathode loadings (0.25 and 0.4 mg_{Pt} cm^{-2}, respectively).

A possible explanation for this phenomenon would be that the PtCo nanoparticles supported on carbon are used more efficiently in the case of ReCatalyst than in the case of the reference materials. From 2D TEM micrographs (Fig. 2), it is evident that all three electrocatalysts feature PtCo nanoparticles that are distributed quite homogeneously on the respective carbon support.

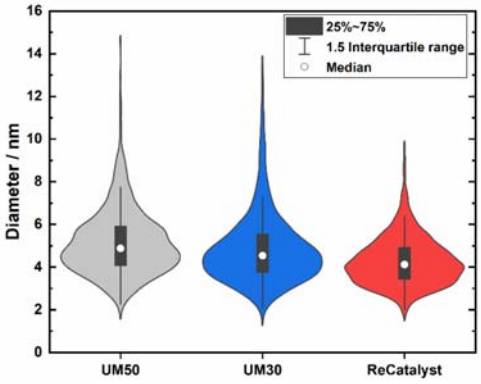

Fig. 3: Violin plots of the particle size distribution for the three PtCo/C catalysts. (© Electrochemical Energy Systems Group)

A more detailed evaluation of the obtained micrographs by measuring at least 2000 individual nanoparticles on several support particles shows that very large PtCo particles are mostly absent, especially in the ReCatalyst sample (Fig. 3). Although there are only small differences in the mean size of the diameters, decreasing from 4.8 nm for UM50 and 4.5 nm for UM30 to 4.1 nm for ReCatalyst, very large particles due to their volume disproportionately strongly lead to a loss of activity as the innermost atoms do not significantly contribute to the ORR. For the ReCatalyst sample, statistically most nanoparticles show the perfect

size for ORR activity, which is believed to be in the range of 4-5 nm.[5]

Although this finding could already provide an explanation for the better MEA performance, STEM tilt series were taken of the UM30 and ReCatalyst sample for tomographic 3D reconstruction (Fig. 4). Recent research suggests that the nanoparticle position (exterior or interior to the carbon support) may also have a crucial influence on the ORR activity.[6]

From preliminary results, it can be estimated that 35 % of PtCo nanoparticles remain exterior on the carbon support surface for the ReCatalyst sample, while only 17 % of PtCo nanoparticles are found on the exterior for the UM30 sample. This could potentially explain the difference observed at high current densities. Further studies are necessary to evaluate the importance of the nanoparticle position in respect to the MEA performance.

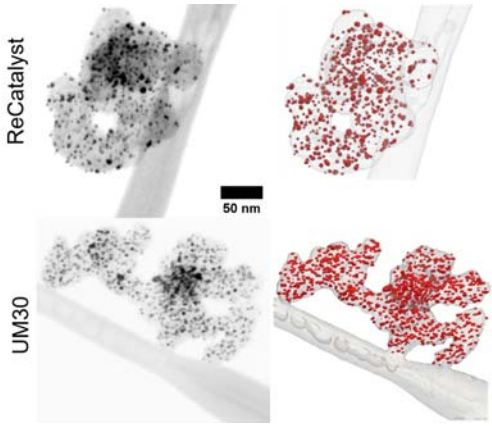

Fig. 4: Raw STEM images (left) and reconstructed 3D models (right) of individual PtCo/C particles. (© Electrochemical Energy Systems Group)

References

1. Nguyen & Heizmann *et al.*, Alternative and facile production pathway towards obtaining high surface area PtCo/C intermetallic catalysts for improved PEM fuel cell performance [Online early access] DOI: 10.26434/chemrxiv-2022-8k3dt

2. M. K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells, *Nature,* 486 (7401), 43–51 (2012)

3. Zhang *et al.*, Recent advances in Pt-based electrocatalysts for PEMFCs, *RSC Adv.,* 11, 13316-13328 (2021)

4. M. Gatalo *et al.,* A Double-Passivation Water-Based Galvanic Displacement Method for Reproducible Gram-Scale Production of High-Performance Platinum-Alloy Electrocatalysts*, Angew. Chem.,* 58(38), 13266–13270 (2019).

5. Wang *et al.,* Monodisperse Pt_3Co Nanoparticles as a Catalyst for the Oxygen Reduction Reaction: Size-Dependent Activity, *J. Phys. Chem. C,* 113(45), 19365–19368 (2009).

6. Harzer *et al.,* Tailoring Catalyst Morphology towards High Performance for Low Pt Loaded PEMFC Cathodes, *J. Electrochem. Soc.,* 165 (10), F770-F779 (2018)

High-resolution neutron imaging of salt precipitation and water transport in CO_2 electrolyzers

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The electrochemical reduction of CO_2 is a pivotal technology for a fossil-free production of feedstocks for the chemical industry. Although first electrolyzers producing carbon monoxide (CO) are already reaching pilot scale [1], they still face major hurdles in achieving the durability needed for industrial commercialization, due to the formation of precipitates in the CO_2 reduction electrode. In a recent publication in the journal nature communications we investigated these processes [2].

The most common cell design is a zero-gap arrangement, where the anode and cathode are in direct contact with an anion conductive membrane, as it offers high energy efficiency [3]. Fig. 1a shows the idealized reactions and water transport processes taking place in a zero-gap electrolyzer. On the cathode side gaseous CO_2 is being reduced under the consumption of water, producing CO and OH^- ions. The OH^- ions partially react with the present CO_2, forming bicarbonate and carbonate ions. These anions can pass the anion exchange membrane to the anode side. The an-

ode is typically supplied with an aqueous potassium hydroxide solution, and oxygen is released in the oxygen evolution reaction.

Over time, potassium ions from the liquid electrolyte can migrate from the anode and accumulate at the gas-fed cathode. When the solubility limit is exceeded, salts will eventually precipitate in the gas diffusion electrode and impede transport of gaseous CO_2 to the active catalyst sites. This can lead to rapid performance decrease, pressure build up and even to total cell failure [4].

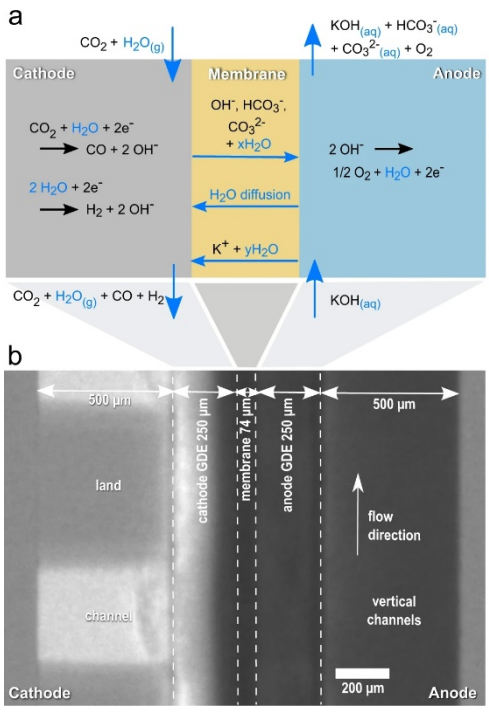

Fig. 1: Transport processes and cell components. (a) Water management highlighted in schematic of reactions and transport processes during operation. (b) enlarged section of a normalized neutron radiographic image of the CO_2 electrolysis cell with approximate dimensions of the components. (adapted from Disch *et al.* [2] CC BY Copyright © 2022)

The zero-gap cell design makes it particularly difficult to investigate such processes in-operando without significant modifications to the membrane electrode assembly, as the utilized components are generally opaque for typical analysis methods. We therefore, used high-resolution neutron imaging for the first time to investigate a zero-gap CO_2 electrolyzer producing CO at application relevant current densities in cooperation with scientists from the Heinz Maier-Leibnitz Zentrum. Fig. 1b shows an enlarged section of a neutron radiographic image of the electrolyzer during operation.

While hydrogen atoms show strong neutron attenuation, other elements like carbon or oxygen are transparent for the neutron beam on the relevant sample sizes of a few centimeters. Thereby, it is possible to quantify small changes in water content even inside the flow fields made from titanium. Due to the strong neutron attenuation of hydrogen atoms, the anode compartment filled with aqueous electrolyte appears dark compared to the gas-fed cathode compartment. The dark dent reaching from the gas diffusion electrode into the cathode channel, is caused by hygroscopic precipitates.

To illustrate the changes at different reduction rates we recorded neutron images at different current densities and normalized them to the image of the cell at zero current, as shown in Fig. 2.

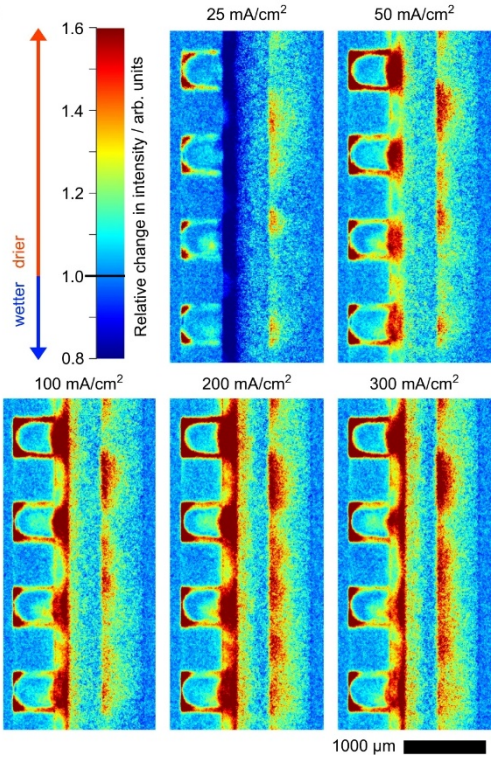

Fig. 2: Neutron radiography of the CO_2 electrolysis cell. The relative change in intensity normalized to the intensity of the zero current cell, which corresponds to a change in water content. (adapted from Disch *et al.* [2] CC BY Copyright © 2022)

The images show that the cathode (left) gets dryer with rising current density up to 200 mA cm^{-2} as the water consumption by the reaction increases. At the same time, the anode side gets “dryer” as oxygen gas bubbles evolve and force out the liquid electrolyte. At 300 mA cm^{-2}, however, the precipitation of hygroscopic and hydrogen containing bicarbonates increases significantly resulting in a slightly brighter (i.e. wetter) cathode area compare to 200 mA cm^{-2}. By these measurements, we found that there are significant differences between channel and land regions for both salt precipitations and water transport. Furthermore, we pointed out that there might also be spatial variations in local current densities. Our work stresses the need for the development of further mitigation strategies for salt precipitation and suggests including flow field design and electrode compression in future works.

References

[1] Masel RI, Liu Z, Yang H, Kaczur JJ, Carrillo D, Ren S et al. An industrial perspective on catalysts for low-temperature CO2 electrolysis. Nat. Nanotechnol. 2021;16(2):118–28. https://doi.org/10.1038/s41565-020-00823-x.

[2] Disch J, Bohn L, Koch S, Schulz M, Han Y, Tengattini A et al. High-resolution neutron imaging of salt precipitation and water transport in zero-gap CO2 electrolysis. Nat Commun 2022;13(1):6099. https://doi.org/10.1038/s41467-022-33694-y.

[3] Wakerley D, Lamaison S, Wicks J, Clemens A, Feaster J, Corral D et al. Gas diffusion electrodes, reactor designs and key metrics of low-temperature CO2 electrolysers. Nat Energy 2022;370:eaba6118. https://doi.org/10.1038/s41560-021-00973-9.

[4] Jesus Gálvez-Vázquez M de, Moreno-García P, Xu H, Hou Y, Hu H, Montiel IZ et al. Environment Matters: CO 2 RR Electrocatalyst Performance Testing in a Gas-Fed Zero-Gap Electrolyzer. ACS Catal. 2020;10(21):13096–108. https://doi.org/10.1021/acscatal.0c03609.

Influence of interstitial Li ions on the electronic properties of LixCsPbI3 as a photobattery material

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The functional integration of a solar-cell absorber with a Lithium-ion battery in one halide perovskite material is a conception of harvesting and storage of energy for portable smart electronic devices. The device with the highest degree of integration uses the photovoltaic absorber as an electrode in the electrochemical storage unit. This requires absorber materials having not only a suitable optical band gap, but also a good ionic conductivity and storage capacity of Lithium.

Halide perovskites are a family of materials that have the potential for high photovoltaic performance and low fabrication cost in solar cells. $CsPbI_3$ is a well-studied prototype for such halide perovskites. A recent report [1] proposes that Li ions can penetrate into and migrate across the perovskite crystal structure. Thus, $CsPbI_3$ is a potential candidate material for an integrated device combining light harvesting and lithium storage.

In this work, the stability of crystalline $CsPbI_3$ with interstitial Li ions is investigated together with the effect that Li has on the electronic structure of the resulting compound Li_xCsPbI_3. Using computational methods of density-functional theory (DFT) we analyze the stability and the band gap of two structural models for Li_xCsPbI_3 at room temperature, the cubic α phase and a distorted structure analogous to the γ phase (γ’ structure) of the halide perovskite. The hypothetical α phase does thermodynamically not allow an uptake of Li and is

likely to be structurally unstable for x > 1/4, while adding Li up to x = 1 in the γ' structure turns out to be energetically favorable. In all cases, Li promotes structural distortions of the perovskite crystal, namely tilting of Pb-I-Pb bond angles $\Delta_{Pb\text{-}I\text{-}Pb}$ and Cs off-center displacements Δr_{Cs}, which lead to a decrease of the solution energy and an increase of the concentration of Li ions in the perovskite (see Figures1a and 1b).

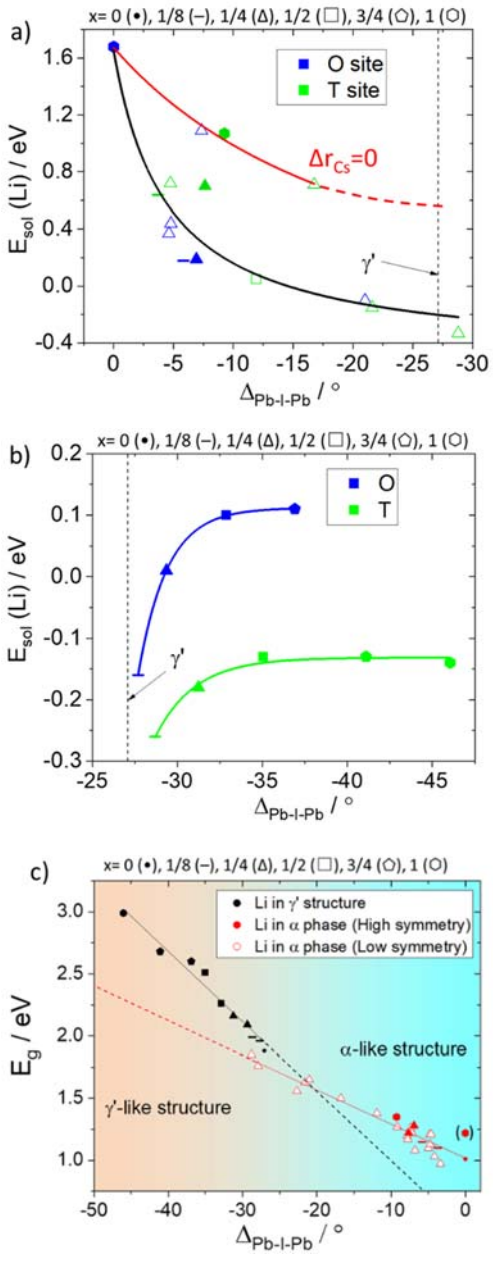

Fig. 1: Relation of Li solution energy Esol and angle distortion ΔPb-I-Pb with varying Li concentration x in a) α phase and b) γ' structure. Fig. c) displays the relation between the band gap Eg and the angular distorsion angle ΔPb-I-Pb caused by the insertion of Li ions into the two perovskite phases. © C. Elsässer's Group

Furthermore, interstitial Li has the following effects on the electronic structure of $CsPbI_3$: i) the induced structural distortion reduces the band dispersion, which leads to a significant increase of the band gap; ii) depending on the electronic charge (Li being considered as neutral atom or charged ion), the screening by mobile electrons in the conduction band leads to a small change in the band gap; iii) Li 2s states hybridize with I and Pb states, but the effect on the band edges and band gap is negligible. Altogether, the change of the band gap is dominated by the $\Delta_{Pb\text{-}I\text{-}Pb}$ angles, i.e., stronger distortion caused by increasing Li content is accompanied by a (linear) increase of the band gap, as plotted in Figure 1c.

Overall, the insertion of Lithium into the halide-perovskite crystal led to an increase of the band gap of Li_xCsPbI_3 compared to $CsPbI_3$. The continuously increasing band gap must be taken into account for potential photobattery applications. It may also provide a sensible measure for the content of Li in (hybrid) halide-perovskite compounds.

References

[1] Z. Li, C. Xiao, Y. Yang, S. P. Harvey, D. H. Kim, J. A. Christians, M. Yang, P. Schulz, S. U. Nanayakkara, and C.-S. Jiang, Extrinsic ion migration in perovskite solar cells, Energy & Environmental Science 10, 1234 (2017).

ThermoBatS – Thermoelectric Battery Systems

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The *liv***Mat**S project ThermoBatS is part of research area A and aims at harvesting thermal energy by developing a micro-thermoelectric generator (*μ*TEG) with two different phase

change materials (PCM) on both sides, acting as heat reservoirs. The concept and idea behind this package – called a ThermoBatS – has been described extensively in previous reports [1,2].

The project can be broken down into two halves: (1) the development and fabrication of the µTEG part and (2) the addition of the PCMs on both sides of the µTEG, forming the ThermoBatS unit. The first part (1) involved synthesis of the thermoelectric materials – n- and p-type, based on Bismuth telluride – and its formulation as a printable ink as well as the whole multi-step process of using the ink to fabricate µTEGs in pre-structured substrates.

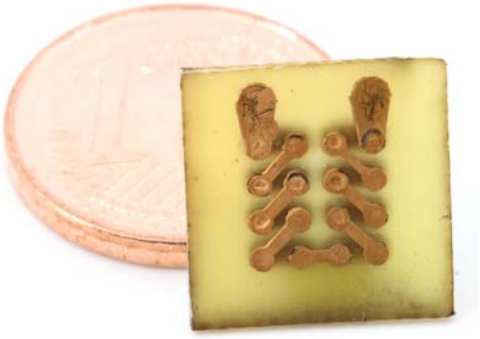

Fig. 1: ThermoBatS μTEG (10 x 10 mm²) on a PCB substrate (© IMTEK/Laboratory for Design of Microsystems)

The whole process along with characterization results has been published in 2021 [3] and an extension/update is prepared at the moment. With the first half of the project successfully finished (Fig. 1), the second half (2) was started in 2021. This involved identification and selection of suitable PCMs as well as overcoming PCM thermal conductivity limitations. The first results and the reasoning behind the PCM selection have been communicated in last years FIT report [4]. The selected, non-toxic and non-corrosive organic PCMs suffer from an intrinsically low thermal conductivity in both liquid and solid state with a maximum approaching only 0.2 W/mK. Prior to any possible integration into a ThermoBatS, the low thermal conductivity had to be addressed.

In order to reliably measure thermal conductivity of paraffin wax PCMs and later its increase, the TACS (temperature adjustmen and control setup) has been developed in-house (Fig. 2).

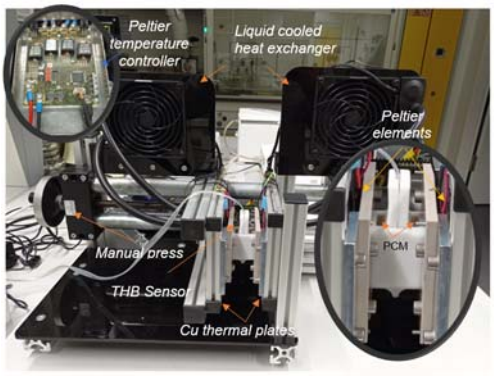

Fig. 2: TACS with THB (see text for details) (© IMTEK/Laboratory for Design of Microsystems)

The TACS and is able to maintain a certain temperature at its copper plates to within 0.1 K. For thermal conductivity measurements at different temperatures, the TACS was combined with a THB (transient hot bridge) system from the company Linseis, which uses wired probes immersed/embeedded in the liquid/solid. The whole setup can measure thermal conductivities at different temperatures with high precision and has been presented at the PowerMEMS conference 2022 in Salt Lake City (Utah, USA) [5].

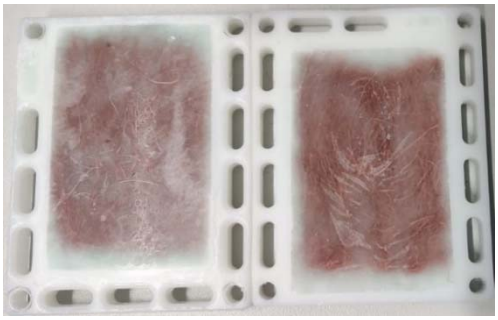

Fig. 3: Solidified PCM-Cu-wool composite (© IMTEK/Laboratory for Design of Microsystems)

In order to increase the thermal conductivity of PCMs, composites with different metal shavings and wools have been fabricated and tested (Fig. 3). A PCM-Cu-wool composite with only 2.8 % Cu is able to enhance the thermal conductivity of a pure PCM +290 % and +125 % in liquid and solid state respectively. Currently the addition of finer graphite or Cu

powders to this composite is under investigation to further increase the thermal conductivity towards 1 W/mK.

While the ThermoBatS project itself came to an end in 2022, its work continues in a multitude of successor projects. A short overview:

A *liv***Mat**S MasterLab student is currently working on further enhancing the thermal conductivity of the PCM-Cu-wool composites in order to finally integrate TEGs with PCM reservoirs, forming ThermoBatS prototypes. His project also involves exploring the possibility of using ThermoBatS as actuators.

The direct *liv***Mat**S follow-up project of ThermoBatS is called ThermoMetaS. This project will finish the ThermoBatS development and use them to develop a “self-contained material system” which is 3D printable and able to (1) harvest thermal energy and (2) can act autonomously to external temperature changes.

In ThermoBatS-RF, a collaborative project with Pennsylvania State University, funded by *liv***Mat**S and the LiMC² (Convergence Center for Living Multifunctional Material Systems), the application of ThermoBatS in responsive facades (RF) of large buildings is investigated both in different theoretical concepts as well as an experimental demonstrator.

References

[1] Subhash, S. K., Pelz, U., Hillebrecht, H., Woias, P. (2019). ThermoBatS – Thermoelectric Battery Systems. FIT-Report 2019, 53.

[2] Subhash, S. K., Pelz, U., Hillebrecht, H., Woias, P. (2020). ThermoBatS – Thermoelectric Battery Systems. FIT-Report 2020, 65.

[3] Subhash, S. K., Gerach, T., Sherkat, N., Hillebrecht, H., Woias, P., Pelz, U. (2021). Fabrication of µ TEGs Based on Nano-Scale Thermoelectric Material Dispersions. Transducers 2021, 471-474, doi: 10.1109/Transducers50396.2021.9495526

[4] Subhash, S. K., Pelz, U., Hillebrecht, H., Woias, P. (2021). ThermoBatS – Thermoelectric Battery Systems. FIT-Report 2021, 74.

[5] Subhash, S. K., W. Ordoñez, W. F. C., Hillebrecht, H., Woias, P., Pelz, U. (2022). Development and Evaluation of a Temperature Control Set-up for the Thermal Conductivity Measurement of Phase Change Materials. PowerMEMS 2022, Salt Lake City, UT, USA, 211-214, doi: 10.1109/PowerMEMS56853.2022.10007609

Realistic Aging Modelling in Fuel Cells

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Project funding: Federal Ministry of Education and Research (BMBF), Project “FC-RAT: Fuel Cell Realistic Aging Trend Modelling”

Mobility is shifting toward zero-emission electrical powertrains. Fuel cells will be an important component of electric powertrains due to their short refuelling times and high energy density. These two benefits are especially important for heavy-duty applications. However, when used in trucks, the lifetime requirement for fuel cells must be increased by a factor of 4 - 8 when compared to the current state of the art for light duty-vehicles. [1-4]

The project "FC-RAT" aims to significantly improve and expand understanding of aging and degradation processes. The aim of the project is to develop models for realistic lifetime assessments under real load profiles in collaboration with the Fraunhofer Institute for Solar Energy Systems (ISE) and AVL Deutschland GmbH,. The goal of the sub-project worked on in FIT, is to characterize and comprehend the aging and degradation mechanisms of various key components of the fuel cell. For the time being, the sub-projects' focus is on membrane aging and degradation.

Membrane electrode assemblies (MEAs) are aged with established accelerated stress tests (ASTs) to improve the understanding of aging processes within a reasonable period. Each AST is selected based on the component and degradation mechanism being examined.

To study membrane degradation with respect to chemical and mechanical degradation, the MEA is held at the open circuit voltage while the relative humidity is varied [3]. The operation at open circuit voltage accelerates chemical degradation, whereas relative humidity variation causes swelling and shrinking of the membrane and thus puts the membrane under mechanical stress. The membrane integrity is

measured in-situ at regular intervals while the AST is conducted.

First experiments indicated that mechanical degradation is the main aging mode for the tested membranes (Fig. 1). In this figure, the H_2 crossover is plotted over time as an indicator of the mechanical integrity of the membrane.

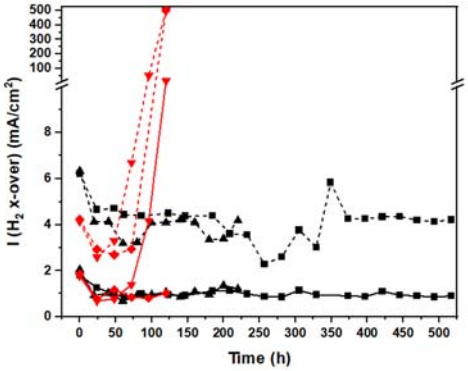

Fig. 1: Gas cross-over versus experimental time for FS-715-RFS membrane combined chemical-mechanical aging (red) versus chemical aging (black), Solid lines: pressure on anode and cathode side is the same, dashed lines: Anode with 50 kPa overpressure against cathode. Cross-over from anode to cathode is measured. Hence, increasing the pressure at the anode increases the cross-over. (© Electrochemical Energy Systems Group)

However, further investigations showed that all membranes show the same failure mechanism in mechanical aging testing. The membranes always tear at the edges of the GDL. A failure point that does only exist in small testing setups but not in larger cells and commercial stacks as there the CCMs are typically framed and the GDL edge is then on the more robust polymer frame instead of the CCM. A framing system for the combinations with our CCMs and flow fields was developed to eliminate this failure point (see Fig. 2a). For lamination, a PEN-foil (Polyethylene naphthalate) with a layer of hot glue on a polyether base was chosen. For good reproducibility, the foils are cut out with a laser. The CCM is then placed between two lamination sheets in a hot-press to seal. The GDL is cut out larger than the active area, so the edges lie on the lamination foil. Tests showed that the lifetime of cells under mechanical aging conditions can be increased by a factor of 3 (compare Fig. 2b) and that the edge of the membrane is not the failure point anymore.

To investigate chemical changes in the membrane during aging, confocal Raman microscopy was used. Previous work of this group showed that Raman microscopy is a good tool to investigate local changes in ion exchange capacity and water content in a membrane. Furthermore, confocal Raman microscopy can resolve different layers of the membrane without the need to cut the membrane, allowing for 2D cross-sections and even 3D chemical maps [5]. As taking 2D images can take multiple hours, it has to be made sure that the sample does not change over time. Therefore, a sample holder is developed in which the sample is submerged in water of controlled temperature.

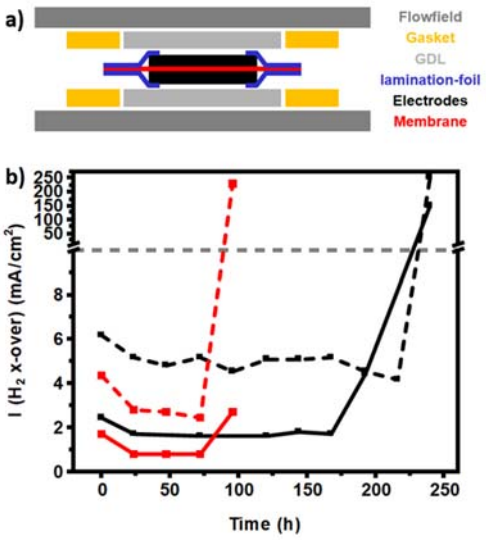

Fig. 2: a) Sketch of the new cell assembly with lamination-foil; b) Comparison of gas crossover during aging test for a sample with old cell assembly (red) and new cell assembly (black). Solid lines: pressure on anode and cathode side is the same, dashed lines: Anode with 50kPa overpressure against cathode. (© Electrochemical Energy Systems Group)

Future work will focus on evaluating local changes in chemistry and water management in different membranes after chemically aging them with the help of the above mentioned and now developed methods.

References

[1] European Commission: Communication COM/2020/301: A hydrogen Strategy for a climate-neutral Europe, 2020

[2] Bundesministerium für Wirtschaft und Energie (MBWi), Die Nationale Wasserstoffstrategie, 2020

[3] The Fuel Cell Technical Team, Fuel Cell Technical Team Roadmap, 2017. https://www.energy.gov/sites/prod/files/2017/11/f46/FCTT_Roadmap_Nov_2017_FINAL.pdf Accessed 1.12.2021

[4] Marcinkoski, J. et al.: *Hydrogen Class 8 Long Haul Truck Targets* (US Department of Energy, 2019); https://www.hydrogen.energy.gov/pdfs/19006_hydrogen_class8_long_haul_truck_targets.pdf Accessed 1.12.2021

[5] Böhm, T. et al.: Spatially Resolved Quantification of Ionomer Degradation in Fuel Cells by Confocal Raman Microscopy. *J. Electrochem. Soc.* 2019, *166* (7), F3044-F3051. DOI: 10.1149/2.0051907jes.

Integrated Photosupercapacitors: Development of a Silicon Solar Cell - Mesoporous N-doped Carbon Photosupercapacitor

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Project funding: German Research Foundation (DFG) – *liv*MatS Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems" – Project A-1

The inorganic SolStore (*i*SolStore) project is held at the University of Freiburg within the framework of the *liv*MatS DFG Cluster of Excellence and is part of the Research Area A (Energy Autonomy).

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Within the inorganic SolStore (*i*SolStore) project we aim at developing multifunctional and autonomous photocharging electrochemical energy storage systems, able to harvest and convert solar energy into electrical energy as well as store and release it at the same time and place. Additionally, such systems should feature the highest possible functional level of integration.

State-of-the-art integrated *i*SolStore devices are based on the so called three-electrode interconnection scheme, with a shared electrode between the photovoltaic (PV) part, a solar cell, and the electrochemical storage unit, a supercapacitor or battery – referred as integration mode II. In this scenario on type of charge carriers photogenerated by the solar cell migrate to and through the shared electrode, which acts simultaneously as a charge acceptor for the storage device. The two remaining electrodes, one at the solar cell and one at the electrochemical unit, close the circuit in the photovoltaic cell and the storage unit, respectively. Here two types of electrochemical photostorage devices can be targeted, namely photobatteries or photosupercapacitors, based on either on batteries or supercapacitors (incl. electrochemical double layer capacitors (EDLCs), pseudocapacitors, hybrid capacitors).

Up to date, as a first proof of concept we successfully developed a photosupercapacitor in the integration mode II based on a solar cell integrated with an EDLC. On the PV side, large area (1 cm^2) $FA_{0.75}Cs_{0.25}Pb(I_{0.8}Br_{0.2})_3$ perovskite solar cells (PSC) with an optimized layer sequence protecting the sensitive absorber from the supercapacitor electrolyte was implemented (Glunz group). As an active material for the EDLC we

used mesoporous N-doped carbon nanospheres (MPNCs) produced via a hard-templating (Fischer group).[1,2] This resulted in a peak overall photoelectrochemical energy conversion efficiency (calculated according to the protocols taken from the literature[3]) of 11.5 %.[4] As a result of this work, all the necessary integration and processing steps were established, incl. (i) the design and processing of the shared electrode interphase between the solar cell and the EDLC; (ii) developing a proper capacitive material for high performance EDLC, including its synthesis, characterization and optimization; (iii) designing and processing the supercapacitor electrodes; and (iv) identifying the proper electrolyte that would provide high ion conductivity and at the same time would be compatible (in terms of stability) with the chosen solar cell.[4,5]

Motivated by the outstanding performance of the perovskite-MPNC-based photosupercapacitor, we extended our approach for the integration of the MPNC-based EDLCs with a crystalline silicon (Si) solar cell - a highly efficient, mature and robust PV technology allowing to aim for reliable and long-lasting devices.[6] Indeed, Si solar cells offer the required chemical stability, enabling the use of aqueous electrolytes which are nontoxic, eco-friendly and cost-effective. Additionally, using Si-based solar cells makes any housing and/or encapsulation unnecessary, which reduces the device's cost and, most importantly, facilitates scaling-up and commercialization.

The electrodes of the electrochemical double layer supercapacitor (EDLC) were assembled out of MPNC particles synthesized by a hard-templating approach. This approach, yielding highly defined MPNC nanospheres, is based on the oxidative polymerization of aniline in the presence of SiO_2 nanoparticles as templates followed by carbonization and template removal (etching) and was reported by us previously for EDLCs and other electrochemical energy applications.[1,2] In this work, highly monodisperse MPNC particles carbonized at 1000°C with a particle size of 320 ± 22 nm and a well-defined continuous porous structure made of 23 nm mesopores (denoted as MPNC-23-1000, where 23 stands for the Silica template size in nm, and 1000 stands for the carbonization temperature in °C) were used (Figure 1 a). The obtained particles have a large specific surface area of 628 m^2/g and pore volume of 1.35 $cm^3\ g^{-1}$, which is a prerequisite for a high capacitive performance of the EDLC. The well-defined porous structure and monodispersity of the MPNC nanospheres (see particle size distribution in Figure 1 a, inset) allowed to produce homogeneous electrode coatings with homogeneously packed MPNC nanospheres along the whole electrode thickness achieving high intra- and interparticle percolation (Figure 1 b).

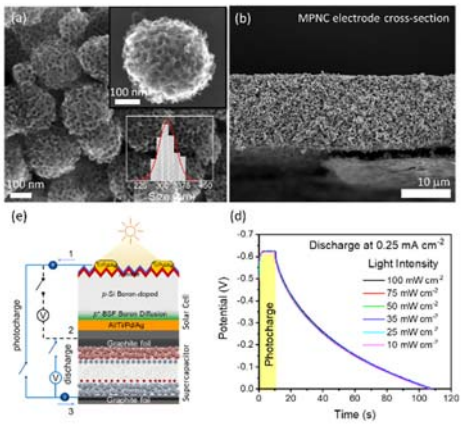

Fig. 1: SEM images of the MPNC-23-1000 (a) and a cross-section (b) of the MPNC-electrode. SEM image MPNC with a diameter of 320 nm and pore size of 23 nm and the particle size distribution in the inset. Scheme of the integrated photosupercapacitor device (b) and photocharge-discharge at low light intensities (f). Reproduced with permission from[6]

The EDLCs were assembled in a symmetric configuration using the produced MPNC electrodes and a semi-solid gel electrolyte, which overall reduced the device complexity making unnecessary any housing or packaging and allowing freestanding structures. The assembled MPNC-EDLC showed a large capacitance (224 F/g at 0.5 A/g), energy densities up to 7.7 Wh/kg with power densities up to 2.4 kW/kg.

As the photovoltaic part, we used an n^+pp^+ c-Si solar cell which showed a high efficiency of 20.5 %, high open-circuit voltage of 0.652 V, short circuit current of 38.8 mA cm^{-2} and fill factor of 81 %. The cell features an excellent illumination linearity and high performance even at low light illumination.

To assess the photoelectrochemical performance of our devices, a test station comprised of a potentiostat/galvanostat together with a solar simulator was utilized to design and perform a set of measurements such as photo-charging, photo-assisted charging as well as charging and discharging of the device.

The monolithic integration of the Si solar cell with the MPNC-EDLC resulted in a free-standing photosupercapacitor that could be photo-charged upon illumination to its maximal voltage of 0.62 V in less than 2 s and discharged on demand, achieving an areal capacitance of 47 mF cm^{-2}. The device could be photo-charged and discharged for more than 15 times, confirming good operation stability. As a result, the photosupercapacitor could deliver an energy density up to 1.25 µWh/cm^2 at a power density of 59.4 µW/cm^2 and 0.5 µWh/cm^2 at 595 µW/cm^2.

More importantly, the photosupercapacitor could be photo-charged even at low light intensities up to its maximal voltage without performance deterioration (43 mF cm^{-2}). These results point out that even under weak illumination conditions the solar cell delivers sufficient current to fully charge the supercapacitor. This only demonstrates the efficiency of our materials, integration approach and resulting devices, paving the way towards new energy autonomous *i*Solstore and *o*SolStore devices.

References

1 J. Melke, R. Schuster, S. Möbus, T. Jurzinsky, P. Elsässer, A. Heilemann and A. Fischer, Carbon N. Y., 2019, 146, 44–59.

2 J. Melke, J. Martin, M. Bruns, P. Hugenell, A. Schökel, S. M. Isaza, F. Fink, P. Elsässer and A. Fischer, ACS Appl. Energy Mater, 2020, 3, 11627.

3 Y. Fu, H. Wu, S. Ye, X. Cai, X. Yu and S. Hou, Energy Environ. Sci., 2013, 6, 805–812.

4 T. Berestok, C. Diestel, N. Ortlieb, J. Buettner, J. Matthews, P. S. C. Schulze, J. C. Goldschmidt, S. W. Glunz and A. Fischer, Sol. RRL, 2021, 5, 1–13.

5 R. D. Andrés, T. Berestok, K. Shchyrba, A. Fischer and U. Würfel, Sol. RRL, 2200614.

6 T. Berestok, C. Diestel, N. Ortlieb, S. W. Glunz and A. Fischer, Adv. Mater. Technol., 2022, 2200237.

Halide-perovskites for battery and solar-battery applications – Fundamental reconsiderations on solubility, lithium intercalation and photo-corrosion

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Within the inorganic SolStore (iSolStore) project, we aim at developing multifunctional solar photocharging electrochemical energy storage systems, able to harvest, convert, store and release energy at the same time and place. Additionally, one goal is to achieve the highest possible and functional level of integration for these systems. One way to achieve this goal is to design a 2-electrode system, involving one multifunctional photo battery elec-

trode capable of energy conversion (PV-functionality) and storage (battery functionality) at the same time and place, which is called integration mode III (Figure 1c).

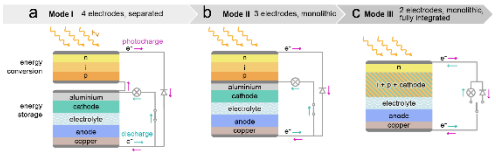

Fig. 1: Schematic of different integration modes. (a) Mode I integration with 4 external contacts, where the energy conversion unit (solar cell) is connected to the energy storage unit (battery) via external wiring. The switch is shown in a closed position. (b) Mode II integration with 3 external contacts, where the p contact of the energy conversion unit (solar cell) and the cathode (positive) contact of the energy storage unit (battery) are merged. The switch is shown in a closed position. (c) Mode III integration with 2 external contacts, where a multifunctional material is used, that is can both convert solar energy and store charges at the same time and place. The switch is shown in an open position (reproduced from [1] under CC BY-NC 4.0 license).

The obvious challenge, especially for a fully integrated 2 electrode mode III device is finding a suitable material providing all the above-mentioned functionalities at once. One candidate proposed are organic-inorganic lead halide perovskites. These materials are known to be very promising and contribute to the fast development of perovskite solar cells (PSC), which after only little more than 10 years of development outperform classic Si-solar cells on a lab scale.[2]

Recently 2-(1-cyclohexenyl)ethyl ammonium lead iodide (CHPI) has been reported as multifunctional photoelectrode material for the design of highly integrated Li-ion photo batteries.[3]

In the present work and based on the somehow conflicting literature reports on organic-inorganic lead halide perovskites for Li-ion rechargeable batteries and Li-ion rechargeable photobatteries[4-7], we revisited the (photo)electrochemical behavior of CHPI and reexplored it's applicability as a multifunctional photoelectrode material for highly integrated Li-ion based mode III photobatteries. We investigated its (photo)electrochemical behavior in very polar carbonate based electrolytes, typically used in LIBs (and previous reports) and a newly developed low polarity electrolyte based on *ortho*-difluorobenzene (*o*-DFB), to probe CHPI-stability against dissolution, possible Li-intercalation and photo-assisted deintercalation (photo charging). In addition, the general behaviour of CHPI under illumination and in contact with liquid electrolyte was assessed.

Model CHPI electrodes on FTO coated glass slides (CHPI-FTO) were prepared via spin-coating precusor solutions containing 2-(1-cyclohexenyl)ethyl amin (CHAI) and lead iodide (2:1 molar ratio) dissolved in a DMF:DMSO (4:1, v:v) solvent mixture (experimental details, see [1]). For comparison CHPI-carbon black (CHPI-CB-FTO) composite electrodes were also prepared.

For the (photo)electrochemical characterization a potentiostat/galvanostat and a solar simulator was used. The electrochemical characterizations were performed with a specifically self-designed photobattery electrochemical cell (see Figure 2b, d). As electrolyte 1M $LiPF_6$ in ethylene carbonate:dimethylcarbonate (1:1, v:v, LP30) and 0.2M Lithium perfluorobutoxyaluminate (Li[*pf*] = $Li[Al(OR^F)_4]$, R^F = $C(CF_3)_3$)Li[*pf*] in *ortho*-difluorobenzene (*o*-DFB): dimethoxyethane (DME): fluoroethylene carbonate (FEC) (59.0:2.6:1.0, v:v:v, = Li[*pf*]-*o*-DFB) were used in combination with a non-woven polymer separator from Freudenberg and a a lithium metal counter electrode.

CHPI-FTO and CHPI-CB-FTO electrodes were the samples investigated. All samples had the same dimensions of 2 cm x 2 cm. All cells were assembled inside an Argon-glovebox (O_2 < 0.1 ppm, H_2O < 0.1 ppm) following the same procedure. In case of photo-electrochemical characterizations, controlled illumination of these cells was realized with a LED-solar simulator (Wavelabs, LS2, AM 1.5 G, 100 mW cm^{-2}, AAA).

Our study demonstrates that the 2D organic-inorganic lead halide perovskite CHPI is fully soluble in polar carbonate based electrolytes, typically used for lithium ion batteries (LiB) (see Figure 2d). When a suitable low polarity electrolyte stabilizing the material is chosen, such as the previously described Li[*pf*]-*o*-DFB based electrolyte, no electrochemical evidence for Li^+ intercalation was found for the

CHPI electrode. Instead purely capacitive behavior was revealed (see Figure 2a, b, c). Attempting an illuminated galvanostatic "charge" of the CHPI-FTO electrode in the specifically designed photobattery setup, while in contact with the electrolyte, leads to photo corrosion and subsequent dissolution of the CHPI phase. This oxidative corrosion can also be achieved by simply oxidizing the material in dark or just illuminating the material without any external voltage.

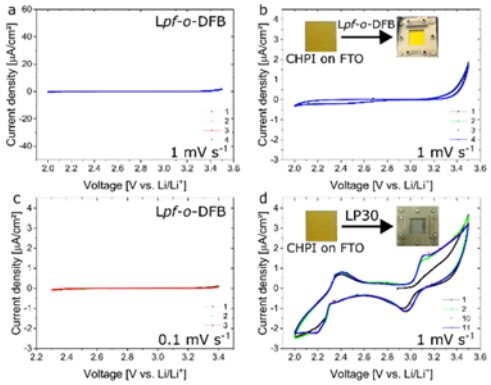

Fig. 2: (a) Cyclic voltammogram (scan rate 1 mV s^{-1}) of spin coated CHPI on FTO as working electrode with a Li counter electrode, Freudenberg non-woven polymer separator and Li[*pf*]-*o*-DFB electrolyte; (b) Zoom in of (a); Inset in (b): Picture of CHPI on FTO before (left) and after (right) contact with Li[*pf*]-*o*-DFB electrolyte. (c) CV (scan rate 0.1 mV s^{-1}) of blank FTO as working electrode with a Li counter electrode, Freudenberg non-woven polymer separator and Li[*pf*]-*o*-DFB electrolyte. (d) spin coated CHPI on FTO as working electrode; Inset in (d): Picture of CHPI on FTO before (left) and after (right) contact with the electrolyte (reproduced from [1] under CC BY-NC 4.0 license).

These dissolved species give rise to faradaic plateaus, but these are neither indicating any Li-ion-intercalation in a solid CHPI phase nor do they correspond to a photo or photo-assisted charging. As such our results contradict the results reported so far on these systems.

The inherent chemical, electro-chemical and photochemical instability of halide perovskites (especially iodide, and bromide containing compounds) and their incompatibility with a Li-ion based intercalation chemistry in our eyes disqualify these materials for any usage in mode III photobattery systems and further its use in direct combination with any polar liquid electrolyte based battery systems, at least if intercalation chemistry is targeted (Figure 3).

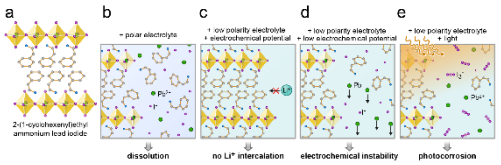

Fig. 3: Schematic of CHPI behavior for different scenarios. (a) Simplified schematic CHPI structure. (b) CHPI dissolution in polar solvents. (c) Stable CHPI in low polarity electrolyte, but no quantitative Li+ intercalation needed for relevant energy storage, occurs. (d) Reductive electrochemical degradation of CHPI with Pb0 formation. (e) Photo corrosion of CHPI under illumination (reproduced from [1] under CC BY-NC 4.0 license).

References

[1] J. Büttner, T. Berestok, S. Burger, M. Daub, H. Hillebrecht, I. Krossing, A. Fischer, *Adv. Funct. Mater.* **2022**, 2206958, 10.1002/adfm.202206958

[2] W. Xiang, S. (Frank) Liu, W. Tress, *Energy Environ Sci* **2021**, 10.1039/d1ee00157d.

[3] S. Ahmad, C. George, D.J. Beesley, J.J. Baumberg, M. De Volder, *Nano Lett* **2018**, *18*, 1856–62, 10.1021/acs.nanolett.7b05153.

[4] G.F. Samu, R.A. Scheidt, P. V. Kamat, C. Janáky, *Chem Mater* **2018**, *30*, 561–9, 10.1021/acs.chemmater.7b04321.

[5] M. Hasan, S. Venkatesan, D. Lyashenko, J.D. Slinker, A. Zakhidov, *Anal Chem* **2017**, *89*, 9649–53, 10.1021/acs.analchem.7b02800.

[6] M. Hasan, S. Venkatesan, D. Lyashenko, J.D. Slinker, A. Zakhidov, *Anal Chem* **2017**, *89*, 9649–53, 10.1021/acs.analchem.7b02800.

[7] A. Mathieson, S. Feldmann, M. De Volder, *JACS Au* **2022**, *2*, 1313–7, 10.1021/jacsau.2c00212.

Novel approach for performance evaluation of photostorage systems: the case of organic solar cell-mesoporous carbon photosupercapacitor

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The SolStore is held within the framework of the *liv*MatS Cluster of Excellence at the University Freiburg and is part of the Research Area A (Energy Autonomy).

The SolStore project tackles the integration of solar cells with the electrochemical energy storage system into one hybrid monolithic device where the solar energy is harvested, converted, stored and released on demand. To realize such self-sufficient photostorage device with a high level of integration, one of the most promising way up to date is the three-electrode design where the respective solar cell is coupled with the storage device via a shared electrode.

Thus far, in the SolStore we developed two types of such photosupercapacitors where the electrochemical double layer capacitors (EDLC, storage units) was integrated either with (i) large area $FA_{0.75}Cs_{0.25}Pb(I_{0.8}Br_{0.2})_3$ perovskite solar cells (PSC), or (ii) highly linear and robust silicon solar cells.[1,2]

The results of these works served not only as the proof of concept but also allowed us to establish all the necessary integration and processing steps, incl. (i) the design and processing of the shared electrode and its interfaces with the solar cell and the EDLC; (ii) developing a proper capacitive material for high performance EDLC, including its synthesis, characterization and optimization; (iii) designing and processing the supercapacitor electrodes; and (iv) identifying a proper electrolyte that would provide high ion conductivity and at the same time would be compatible (in terms of stability) with the chosen solar cell.

However, despite the successful integration of the photosupercapacitors, there were still no clear measurment and characterization protocols for performance evaluation of such hybrid devices, which renders a fair comparison among different photostorage devices difficult. Thus, in this work we developed a new approach to evaluate the performance of an integrated solar energy conversion and storage system and applied it to an integrated photosupercapacitor composed of a EDLC monolithically assembled with an organic solar cell (OSC).

As an electroactive material for the EDLC electrodes we used mesoporous N-doped carbon nanospheres (MPNC) with a pore size of 23 nm. The synthesis approach is based on the oxidative polymerisation of aniline in the presence of Silica template (with 23 nm diameter in this case), followed by carbonisation (1000 °C in this case) and template etching.[1-4] This resulted in highly monodisperse 320 ± 22 nm MPNC particles with well-defined porous structure with 23 nm mesopores (denoted as MPNC-23-1000, where 23 stands for the Silica template size in nm, 1000 – stands for the carbonization temperature in °C). The obtained MPNCs have large specific surface area of 628 $m^2 g^{-1}$ and pore volume of 1.35 $cm^3 g^{-1}$,

which is essential for an efficient charge accommodation and hence for high capacitive performance of the EDLC. At the same time, the MPNCs feature well-defined mesoporous structure and homogeneous particle size distribution, which is important while processing the particles onto electrodes. This results in 3D porous and accessible electrodes with fixed intraparticular diffusion pathways and maximized electrode percolation.

As the solar cell, we used a highly efficient OSC based on the absorber blend D18:Y6. Under "1 sun" illumination (AM1.5G, corrected for spectral mismatch), the OSC showed high open-circuit voltage of 0.84 V and large short-circuit current density of 24.9 mA cm^{-2} resulting in high power conversion efficiency (PCE) of 14%. This was the main trigger for fast photo-charging of the OSC-MPNC photosupercapacitor (when integrated) of up to 0.84 V. Additionally, excellent capacitive performance (with the areal capacitance up to 120 mF cm^{2}) of the MPNC-EDLC enabled to efficiently store the charge delivered by the solar cell, favoring high storage efficiency of 98.5 %. The resulted OSC-MPNC photosupercapacitor delivered 0.01 mWh cm^{-2} and 4.6 mW cm^{-2} energy and power density, outperforming reported works.[5]

As widely reported in the literature, the efficiency of the integrated photosupercapacitors is calculated using a photoelectrochemical energy conversion efficiency definition:[5]

$$\eta = \eta_{\text{conversion}} \cdot \eta_{\text{storage}} = \frac{E^{\text{output}}_{\text{solar cell}}}{E_{\text{light}}} \cdot \frac{E^{\text{output}}_{\text{storage}}}{E^{output}_{\text{solar cell}}} = \frac{0.5 \cdot C \cdot V^2}{P_{\text{i}} \cdot \Delta t \cdot A_{\text{solar cell}}} \quad \text{Eq.1}$$

Where C is the capacitance, V is the voltage when charged, P_i is the power input, Δt is the photocharging time, and $A_{solar\ cell}$ is the active photosensitive area.

This summed up to an unprecedentedly high overall photoelectrochemical peak energy conversion efficiency (η) of 17.3%, which outperforms photosupercapacitors reported in the literature so far.[6,7]

However, this equation implies that all the energy provided by the solar cell is actually stored in the supercapacitor. In real devices however, losses are expected due to the circuitry and non-ideal supercapacitor behavior. Additionally, the energy stored is not the same as the energy output for non-ideal supercapacitors.

Thus, we proposed a new definition ($\eta_{photostorage}$) to accurately calculate the efficiency of the photosupercapacitor (Eq. 2) which includes the losses occurring during the illumination. It gives the instantaneous ratio of the energy stored in the supercapacitor to the energy input:

$$\eta_{\text{photocharge}} = \frac{E_{\text{stored}}}{E_{\text{light}}} = \frac{\int_0^{t_c} (V_{\text{cap}}(t)\, J_{\text{solar cell}}(t) - J^2_{\text{solar cell}}(t) R_{\text{loss}})\, dt}{\int_0^{t_c} P_{\text{i}}\,(t)\, dt} \quad \text{Eq.2}$$

Where, E_{light} is the energy of the incoming light, $V_{cap}(t)$ is the measured voltage between the supercapacitor terminals, $J_{solar\ cell}(t)$ is the current between OSC and EDLC, t_C is the illumination time, and R_{loss} is the measured overall resistance of the losses in the system, i.e., circuitry, solar cell, and supercapacitor series resistance.

Nevertheless, Eq. 2 does not include the supercapacitor characteristics apart from the series resistance, and thus is only valid to evaluate the illuminated cycle. To calculate the complete efficiency of a photocharge and discharge cycle, the energy delivered during discharge should also be considered. Thus, we introduced a new figure of merit – a cycle efficiency (η_{cycle}), which takes into account these parameters in a correct manner (Eq. (3):

$$\eta_{\text{cycle}} = \eta_{\text{conversion}} \times \eta_{\text{storage}} = \frac{E^{\text{output}}_{\text{solar cell}}}{E_{\text{light}}} \times \frac{E_{\text{output}}}{E_{\text{stored}}} = \frac{\int_0^{t_c} V_{\text{solar cell}}(t)\, J_{\text{solar cell}}(t)\ dt}{\int_0^{t_c} P_{\text{i}}\,(t)\, dt} \times \frac{\int_{t_c}^{t_d} V_{\text{cap}}\,(t)\, J_{\text{GD}}(t)\, dt}{\int_0^{t_c} V_{\text{cap}}\,(t)\, J_{\text{solar cell}}(t) - J^2_{\text{solar cell}}(t)\, R_{\text{loss}}\, dt} \quad \text{Eq.3}$$

Where t_d is the discharge time, $V_{solar\ cell}(t)$ is the voltage of the solar cell, and $J_{GD}(t)$ is the current density applied during the discharge.

The performance evaluation using our new definition resulted in a complete cycle efficiency of 2%. This is a much more realistic figure of merit for the overall device performance

as it includes the cycle energy utilization of the complete device.[8]

We believe this new definition will help in the future to benchmark new photosupercapacitors and enable a reliable comparison among different systems.

References

1 T. Berestok, C. Diestel, N. Ortlieb, J. Buettner, J. Matthews, P. S. C. Schulze, J. C. Goldschmidt, S. W. Glunz and A. Fischer, Sol. RRL, 2021, 5, 1–13.

2 T. Berestok, C. Diestel, N. Ortlieb, S. W. Glunz and A. Fischer, Adv. Mater. Technol., 2022, 2200237.

3 J. Melke, R. Schuster, S. Möbus, T. Jurzinsky, P. Elsässer, A. Heilemann and A. Fischer, Carbon N. Y., 2019, 146, 44–59.

4 J. Melke, J. Martin, M. Bruns, P. Hugenell, A. Schökel, S. M. Isaza, F. Fink, P. Elsässer and A. Fischer, ACS Appl. Energy Mater, 2020, 3, 11627.

5 A. Bhat, S. Anwer, K. S. Bhat, M. I. H. Mohideen, K. Liao and A. Qurashi, npj 2D Mater. Appl., 2021, 5, 1–21.

6 R. Liu, M. Takakuwa, A. Li, D. Inoue, D. Hashizume, K. Yu, S. Umezu, K. Fukuda and T. Someya, Adv. Energy Mater., 2020, 10, 1–8.

7 H. Wei, D. Cui, J. Ma, L. Chu, X. Zhao, H. Song, H. Liu, T. Liu, N. Wang and Z. Guo, J. Mater. Chem. A, 2017, 5, 1873–1894.

8 R. D. Andrés, T. Berestok, K. Shchyrba, A. Fischer and U. Würfel, Sol. RRL, 2022, 2200614.

Development of integrated and flexible manufacturing processes for micro-Thermoelectric generators – MiTEG

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For achieving the best results in system design and manufacture of micro thermoelectric generators (µTEGs), electrical and thermal characterization is the essential part. This study describes a fully integrated in-situ measurement setup for determining contact resistance and characterizing the thermoelectric properties of thermoelectric materials and thermoelectric thermolegs used in a µTEG. Printing technology is a popular process for TEG and thermoleg manufacture and dispenser printing is the simplest technique in this field [1]. As a result, dispenser printing was employed in this work for µTEG manufacturing, based on a prior µTEG fabrication idea established in printed circuit board (PCB) material [2]. To evaluate the effect of the paste dispensing process, compacting, and the pressure and temperature during the hot-pressing processes of previously dispensed µTEG thermolegs, a measurement setup was implemented in a PCB substrate similar to the one carrying the entire µTEG, allowing measuring the contact resistance between the TE material and the PCB substrate. The traditional transfer length technique (TLM) is employed for contact measurement in this arrangement, however it is applied in an unconventional vertical way alongside the thermo-legs. Based on this configuration, a full measuring platform (ZT-Card) is designed and ready to be manufactured to assess all important thermoelectric material parameters as well as contact resistance [3].

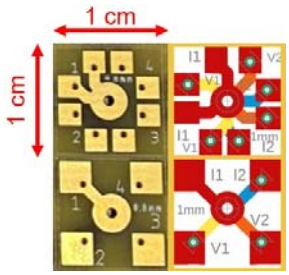

Fig. 1: Top view of contact resistance measurement units, each unit consists of a of single thermoleg in the middle and surrounding electrical Cu contacts. © IMTEK/Laboratory for Design of Microsystems

A 10 × 10 mm² FR4-based 4-layer PCB substrate serves as the measuring platform for contact resistance measurement. Vertical TLM structures are made up of four 110 µm thick Cu layers with three 260 µm thick FR4 layers in between. A single cylindrical cavity in the middle is surrounded by four copper ring contacts and is filled with p-type or n-type TE material (Fig. 1). The contact resistance is calculated using the authorized TLM technique by measuring the varying resistances between

the copper layers and graphing the results with relation to the distance between the Cu layers (Fig. 2). The linear regression extrapolated to zero distance gives double the contact resistance R_C as in a regular TLM system (Fig. 2). The simulation study with COMSOL 5.6 is also applied for the desined electrical contact resistance measurement setup and the fluctuation of contact resistances under hot-pressing conditions used for thermoleg manufacturing is investigated. More information and discussion can be found in the published literature [2].

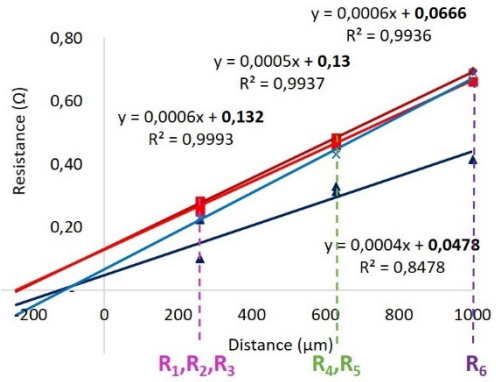

Fig. 2: Contact resistance calculation for a measurement platform filled with n-type TE material at its respective distance alongside the thermoleg. Red data points data are corresponding to the simulation values and blue data points are corresponding to the measurement values. © IMTEK/Laboratory for Design of Microsystems

The whole ZT-Card is designed as a FR4-based multilayer PCB substrate with dimensions of 20 × 10 mm² (Fig. 3). In order to characterize both p-type and n-type TE material, it combines the previously explained electrical contact resistance measurement at the manufactured thermolegs with a Seebeck measuring setup. The same method is employed to fabricate both samples and the final µTEG, therefore the outcomes of material characterization may be directly correlated with process variables. Additionally, a four-point measurement for determining electrical conductivity may be used with this measuring platform, which is currently under manufacturing, by reusing the TLM connections. Thermocouples from the top and bottom, along with the heating system on board (Fig. 3), will make it possible to measure the Seebeck voltage of each leg. The ZT of the n- and p-type materials can be calculated using only the ZT-Card [3]. Current work focuses on getting results and evaluating this fully integrated measurement platform.

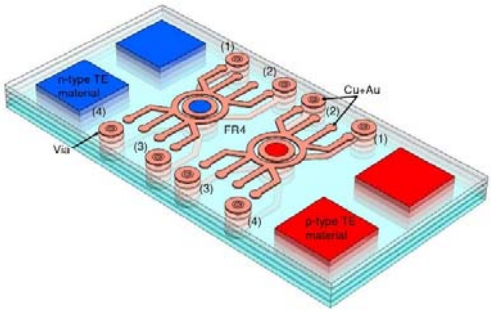

Fig. 3: 3D view of the design of the ZT-Card consists of contact resistance measurement together with the TE material characterization [3]. © IMTEK/Laboratory for Design of Microsystems

References

[1] Burton, Matthew, et al. "Printed Thermoelectrics." Advanced Materials (2022): 2108183.

[2] Sherkat, Negin, et al. "Fabrication and simulation study for vertical micro-TEGs based on printed circuit board manufacturing processes." Smart Materials and Structures (2022).

[3] Sherkat, Negin, Athira Kattiparambil Sivaprasad, Peter Woias, and Uwe Pelz. "A Fully Integrated Measurement Setup for the In-Situ Characterization of Vertical Thermolegs with the Help of the Transfer Length Method." In 2022 21st International Conference on Micro and Nanotechnology for Power Generation and Energy Conversion Applications (PowerMEMS), pp. 252-255. IEEE, 2022. 252-255, doi: 10.1109/PowerMEMS56853.2022.10007585.

FUTURE FIELD "NEW MATERIALS: SOCIETAL CHALLENGES"

Tiered Approach for Prospective Assessment of Benefits and Challenges (TAPAS)

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The ultimate goal of this project from Research Area D of *liv*MatS is the design of a new, tiered methodological framework (TAPAS) for a prospective assessment of the sustainability aspects of novel technologies and materials systems. TAPAS aims to detect associated benefits and challenges. Hence, the approach serves both as an "early warning system" for less sustainable options and as an "early encouraging system" for favorable paths of innovation. Within this context, TAPAS operationalizes relevant normative frameworks for the sustainability assessment, with particular focus on the 2030 Agenda [1] and the concept of Planetary Boundaries [2].

Important basic work was dedicated to the methodological interface between biomimetics and sustainability research. By using the plant growth form of lianas as an example, existing biological concepts were analyzed in close collaboration with Research Areas B, C and the Demonstrator line of *liv*MatS in order to sharpen the three sustainability strategies of efficiency, consistency and sufficiency and to derive practical design principles for more sustainable products in the technosphere [3].

Based on this methodological groundwork, TAPAS was designed to allow users to analyze potential impacts of their development work by themselves [4]. Depending on the maturity of the analyzed object as well as on the data available, different low-threshold instruments are applied: In the first stage, qualitative online surveys are used to obtain an overview of, e.g., the functions and materials used in the analyzed object. In the second stage, "Cognitive-Affective Maps" as a method from social sciences come into play for analyzing social acceptance. In the third stage, a prospective screening of chemicals and an analysis of the criticality of raw materials are carried out. The fourth stage is followed by detailed benefit analyses with an indicator set derived from the 2030 Agenda. In this respect, new methodological ground was broken and a set of indicators was developed that allows for the first time the assessment of societal benefits with regard to the 2030 Agenda, its 17 Sustainable Development Goals (SDG) as well as the 169 SDG targets [5]. In the case of more advanced technologies or materials systems, life cycle oriented approaches, e.g. in the form of a life cycle assessment, are performed in a fifth stage. At any stage, TAPAS develops recommendations in order to accompany and enhance the *liv*MatS developments.

In order to evaluate the practical applicability of TAPAS, two case studies were carried out in which selected instruments of TAPAS were applied and tested in cooperation with two *liv*MatS projects (SolStore and ThermoBatS) from Research Area A. The testing covered the tools of prospective chemicals assessment, benefit analysis as well as orienting life cycle assessments. These case studies showed that the developed tools are generally suitable for projects in the field of basic research. Furthermore, their application also provided concrete suggestions for the substitution of solvents of toxicological concern (e.g., DMF) [6].

With the completion of the TAPAS project, it can be summarized that a field-proven approach for early sustainability assessment of novel technologies and materials systems is now available. Due to its consistent alignment with the 2030 Agenda, TAPAS combines a high degree of commitment with regard to its indicators with the pragmatic approach of self-reflection. By locating the steps of analysis and assessment in the hands of scientists as the actors of the innovation process, it is not

only possible to provide the best possible database; further advantages also arise in terms of "capacity building", i.e. strengthening the methodological knowledge and skills for a sustainability assessment among the users.

References

[1] United Nations. (2015). Transforming our world: the 2030 Agenda for sustainable development (Resolution A/RES/70/1 adopted by the General Assembly on 25 September 2015). United Nations. https://www.un.org/en/development/desa/population/migration/generalassembly/docs/globalcompact/A_RES_70_1_E.pdf

[2] Rockström, J., Steffen, W., Noone, K., Persson, A., Stuart Chapin III, F., Lambin, E. F., Lenton, T. M., Scheffer, M., Folke, C., Schnellnhuber, H. J., Nykvist, B., de Wit, C. A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P. K., Costanza, R., Svedin, U., …, Foley, J. A. (2009). A safe operating space for humanity. Nature, 461(7263), 472–475. https://doi.org/10.1038/461472a

[3] Speck, O., Möller, M., Speck, T., & Grießhammer, R. (2022). Biological concepts as a source of inspiration for efficiency, consistency, and sufficiency. Sustainability 14(8892). https://doi.org/10.3390/su14148892

[4] Möller, M., Höfele, P., Reuter, L., Tauber, F. J., & Grießhammer, R. (2021). How to assess technological developments in basic research? Enabling formative interventions regarding sustainability, ethics and consumer issues at an early stage. TATuP – Journal for Technology Assessment in Theory and Practice, 30(1), 56–62. https://doi.org/10.14512/tatup.30.1.56

[5] Möller, M., & Grießhammer, R. (accepted). Product-related benefit analysis based on the Sustainable Development Goals – integrating the voice of society into Life Cycle Sustainability Assessment. Journal for Industrial Ecology.

[6] Möller, M. (2022). Entwicklung eines mehrstufigen Methodenrahmens für eine prospektive Nachhaltigkeitsbewertung von neuartigen Technologien und Materialsystemen (TAPAS). Dissertation, November 2022 (previously unpublished).

'System' as an interdisciplinary concept and the research on living materials systems

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Since the societal and ecological implications of new technologies are too complex to be suitably overseen by any scientific discipline alone, interdisciplinary research now is more necessary than ever. Thereby, the term 'system' is a core concept in various disciplines involved in livMatS, and in the current discourse on sustainability and the socio-ecological transformation of society. It is used to describe properties of nature, technology, and society alike, as well as their interactions (see e.g. Figure 1 to demonstrate different types of systems as identified in systems theory). Hence, the mutual understanding of the concept 'system' is highly relevant for interdisciplinary research. Because humanity is identified as the driving force behind ostensibly natural events like climate change and mass extinction, not even the combined expertise of the natural sciences is sufficiently equipped to understand all relevant dimensions of such phenomena. As they are the result of historically specific interactions between nature, society, and technology, their analysis can't be reduced to either of these spheres and is reliant on concepts that illuminate such interactions [1].

Based on these considerations, we assume that a thorough analysis of the concept of 'system' and its different meanings is an important contribution to the research on the origins of and possible solutions to the multiple ecological crises. An assumption affirmed by the latest report of the IPCC, which explicitly calls for systemic solutions and a systemic perspective on the development of new technologies [2].

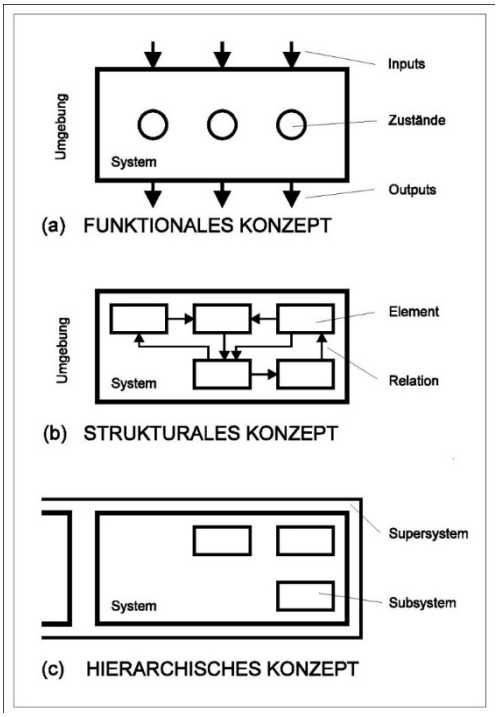

Fig. 1: "Konzepte der Systemtheorie" by Günter Ropohl is licenced under CC BY-NC-ND 4.0.

This assumption of system as both essential part and intermediary between realms normally separated in western thinking, potentially allows for the declared aim of livMatS to achieve a "systemic transfer of functional principles of biological models into technical applications" [3]. This transfer can only succeed if the functional biological principle fits the respecitive technical system, which again requires some sort of systemic familiarity between the biological model and its technical application. In this project, we would like to take this hypothesis of an ontological fitting even one step further: From the perspective of systems theory, new technologies only succeed in being sustainable in the threefold sense of the 2030 Agenda if they fit into various already existing systems: Into other technical systems, in the sense that they need to become an integral part of an already existing infrastructure to have an impact; into social systems, in the sense that they need to be considered useful, affordable and just to become accepted by the respective societies (or at least a relevant part of it); and into the respective ecosystems and the earth system as a whole, in the sense that they need to be part of the material and energy cycle in a way that supports rather than harms life on earth.

For scientists to collaboratively facilitate those systemic transfers and integrations, it is indispensable that all participating actors have a mutual understanding of the systems terminology. Because even if the language of systems theory is used by natural, social, and engineering sciences alike, the semantics can vary profoundly. Hence, this project aims to help clarifying the different meanings of 'system' and strives to thereby strengthen its utility as an interdisciplinary concept and mediator.

References

[1] Öberg, G. (2011). Interdisciplinary Environmental Studies. A Primer. Wiley-Blackwell.

[2] IPCC (2022). Climate Change 2022. Mitigation of Climate Change. Working Group III Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. URL: https://www.ipcc.ch/report/ar6/wg3/.

[3] Möller, M., Höfele, P., Kiesel, A., Speck, O. (2021): Reactions of Sciences to the Anthropocene. Highlighting inter- and transdisciplinary practices in biomimetics and sustainability research. Elementa. Science of the Anthropocene 9(1), 035.

Cognitive-Affective Mapping (CAMing) as Measurement Tool – Elaboration of Reliability Criteria.

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Cognitive-Affective Mapping (CAMing) is a novel method that can be used for exploring individual assessment e.g. for technology acceptance by displaying relevant concepts, their affective connotation and their relationship to each other in a network [1] [2]. Cognitive-Affective Maps (CAMs) can be used in large-scale online surveys by asking participants to draw a Cognitive-Affective Map (CAM) online with several possible software

packages called EMPATHICA [1], Valence [3] or C.A.M.E.L. [4]. An example how a CAM can look like is shown in Figure 1. In recent years, the implementation of the method of CAMing advanced, quantitative as well as qualitative analysis methods were explored concerning CAMing and CAMing was applied successfully on several research questions [5] [6] [7].

Fig. 1: This is an exemplary CAM out of our prestudy dataset. As CAM-Architecture, we can observe a neutral axis which serves as kind of a semantic scaffold for the further assessment by the participant. Positive concepts are sorted left, while negative concepts are sorted right. In addition, this CAM is rich in connections and causal chains. (© Wilhelm Gros @ *liv***Mat**S)

In this project, we aim to gain further knowledge of the core quality criteria of CAMing, which are objectivity, reliability and validity. Objectivity means that a measurement method delivers equal results no matter which user (here researcher) applies it. Reliability estimates how much of the observed score on the one hand is due to the true underlying topic of measurement and on the other hand due to measurement errors. Validity considers whether a measurement method measures what its supposed to measure (e.g. technology acceptance) or rather something else (e.g. preference for specific design or colors). Since we use a standardized instruction (objectivity) and the participants draw the CAMs on their own (validity), we have the most concerns on reliability right now (which doesn't mean, that objectivity and validity can be assumed without further research).

To assess the reliability of CAMing we apply a test-retest reliability approach. We measure a psychological measurement object, which is justifiable stable, at a first measurement time point and at a second measurement time point one week later. Since values are known to be very stable even over larger periods of time [8], we use them as measurement object operationalized with the Portrait Value Questionnaire [9]. In a prestudy, we recruited 27 students of psychology. For the main study we computed a demand of 67 participants and add a 20% potential dropout.

CAMs deliver different parameters such as mean valence (averaged valence of all concepts, where positive concepts are quantified from 1 to 3 and negative concepts are quantified from -3 to -1, see Figure 2), density (total drawn connections in relation to total possible connections) and the number of drawn concepts. Statistically, we correlate pre and post measurements of these CAMing parameters. The resulting coefficients can range between 0 and 1 with the former meaning no reliability and the latter meaning perfect reliability. By convention, a correlation above .7 is "acceptable". Preliminary results of the pre-study are shown in Figures 2, 3 and 4.

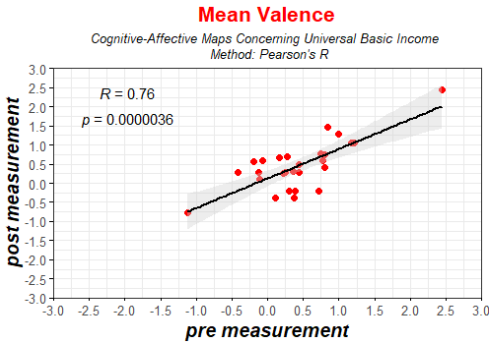

Fig. 2: Scatter plot of the correlation between the pre and post measurements concerning the mean valence from our pilot study (N = 27) with regression line and confidence intervals. The graph indicates a significant "acceptable" Pearson reliability of .76 after one week. The mean valence could range between -3 (strongly negative) and +3 (strongly positive). (© Wilhelm Gros @ *liv***Mat**S)

In addition, we aim to assess reliabity in terms of content of the CAMs. For this, we identified value-related concepts confirming that we measured the stable measurement object as intended. A comparison of individual CAMs revealed that there are CAMs with almost perfect test-retest reliability as well as CAMs with almost 50% different concepts at the second measurement timepoint. Next steps will be to

compare reliability depending on parameters and content-wise.

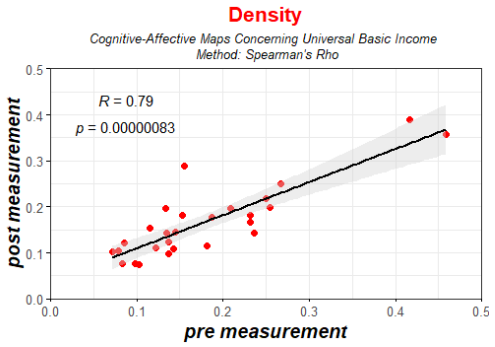

Fig. 3: Scatter plot of the correlation between the pre and post measurements concerning the density from our pilot study (N = 27) with regression line and confidence intervals. The graph indicates a significant "acceptable" Spearman reliability of .79 after one week. The density could range between 0 (no connections) and 1 (each concept connected to all other concepts). (© Wilhelm Gros @ *liv***Mat**S)

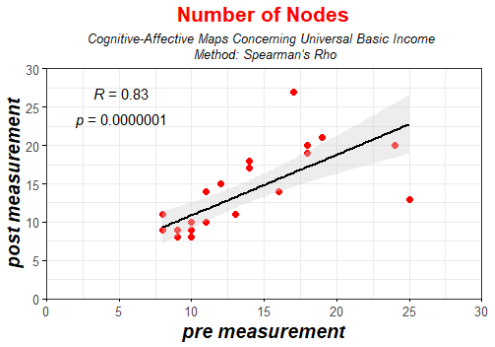

Fig. 4: Scatter plot of the correlation between the pre and post measurements concerning the number of drawn concepts from our pilot study (N = 27) with regression line and confidence intervals. The graph indicates a significant "good" Spearman reliability of .83 after one week. The number of drawn concepts ranged between 8 and 27. (© Wilhelm Gros @ *liv***Mat**S)

Taken together, the described prestudy gives a first hint at an acceptable reliability of CAMs when considering CAMing parameters. It thus is a first step on the three goals of our project: (1) consider the reliability of CAMing with established methods, (2) formulate a CAMing-tailored quantitative-qualitative definition of reliability and (3) give advice on how to best implement CAMing for high reliability. This will help to better understand and implement this method. In the end, the assessment of the acceptance of living materials systems via CAMing in general becomes more credible.

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References

[1] Thagard, P. (2010, July). EMPATHICA: A computer support system with visual representations for cognitive-affective mapping. In *Workshops at the Twenty-Fourth AAAI Conference on Artificial Intelligence*.

[2] Reuter, L., Mansell, J., Rhea, C., & Kiesel, A. (2021). Direct Assessment of Individual Connotation and Experience: An Introduction to Cognitive-Affective Mapping. *Politics and the Life Sciences*. https://doi.org/10-1017/pls.2021.31

[3] Rhea, C., Reuter, L., & Piereder, J. (2020). Valence Software Release. https://doi.org/10.17605/OSF.IO/9TZA2

[4] Fenn, J., Gouret, F., & Kiesel, A. (2022). *Cognitive-Affective Maps extended logic* (Version 1.0.5) [Computer software]. https://camgalaxy.github.io/

[5] Höfele, P., Reuter, L., Estadieu, L., Livanec, S., Stumpf, M., & Kiesel, A. (2022). Connecting the methods of psychology and philosophy: Applying cognitive-affective maps (CAMs) to identify ethical principles underlying the evaluation of bioinspired technologies. *Philosophical Psychology*. https://doi.org/10.1080/09515089.2022.2113770

[6] Mansell, J., Reuter, L., Rhea, C., & Kiesel, A. (2021). A Novel Network Approach to Capture Cognition and Affect: COVID-19 Experiences in Canada and Germany. *Frontiers in Psychology, 12*:663627. https://doi.org/10.3389/fpsyg.2021.663627

[7] Reuter, L., Fenn, J., Bilo, T. A., Schulz, M., Weyland, A. L., Kiesel, A., & Thomaschke, R. (2021). Leisure walks modulate the cognitive and affective representation of the corona pandemic: Employing Cognitive-Affective Maps within a randomized experimental design. *Applied Psychology: Health and Well-Being, 13*(4), 952-967. https://doi.org/10.1111/aphw.12283

[8] Vecchione, M., Caprara, G., Dentale, F., & Schwartz, S. H. (2013). Voting and values: Reciprocal effects over time. *Political Psychology*, *34*(4), 465-485.

[9] Schwartz, S. H. (2017). The Refined Theory of Basic Values. In S. Roccas & L. Sagiv (Eds.*), Values and Behavior* (pp. 51-72). Springer. https://doi.org/10.1007/978-3-319-56352-7_3

CORE FACILITY "MODELLING AND SIMULATION OF MATERIALS SYSTEMS"

Estimation of bond breaking forces for syn-Cl-gCFC and anti-Cl-gCFC molecules

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Mechanochemistry is the chemistry under the influence of external forces. External forces may enable or promote reactions that are not feasible by thermal or photonic sources. There are accurate single polymer chain experiments under force control [1], but the correct theoretical description of the corresponding effects is still challenging. Here we present a simplified viewpoint that nevertheless allows to predict experimentally observed rupture forces to good accuracy.

Generally, theoretical modeling can help to comprehend mechanochemical processes that are difficult to witness directly in experiments. A popular and facile approach in this direction is the constraint geometry simulates external force (CoGEF) method [2] that can be used to explore the nature of force-induced responses. However, certain important shortcomings of the CoGEF approach were also found. In general, rupture forces computed using the CoGEF approach are consistently larger than experimentally observed values [3], owing to the disregard of temperature effects.

Here we address the mechanical activation for ring opening of two isomers, namely syn-chloro-gem-chlorofluorocyclopropane (syn-Cl-gCFC) and anti-chloro-gem-chlorofluorocyclopropane (anti-Cl-gCFC), which are depicteded in Fig. 1. Previous experimental as well as theoretical studies [1] revealed similarities as well as differences. The single-molecule force spectroscopy experiment on the mixture of two isomers observed that anti-Cl-gCFC requires less force for ring opening reaction as compared to syn-Cl-gCFC. It was shown theoretically that both isomers undergo disrotatory outward reaction during ring opening, where the difference of the corresponding barriers in the absence of force D_e is quite large (> 0.35 eV).

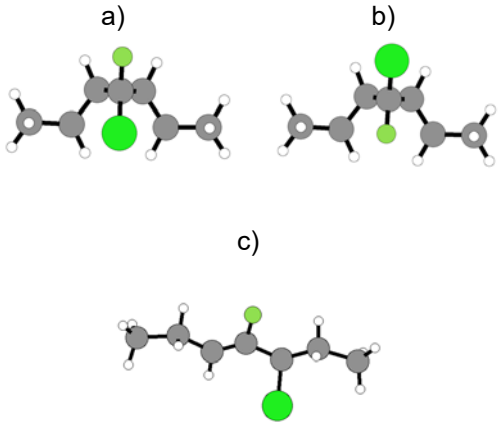

Fig. 1: Initial structure of a) syn-Cl-gCFC (Cl in front) and b) anti-Cl-gCFC (Cl at the back) and c) the final state for a disrotatory outward ring opening reaction for both isomers (© Functional Nanosystems Group)

Our goal is to predict the experimentally measured rupture force purely by computational methods. Bonds are broken by temperature that allows to overcome (force dependent) barriers. This is a stochastic process, such that a most probable force can be given only. Some of us have previously shown that the force dependent barrier $\Delta H^{\ddagger}(F)$ to break a bond depends mainly on two quantities to good accuracy [4]: the force required for spontaneous bond break F_{max} and dissociation energy in the absence of force D_e. The force dependent barrier then follows

$$\Delta H^{\ddagger}(F) = D_e \left(1 - \frac{F}{F_{max}}\right)^2 \qquad (1)$$

to good accuracy.

Table 1: DFT barriers and F_{max} using CoGEF and NEB approaches. 1eV=96 kJ/mol.

Structure	CoGEF		NEB
	D_e (eV)	F_{max} (nN)	D_e (eV)
syn-Cl-gCFC	3.67	3.4	1.97
anti-Cl-gCFC	1.72	3.36	1.59

We perform our calculations within density functional theory (DFT) susing the GPAW package co-developed at FIT. In the first approach, both the barrier D_e as well as the maximal force F_{max} are obtained from CoGEF as was done in Ref. [3] and the results are presented in Table 1. We also calculate D_e using the nudged elastic band (NEB) method [5]. The D_e from NEB is much lower than the value from CoGEF as the latter contains contributions from elastic region of molecule [4]. The value of F_{max} from CoGEF is in accordance with force dependent NEB results (not shown), however.

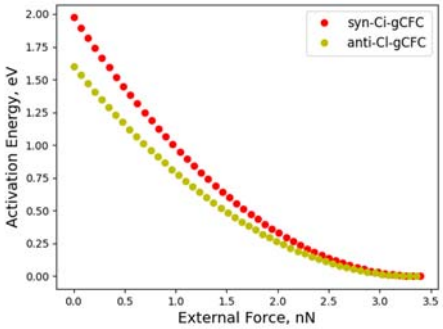

Fig. 2: Force dependent barrier obtained from activation energy formula (Eq. (1)) © Functional Nanosystems Group)

Using D_e from NEB and F_{max} from CoGEF, the variation of the expected activation enthalpy with external force according to Eq. (1) for two isomers is depicted in Fig. 2. We see the difference in barrier between two isomers at $F = 0$ is 0.38 eV in agreement with previous results [1].

The most probable force depends on experimental temperature and also on the rate of force increase, the loading rate α. We assume room temperature and estimate α based on the experimental force extension curves [1]. The most probable force F^* is obtained via the probability for an intact bond at given external force $P(F)$ as [6]

$$F^* = \int_0^\infty F \frac{dP(F)}{dF} dF, \qquad (2)$$

where $\frac{dP(F)}{dF} = \frac{k_0}{\alpha} e^{(-\Delta H^\ddagger(F)/k_B T)} P(F)$, k_0 is the Arrhenius prefactor and k_B is the Boltzmann constant.

Table 2: Most probable force comparison with experimental measurements [1].

	Exp F^*(nN)	Our F^* (nN)
syn-Cl-gCFC	1.5±0.07	1.49±0.02
anti-Cl-gCFC	1.29±0.07	1.21±0.03

The comparison of our predictions with the experimental rupture force is shown in Table 2. First of all, the experimental values are substantially lower than the F_{max} from CoGEF (c.f. Table 1). In contrast to that, our F^* are in excellent agreement with experimental measurements. We thus have shown the possibility to predict measure forces from single molecule force spectroscopy experiments purely from DFT calculations.

References

[1] Wang, J.; Kouznetsova, T. B. & Craig, S. L (2015) “Reactivity and Mechanism of a Mechanically Activated *anti* -Woodward–Hoffmann–DePuy Reaction,” *J. Am. Chem. Soc.*, 137, 11554–11557

[2] Beyer, M. K. (2000) “The mechanical strength of a covalent bond calculated by density functional theory”, *J. Chem. Phys.* 112, 7307

[3] Klein, I.M.; Husic, C.C.; Kovács, D.P.; Choquette, N.J. & Robb, M.J. (2020) “Validation of the CoGEF Method as a Predictive Tool for Polymer Mechanochemistry,” *J. Am. Chem. Soc.*, 142, 16364–16381,

[4] Khodayeki, S.; Maftuhin, W. & Walter, M. (2022) “Force Dependent Barriers from Analytic

Potentials within Elastic Environments," *ChemPhysChem*, 202200237

[5] Henkelman, G.; Uberuaga, B.P. & Jónsson, H. (2000) "A climbing image nudged elastic band method for finding saddle points and minimum energy paths," *J. Chem. Phys.*, 113, 9901–9904

[6] Brügner, O. & Walter, M. (2018) "Temperature and loading rate dependent rupture forces from universal paths in mechanochemistry," *Phys. Rev. Materials*, 2, 113603

Theoretical modeling of NEXAFS spectra in Li-S batteries

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Lithium-sulfur (Li-S) batteries are a highly promising energy storage technology due to their light weight, abundant active material, high theoretical capacity, and high energy density relative to existing Li-ion batteries.[1] Organic polymers with isolated redox-active sites are attractive materials for battery electrodes because of their structural tunability, solution-processability, the absence of heavy metals and possible commercial scale production.[2,3] Such redox polymers feature redox reactions at distinct potentials and, consequently, enable the construction of organic batteries with stable charge/discharge voltages. However, limitations exist in terms of stability, specific capacities and energies.

Our project involves the design, synthesis, characterization (Chemnitz University of Technology) and theoretical modelling (University of Freiburg) of novel materials for Li-S batteries with additional organic redox couples, and their investigation using highly advanced operando X-ray spectroscopy methods[4] (Physikalisch-Technische Bundesanstalt, PTB). Inverse vulcanization of sulfur with redox active divinyl monomers of varying redox potential will be done to produce sulfur/comonomer networks in which additional charge can be stored on the redox active comonomer. The University of Freiburg contributes to these investigations by using density functional theory (DFT) simulations to probe the stability and the electronic structure of the various species involved, as well as the prediction of near edge X-ray absorption fine structure (NEXAFS) spectra on an absolute scale. With this joint theoretical and experimental project we hope to gain an enhanced mechanistic understanding as well as more stable, and eventually more efficient, materials for both Li-S and organic batteries.

For workflow management we employ the Atomic Simulation Environment (ASE)[5]. All calculations were based on density functional theory (DFT) and were done using GPAW[6,7]. Both packages are actively co-developed in our group.

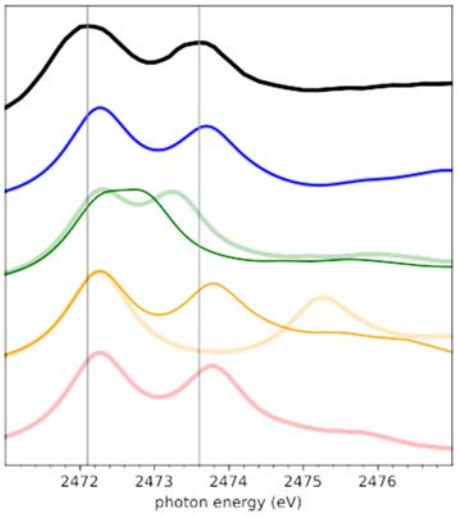

Fig. 1: Dimethyl disulfide x-ray absorption spectra by different methods. black - experimental spectrum, blue - PBE transition potential, green - PBE full core hole, yellow - PBE0 with unoccupied orbitals, red - PBE0 IVO. Calculations without spin polarization are shown as thin, dark lines, spin polarized shown as thick, lighter lines. © Functional Nanosystems Group and PTB Berlin

The experimental (black) and theoretical spectra of dimethyl disulfide (DMDS) are shown in Figure 1. Our chosen method, calculation by the transition potential method and the PBE functional, is shown in blue. An excellent agreement with experiment is observed in the peak shapes, as well as energies. The latter is accomplished by the use of a semiempirical

correction to the transition energies developed in our group[8].

In the transition potential method, half a core hole is applied to the atoms. In the full core hole method (green) a full electron is removed from a core orbital. The agreement with experiment is quite poor for this method – the difference in energy between the main transitions is too small, especially with spin polarization. A hybrid functional (very computationally expensive in GPAW), PBE0[9], was also investigated. The yellow spectra correspond to PBE0 calculated with the convergence of a number of unoccupied orbitals. Without spin polarization a good agreement is achieved with experiment, but when spin polarization is included the gap between the peaks is grossly overestimated. The red spectrum corresponds to PBE0 with improved virtual orbitals (IVO)[10]. Here, a good agreement is observed when the calculation is spin polarized. We were not able to converge the calculation without spin.

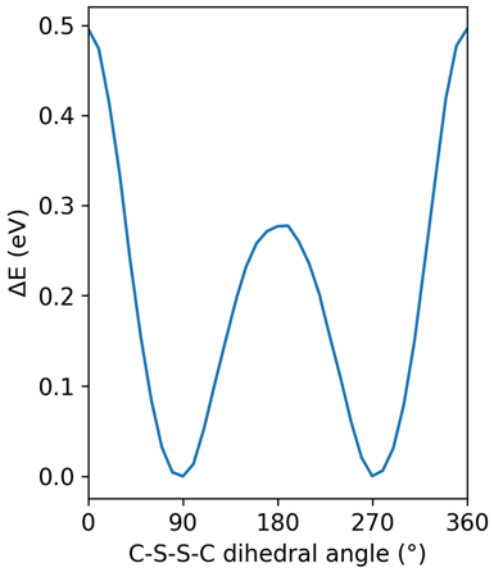

Fig. 2: Dependence of energy on the C-S-S-C dihedral angle in DMDS © Functional Nanosystems Group

We also investigated the dependence of peak position with conformation for DMDS (Figure 2), specifically the C-S-S-C dihedral angle. Two minima occur at dihedral angles of 90 and 270°. A local maximum occurs at 180°, and the global maximum is at 0°.

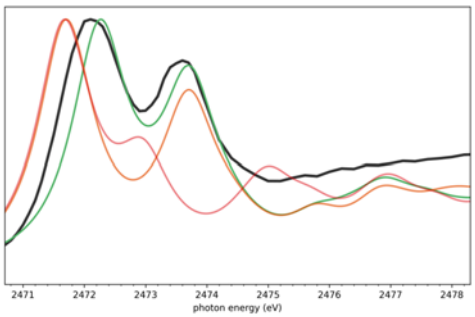

Fig. 3: Spectra of DMDS in different conformations. black – experimental spectrum, green – minimum energy, orange – local maximum, red – global maximum. © Functional Nanosystems Group and PTB Berlin

Spectra of different conformations are shown in Figure 3, along with the experimental spectrum in black. The spectrum for the lowest energy conformer is shown in green. In orange is shown the local maximum, and in red the global maximum, in which the carbon atoms are in an eclipsed configuration. The spectra clearly show a clear dependence on the dihedral angle. Flat and eclipsed configurations have their maximum peak well below that of the lowest energy structure.

While this is not relevant for gas-phase molecules that can freely relax to the minimum of the potential (Fig. 2), additional constraints, e.g. by the connection to rigid partners through inverse vulcanization, might be able to force such a configuration. Our calculations show that even such structural detail may be detectable by NEXAFS spectra.

References

[1] Z. Zeng & X. Liu, Adv. Mater. Interfaces 5, 1701274 (2018)

[2] S. Muench, A. Wild, C. Friebe, B. Haüpler, T. Janoschka & U.S. Schubert, Chem. Rev. 116, 9438 (2016)

[3] T. Janoschka, M. D. Hager & U.S. Schubert, Adv. Mater. 24, 6397 (2012)

[4] C. Zech, P. Hönicke, Y. Kayser, S. Risse, O. Grätz, M. Stamm & B. Beckhoff, J. Mater. Chem. A 9, 10231–10239 (2021)

[5] A.H. Larsen, J.J. Mortensen, J. Blomqvist, I.E. Castelli, R. Christensen, M. Dułak, J. Friis, M.N. Groves, B. Hammer, C. Hargus, E.D. Hermes, P.C. Jennings, P.B. Jensen, J. Kermode, J.R. Kitchin, E.L. Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J.B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiøtz, O. Schütt, M. Strange, K.S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng & K.W.

Jacobsen, J. Phys.: Condens. Matter **29,** 273002 (2017)

[6] J.J. Mortensen, L.B. Hansen & K.W. Jacobsen, Phys. Rev. B **71**, 035109 (2005)

[7] J. Enkovaara, C. Rostgaard, J.J. Mortensen, J. Gavnholt, C. Glinsvad, V. Haikola & H.A. Hansen, J. Phys. Condens. Matter 22, 253202 (2010)

[8] M. Walter, M. Moseler & L. Pastewka, Phys. Rev. B 94, 041112 (2016)

[9] C. Adamo & V. Barone, J. Chem. Phys. 110, 6158 (1999)

[10 S. Huzinaga & C. Arnau, J. Chem. Phys. 54, 1948 (1971)

Decoding the signals of retinal isomers from an optical whispering gallery mode biosensor

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Highly sensitive optical biosensors can detect molecules through effects of their polarizability [1-3]. The biosensing technique relies on the resonance properties of an optical whispering gallery mode (WGM) confined to a spherical micro-resonator, which can be studied analytically using the WGMode MATLAB toolbox . Figure 1 shows the results from a WGMode simulation, corresponding to an optical WGM confined to a 45 micro-meter glass microcavity. Molecules at the surface of the biosensor, in the vicinity of the evanescent field, are detected through a shift in the WGM resonant wavelength. It is predicted that the shift is proportional to the polarizability of the molecule and depends on the magnitude of the evanescent field at the position of the molecule [1].

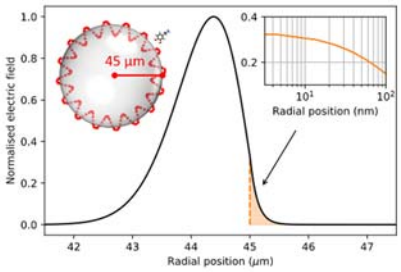

Fig. 1: Simulation of the optical whispering gallery mode biosensor using the WGMode MATLAB toolbox [5]. The whispering gallery mode is confined to a glass microsphere with a radius of 45 micro-meters. The simulation results show the variation of the normalized electric field as a function of the radial position. Most of the mode volume is contained within the cavity, but there is an evanescent tail that extends outside of the boundary of the glass cavity, highlighted on the plot in orange. The inset shows that the electric field is approximately constant in the first 10 nm from the surface of the microcavity but is dramatically reduced by 100 nm from the surface. Molecules in the evanescent field of the biosensor are detected through effects of their polarizability. (© Modelling and Simulation of Materials Systems Group)

This technique has been used to study photoinduced transformations of bacteriorhodopsin, a protein responsible for light detection in bacteria. The photoactive part of bacteriorhodopsin is the retinal chromophore, which transforms from all-trans to 13-cis isomers upon the absorption of photon at 532 nm (2.33 eV) [4]. Topolancik and Vollmer [2] detected a change in average polarizability between the all-trans and 13-cis isomers, which they attributed to the photoinduced isomerization of retinal in its complex proteolipid environment. The open questions relating to the biosensing experiment are whether the orientation of the molecule with respect to the biosensor plays a significant role in these measurements.

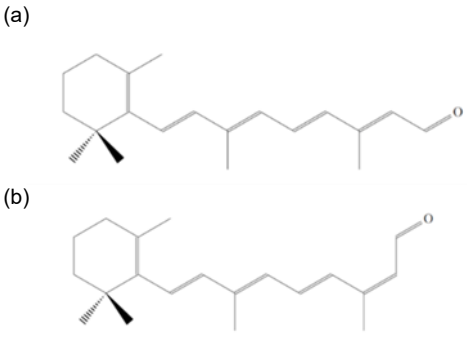

Fig. 2: Model structure of retinal in the a) all-trans ground-state and b) 13-cis photo-excited structure.

In order to test this hypothesis, we apply different polarizability models to study the relationship between molecular structure and polarizability, focusing on the all-trans and 13-cis retinal isomers model structures. The structures for all-trans retinal and 13-cis retinal are downloaded from the PubChem database [11] and are shown in Fig. 2.

Additive atomistic polarizability models and electronic structure calculations can be used to quantify the change in polarizability due to photoisomerization and to decode the signals measured in biosensing experiments. As a first approximation, we calculate the the sum of Hirshfeld-partitioned atomic polarizabilities [6], which accounts for the effect of local chemistry. We then include the effect of interacting atoms, either through the modified point dipole interaction model (Thole model)]7] or the quantum Drude oscillator (QDO) model [8]. We further compare the results from the above additive atomistic models with finite field calculations of the static polarizability using density functional theory code. As a final comparison, we include the results from AlphaML; a machine learning algorithm trained on coupled cluster (CCSD) polarizability data [9, 10].

The Hirshfeld volume ratios and finite field calculations are calculated using the open-source GPAW density functional theory code co-developed at FIT [12, 13]. We calculate the Thole molecular polarizability tensor using a local python script that will be added to a future release of the Atomic Simulation Environment (ASE) co-developed at FIT [14]. The QDO molecular polarizability tensor is calculated using the code in Libmbd [15].

Table 1: Change in isotropic polarizability, $\Delta\overline{\alpha}$, and change in longitudinal component of polarizability, $\Delta\alpha_{\parallel}$, upon photoisomerization from all-trans to 13-cis retinal. All units are in atomic units (Bohr^3).

	$\Delta\overline{\alpha}$	$\Delta\alpha_{\parallel}$
Hirshfeld atoms	0	n/a
Interacting atoms (Thole model)	-1	-15
Interacting atoms (QDO model)	0	-8
Finite field	-15	-61
AlphaML (CCSD trained)	0	-17

The anisotropy of retinal changes significantly depending on how the tail of the molecule is oriented. The eigenvalue along the longitudinal axis of retinal, $\alpha_{\parallel}$, is reduced in the case of the 13-cis isomer because the tail of the molecule turns away from the long axis, effectively reducing the length of the molecule.

Our computational results are presented in Table 1. All approaches that consider anisotropy predict that all-trans retinal has larger anisotropy than 13-cis retinal. The AlphaML results are also in good agreement with the above observations. The result for the change in isotropic polarizability, $\Delta\overline{\alpha}$, is not so unanimous between the different models. Whilst the Thole model, QDO model and AlphaML do not predict a significant change in $\Delta\overline{\alpha}$, the finite field calculation and the electronic structure calculations by Junior et al. [16] suggest that the isotropic polarizability of 13-cis retinal is approximately 2 – 4% reduced than for all-trans retinal. This may be an effect that can only be captured by electronic structure calculations because in the atomistic picture, the main contributions to the polarizability are the atomic species and the number of atoms. Since the isomers have, by definition, the same number and types of atoms, the atomistic models may not be able to distinguish between the isotropic polarizabilities of all-trans and 13-cis retinal.

The results from the polarizability models suggest that a large change is observed for the longitudinal component of the polarizability, $\alpha_{\parallel}$, between all-trans and 13-cis retinal, which may account for the large change in polarizability measured by the biosensor. The reasons for the quantitative differences between the different models are not clear currently.

An open question from the simulation side is whether including the protonated Schiff base between the retinal chromophore and the rest of the bacteriorhodopsin molecule. Whether this will significantly affect the polarizability results is under current investigation. Finding the answer to these questions will help us to understand the signals and detection mechanisms of the optical WGM biosensor.

References

[1] S. Arnold, M. Khoshsima, I. Teraoka, S. Holler, and F. Vollmer, ‘Shift of whispering-gallery modes in microspheres by protein adsorption’, Opt. Lett., vol. 28, no. 4, pp. 272–274, Feb. 2003, doi: 10.1364/OL.28.000272.

[2] J. Topolancik and F. Vollmer, ‘Photoinduced Transformations in Bacteriorhodopsin Membrane Monitored with Optical Microcavities’, Biophys. J., vol. 92, no. 6, pp. 2223–2229, Mar. 2007, doi: 10.1529/biophysj.106.098806.

[3] D. Yu, M. Humar, K. Meserve, R. C. Bailey, S. N. Chormaic, and F. Vollmer, ‘Whispering-gallery-mode sensors for biological and physical sensing’, Nat. Rev. Methods Primer, vol. 1, no. 1, pp. 1–22, Dec. 2021, doi: 10.1038/s43586-021-00079-2.

[4] E. Nango et al., ‘A three-dimensional movie of structural changes in bacteriorhodopsin’, Science, vol. 354, no. 6319, pp. 1552–1557, Dec. 2016, doi: 10.1126/science.aah3497.

[5] S. Balac, ‘WGMode : A Matlab toolbox for whispering gallery modes volume computation in spherical optical micro-resonators’, Comput. Phys. Commun., vol. 243, pp. 121–134, Oct. 2019, doi: 10.1016/j.cpc.2019.05.002.

[6] F. L. Hirshfeld, ‘Bonded-atom fragments for describing molecular charge densities’, Theor. Chim. Acta, vol. 44, no. 2, pp. 129–138, 1977, doi: 10.1007/BF00549096.

[7] B. T. Thole, ‘Molecular polarizabilities calculated with a modified dipole interaction’, Chem. Phys., vol. 59, no. 3, pp. 341–350, Aug. 1981, doi: 10.1016/0301-0104(81)85176-2.

[8] A. P. Jones, J. Crain, V. P. Sokhan, T. W. Whitfield, and G. J. Martyna, ‘Quantum Drude oscillator model of atoms and molecules: Many-body polarization and dispersion interactions for atomistic simulation’, Phys. Rev. B, vol. 87, no. 14, p. 144103, Apr. 2013, doi: 10.1103/PhysRevB.87.144103.

[9] D. M. Wilkins, A. Grisafi, Y. Yang, K. U. Lao, R. A. DiStasio, and M. Ceriotti, ‘Accurate molecular polarizabilities with coupled cluster theory and machine learning’, Proc. Natl. Acad. Sci., vol. 116, no. 9, pp. 3401–3406, Feb. 2019, doi: 10.1073/pnas.1816132116.

[10] Y. Yang, K. U. Lao, D. M. Wilkins, A. Grisafi, M. Ceriotti, and R. A. DiStasio, ‘Quantum mechanical static dipole polarizabilities in the QM7b and AlphaML showcase databases’, Sci. Data, vol. 6, no. 1, Art. no. 1, Aug. 2019, doi: 10.1038/s41597-019-0157-8.

[11] S. Kim et al., ‘PubChem in 2021: new data content and improved web interfaces’, Nucleic Acids Res., vol. 49, no. D1, pp. D1388–D1395, Nov. 2020, doi: 10.1093/nar/gkaa971.

[12] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, ‘Real-space grid implementation of the projector augmented wave method’, Phys. Rev. B, vol. 71, no. 3, p. 035109, Jan. 2005, doi: 10.1103/PhysRevB.71.035109.

[13] J. Enkovaara et al., ‘Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method’, J. Phys. Condens. Matter, vol. 22, no. 25, p. 253202, Jun. 2010, doi: 10.1088/0953-8984/22/25/253202.

[14] A. H. Larsen et al., ‘The atomic simulation environment—a Python library for working with atoms’, J. Phys. Condens. Matter, vol. 29, no. 27, p. 273002, Jun. 2017, doi: 10.1088/1361-648X/aa680e.

[15] A. Ambrosetti, A. M. Reilly, R. A. DiStasio, and A. Tkatchenko, ‘Long-range correlation energy calculated from coupled atomic response functions’, J. Chem. Phys., vol. 140, no. 18, p. 18A508, May 2014, doi: 10.1063/1.4865104.

[16] L. A. Junior, G. Colherinhas, T. L. Fonseca, and M. A. Castro, ‘Solvent effects on the first hyperpolarizability of retinal derivatives’, Chem. Phys. Lett., vol. 598, pp. 43–47, Apr. 2014, doi: 10.1016/j.cplett.2014.02.051.

PROJECTS

IPROM—INTERACTIVE AND PROGRAMMABLE MATERIALS

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www.fit.uni-freiburg.de/iprom

One of the core principles in the design of technical objects is the static nature of the materials: They have more or less unchangeable properties. In nature, on the other hand, the (bio-)materials used by living systems are geared towards enabling the best possible adaptation to the respective environmental conditions in order to be best react to changes in the surrounding. The aim of the Research Cluster "Interactive and Programmable Materials (IPROM)" funded by the Carl Zeiss Foundation is the development of innovative technical materials that respond to changing environmental conditions with a response, which is preprogrammed into the material and thus triggers a material adaptation to changes in the surrounding and the load conditions. In order to do so, they have to be able to change their internal structure and/or their external shape as a consequence of an external stimulus, e.g. by adapting the adhesion, wettability or mechanical properties of the materials. This concept opens up new opportunities for the production of complex objects in many areas such as optics, medical technology or architecture.

“The IPROM cluster will bring forth a paradigm shift in materials research from static to dynamic materials. The novel materials generated will dynamically adapt their properties to the constantly changing conditions of their environment in a previously programmed manner.”

Fig. 1: IPROM – Interactive and Programmable Materials (www.fit.uni-freiburg.de/iprom)

IPROM projects include the following topics:

TP 1: Bio-inspired programmable material systems (PI: Thomas Speck)
TP 2: Multiparameter / Multimaterial 4D Printing (PI: Bastian E. Rapp)
TP 3: Light-responsive surfaces (PIs: Jürgen Rühe & Bastian E. Rapp)
TP 4: Nonlinear micromechanics of programmable materials (PIs: Christoph Eberl & Lars Pastewka)
TP 5: Sustainable materials for 4D printing (PI: Dorothea Helmer)
TP 6: Programmable Tribology (PIs: Jürgen Rühe & Lars Pastewka)
TP 7: Biocompatible, programmable materials for soft micro-robots (PI: Karen Lienkamp)
TP 8: Bioelectroactive Interfaces for dynamic interaction with biology (PI: Maria Asplund)
TP 9: Autonomous and reconfigurable metamaterials and soft robots (PI: Andreas Walther)
TP 10: Digitized dynamic illumination (PI: Hans Zappe)

GROWBOT—TOWARDS A NEW GENERATION OF PLANT-INSPIRED GROWING ARTEFACTS

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www.growbot.eu

GrowBot proposes a disruptively new paradigm of movement in robotics inspired by the moving-by-growing abilities of climbing plants.

Fig. 1: GrowBot - Towards a new generation of plant-inspired growing artefacts. Figure from www.growbot.eu.

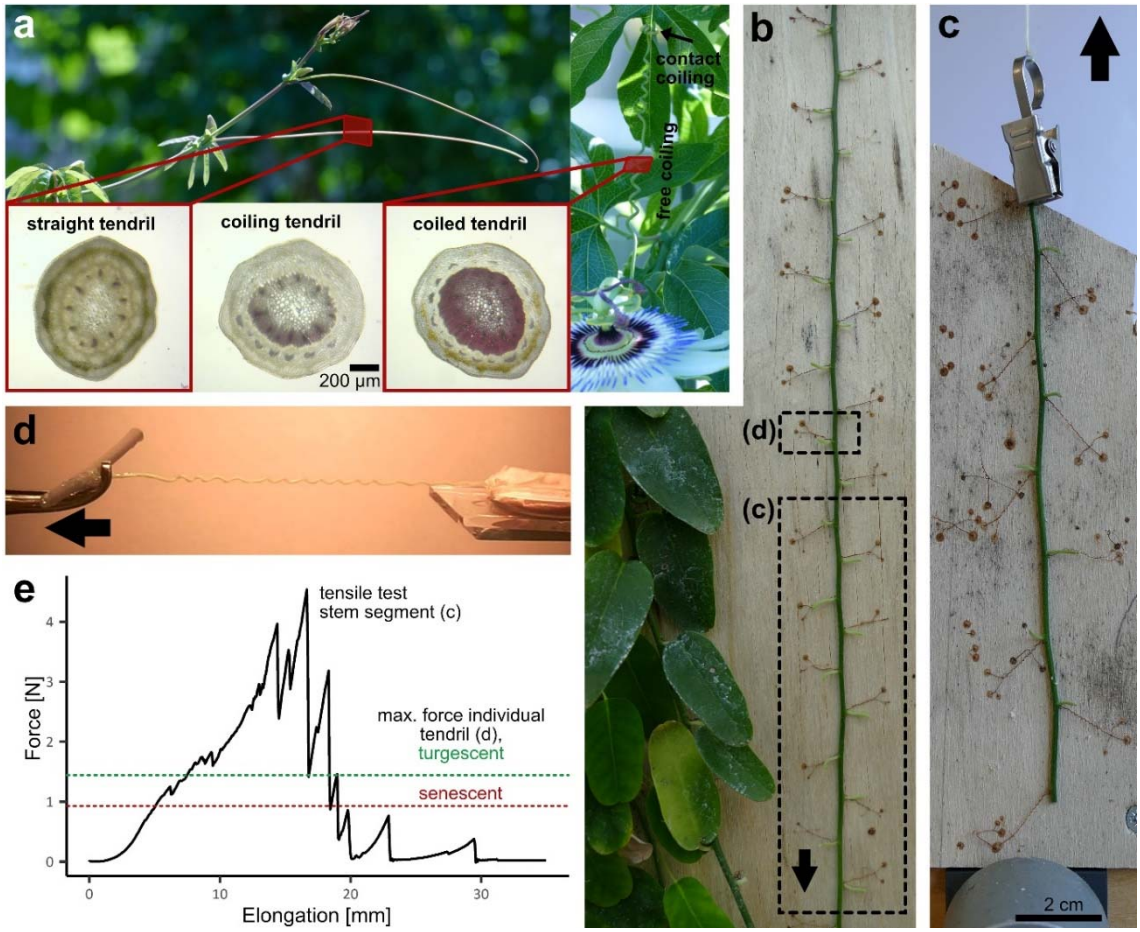

Fig. 2: Tendrils of the passion flower *Passiflora caerulea* in the pre-mature state, i.e. uncoiled (left) and in the mature state showing contact and free coiling (right) (a). *Passiflora discophora* stem attached via multiple tendrils showing adhesive pads (b) that act together when the stem is placed under tension (c). This structure allows the plant to sustain higher forces before failing/detaching than would be the case for individual tendrils (d, e). Thick black arrows indicate direction of force application. Figure from [2].

Plants are still a quite unexplored models for robotics and soft machines, as their sessile nature leads to think that they do not move. Instead, they move considerably, however, on a different time scale. To move from one point to another, plants must grow and continuously adapt their body to the external environmental conditions. This continuous growth is particularly evident in climbing plants.

By mimicking them, the GrowBot objective is to develop low-mass and low-volume robots capable of anchoring themselves, negotiating voids, and more generally climbing, where current climbing robots based on wheels, legs, or rails would get stuck or fall. Specifically, the ability to grow will be translated by additive manufacturing processes inside the robot, which creates its body by depositing new materials with multi-functional properties, on the basis of the perceived external stimuli (without a pre-defined design). Perception and behaviour will be based on the adaptive strategies that allow climbing plants to explore their environment. GrowBot is based on a strongly interdisciplinary approach and can open the way for a new technological paradigm around the concept of growing robots, fostering a European innovation eco-system for several high-tech sectors [1]. The Plant Biomechanics Group Freiburg is contributing to this task based on their long experience on eco-biomechanics and stem structure of climbing plants and on the various attachment systems existing in climbing plants.

A main focus is on the sophisticated anchoring system(s) of various *Passiflora* species. Since these plants do not have a massive solid trunk, they are not self-supporting and thus depend on support structures to which they must somehow anchor themselves. Many species have evolved tendrils for this purpose, which are able to "grasp" thin supports (so-called contact coiling) (figure 2a), while other species develop adhesive pads at the tendril tips that enable them to adhere to a wide range of different substrates (figure 2b) [2]. In addition to the performance of individual tendrils or even individual adhesive pads [3], the interaction of multiple tendrils is currently the main target of investigation (figure 2 c & e) [2]. Using the example of *Passiflora discophora*, it could be shown that, while being loaded, the adhesive pads of several tendrils act together (and do not snap off one after the other). The plant can thus withstand relatively large external forces before it is ripped off its substrate.

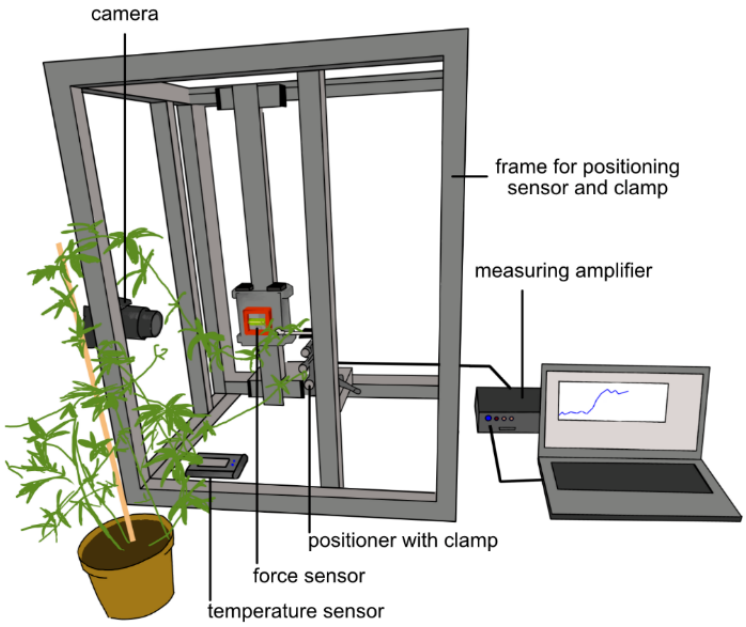

Fig. 3: Experimental set-up for measuring the tensile forces generated during the coiling process in *Passiflora caerulea*.

What all *Passiflora* tendrils have in common is that they coil around their length axis during maturation, thus shortening themselves. The resulting forces lash the plant stem firmly to its support structure. Using an in-house developed experimental set-up (figure 3), we were able to measure for the first time the forces in vivo during this coiling process and even relate them to the hydration status of the plant [4]. Along with anatomical studies, these measurements allow for a profound understanding of the form-structure-function relationship and thus for a transfer into first biomimetic artificial tendrils that can be actuated by various external stimuli [5].

References

[1] B. Mazzolai, F. Carpi, K. Suzumori, M. Cianchetti, T. Speck, S.K. Smoukov, I. Burgert, T. Keplinger, G. De Freitas Siqueira, F. Vanneste, O. Goury, C. Duriez, T. Nanayakkara, B. Vanderborght, J. Brancart, S. Terryn, S. Rich, R. Liu, K. Fukuda, T. Someya, M. Calisti, C. Laschi, W. Sun, G. Wang, L. Wen, R. Baines, S. Patiballa, R. Kramer-Bottiglio, D. Rus, P. Fischer, F.C. Simmel & A. Lendlein (2022): Roadmap on Soft Robotics: Multifunctionality, adaptability and growth without borders. Multifunctional Materials, 5(3): 032001. DOI.org/10.1088/2399-7532/ac4c95

[2] T. Speck, T. Cheng, F. Klimm, A. Menges, S. Poppinga, O. Speck, Y. Tahouni, F. Tauber & M. Thielen (2023): Plants as inspiration for material-based sensing and actuation in soft robots and machines. MRS Bulletin Impact (in press).

[3] F. Klimm, S. Schmier, H.F. Bohn, S. Kleiser, M. Thielen & T. Speck (2022): Biomechanics of tendrils and adhesive pads of the climbing passionflower Passiflora discophora. Journal of Experimental Botany, 73(4): 1190 – 1203. DOI.org/10.1093/jxb/erab456

[4] F. Klimm, T. Speck & M. Thielen (2023): Force generation in the coiling tendrils of Passiflora caerulea (under review).

[5] M. Farhan, F. Klimm, M. Thielen, A. Rešetič, A. Bastola, M. Behl, T. Speck & A. Lendlein (2023): Artificial tendrils mimicking plant movements by mismatching modulus and strain in core and shell (under review).

LIVING, ADAPTIVE AND ENERGY-AUTONOMOUS MATERIALS SYSTEMS (*liv*MATS)

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The Cluster of Excellence "Living, Adaptive, and Energy-autonomous Materials Systems" (*liv*MatS) develops bioinspired materials systems that adapt autonomously to various environments and harvest clean energy from their surroundings. The intention of these purely technical – yet in a behavioral sense quasi-living – materials systems is to meet the demands of humans with regard to pioneering environmental and energy technologies. The societal relevance of autonomous systems and their sustainability thus plays a crucial role in their development within the framework of *liv*MatS. The cluster receives funding from the German Research Foundation (DFG) under Germany's Excellency Strategy – EXC-2193/1 39051807 since January 2019.

Goal of the Cluster is that bioinspired materials, efficient energy materials systems (harvesting, conversion, and storage), and interactive, self-repairing materials with different and often even contradictory properties and functional conditions all meet to form a quasi-living materials system. Energy autonomy, adaptivity, longevity, and sustainability are the core properties of the materials systems to be developed in *liv*MatS. These challenging topics are investigated and combined with each other in four research areas: A – Energy Autonomy, B – Adaptivity, C – Longevity, and D

– Sustainability (cf. Fig. 1). Research from all four areas feeds into demonstrator projects [1].

Fig. 1: Interplay of the closely interconnected Research Areas in *liv*MatS (A – Energy Autonomy, B – Adaptivity, C – Longevity, D – Sustainability and Societal Implications). © *liv*MatS / Daniel Hellweg.

Research area A – Energy Autonomy - studies novel methods of energy harvesting and/or energy storage within a single highly integrated system, i.e. aims for the development of materials systems with embedded energy and energy management. Light, temperature differences, and vibrations are used as potential sources of energy. Once harvested, the energy is either consumed directly or stored for later use. Another important factor is the transformation of energy to make it available in mechanical, chemical, or thermal form or as light energy for adaptive processes within a materials system.

Research area B – Adaptivity - develops new concepts for adaptive materialls systems with complex energy landscapes that recognize and can react to sensory input from their environment. The recognition of the sensory input and the reaction to it are not performed by a sensor/computer combination but directly by the material or the materials system itself, using energy harvested from the environment. The goal of the research in area B is to develop a materials system with a “memory” that can adapt to its environment and improve itself.

Research area C – Longevity - develops strategies that focus on the longevity and “self-control” of complex materials systems, drawing inspiration from living nature, particularly plant life, i.e. aims for the development of materials systems with embedded intelligence. Mechanisms for self-repair, the shedding and replacement of damaged parts, or also a training-based strengthening of system parts under special stress help to prevent minor damages from leading to a loss of functioning of the entire system.

Research area D – Sustainability - considers the societal dimension of autonomous, quasi-living materials systems and their sustainability. A societal discourse on disruptive technologies, such as autonomous driving or expert systems, is often conducted only after the development and introduction of these technologies. In *liv*MatS, this discourse is initiated even as the technologies are being developed. The goal is to strengthen the development of the materials systems by means of concurrent sustainability analyses and to actively explore their societal dimension by engaging in critical philosophical reflection and conducting psychological studies.

There are myriad potential applications for the materials systems developed in *liv*MatS. Examples are “soft” machines that can recognize and grasp objects by feeling them, without the help of a computer, or can autonomously walk controlled by pneumatic logic gates. The capability of a materials system to adapt itself to temperatures, lighting conditions, or pressure opens up perspectives in a wide range of application areas, such as protective clothing like helmets and back protectors or prostheses that can adjust themselves to fit the wearer automatically, autonomously and without needing external energy supply – for instance through the use of body heat. Other ideas include packaging materials that grow stronger automatically when placed under stress and building envelopes that level out temperature differences, for example to prevent overheating.

*liv*MatS is based at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT) and unites researchers from the Faculty of Engineering, the Faculty of Chemistry and Pharmacy, the Faculty of Biology, the

Faculty of Mathematics and Physics, the Faculty of Economics and Behavioral Sciences, and the Faculty of Humanities. Our institutional composition reinforces the university's strategic alliance with Freiburg's Fraunhofer Institutes, with the Fraunhofer Institute for Solar Energy Systems (ISE) and the Fraunhofer Institute for Mechanics of Materials (IWM) as partner institutions within the Cluster and is complemented by the Institute for Applied Ecology (Öko-Institut e.V.).

*liv*MatS uses the ideas factory (IDEASfactory@FIT) to implement new forms of scientific exchange and interdisciplinary cooperation. Three Shared Laboratories, one for the Research Areas A, B and C each, foster close collaboration between researchers within and across research areas. Shared Lab A provides equipment for synthesis, modification, and processing (2D and 3D) of energy materials as well as advanced photo-, electrochemical and microscopic characterization. In 2022, the facilities of Shared Lab A have been complemented by two atomic layer deposition (ALD) reactors that allow for interface and interphase optimization in energy materials in both powder and planar ('wafer') samples. Shared Lab B focuses on microscopy, spectroscopy and rheology, with additional equipment for wet lab chemistry and sample preparation, and also provides an X-ray photoelectron spectroscopy system (XPS) for surface analysis with microscopic resolution and depth profiling. In 2022, the Shared Lab B has been complemented by an ultrahigh performance liquid chromatography time of flight mass spectrometry system (UHPLC/MS/QTOF) for adaptive peptide analysis. Shared lab C provides additional options for microscopy and imaging but has its main focus on materials testing from macro- to microscale, 3D printing, and sample preparation. Core equipment includes a MicroCT system with an integrated mechanical testing device for the quantitative structural analysis of biological structures and biomimetic materials systems, and an electrospinning setup for the processing of polymer and polymer-composite materials into porous felts, among others.

Since 2019, the Cluster has developed and set up three different types of projects to provide flexible formats for the implementation of its research agenda. Doing so has allowed us to strike a balance between long-term projects (36 months) and complementary booster and impulse projects (six to eight and three months respectively). Within the *liv*MatS Call for Projects 2022, 16 new long-term projects were selected that will start in January and February 2023. In addition, 21 booster projects will be carried out in 2023, adding to the cluster's scientific positioning and research output. The *liv*MatS Call for Projects 2023 has been published in December 2022. The final round of long-term projects within the cluster's first funding period are currently being conceptualized and will start in summer 2023.

Over the past 4 years, *liv*MatS has been able to recruit excellent early career researchers for its projects. Currently a total of 114 researchers at all levels, from doctoral researchers to experienced principal investigators, are working in long-term projects directly funded by the Cluster or associated to it. Recruitment for the 27 new PhD positions and the 2 new postdoc positions from the *liv*MatS Call for Projects 2022 is ongoing.

With a slight relaxation of pandemic-related constraints in 2022, *liv*MatS has taken great efforts to strike a balance between virtual and onsite formats in its efforts to promote internal and external scientific exchange and interaction with the public. Scientifc exchange was facilitated in several formats throughout 2022. The *Rising Stars Conference* took place in a hybrid format from March 21st – 24th, 2022, and brought international early career researchers to Freiburg for a varied conference program and research stays for selected candidates. After a virtual event in 2021, the *first onsite visit of the cluster's Scientific Advisory Board* took place from July 27th – 28th, 2022, with vivid scientific exchange during presentations and a poster session, complemented by a tour of the cluster's infrastructure in the Shared Laboratories A, B and C. All members of the *liv*MatS community came together for the Cluster's *fourth scientific retreat* from September 28th – 30th September, 2022. During the onsite event in Karlsruhe, the current status, challenges, interfaces and goals of collaborative research in *liv*MatS were presented

and discussed, with a special focus on interactive formats such as world cafès to maximize direct exchange. Finally, a total of 22 *liv*MatS colloquia with external guest speakers offered the *liv*MatS community ample opportunity to discuss current developments in their field with renowned international research, covering a wide range of topics and disciplines.

The cluster has further consolidated its activities within the *Convergence Center for Living Multifunctional Material Systems* (LiMC²) founded in 2019, uniting researchers from the Penn State University and the University of Freiburg. An eSeminar Series, LIMtalks, has been set up, with a total of five seminars in 2022. In addition, five LiMC2 Seed Grants, where researchers from Penn State and *liv*MatS join forces to maximize the center's potential, have been funded to be carried out in 2023. In September 2022, a collaboration agreement was signed for a *European Network on Nature-Inspired Materials*, funded by the Royal Society of Edinburgh within its RSE Saltire Facilitation Network Award Program. Partners currently include *liv*MatS, the NCCR Bio-inspired Materials, and the Universities of Strathclyde and Hariot-Watt.

Throughout 2022, *liv*MatS has worked on the implementation and further development of its early career advancement objectives. In September 2022, *liv*MatS issued a second call for its Agnes Pockels and its Hermann Staudinger Doctoral Fellowship Programs, which invite outstanding candidates to propose PhD projects to be carried out in *liv*MatS. During a two-tiered selection process, two male and three female candidates have been selected to carry out their PhDs in *liv*MatS. The cluster's successful Master Lab program saw its fourth iteration completed in 2022. Twelve master students in summer term 2022 worked independently on research ideas in various fields under the supervision of a researcher from the Cluster. A fifth iteration began in October 2022 with 13 new Master students working on numerous research challenges, which were showcased at a Meet the Labs recruiting event at FIT on 1 July 2022. The event was attended by circa 30 students from various *liv*MatS relevant study programs. Thus, a total of 46 master students will have completed the *liv*MatS Master lab by the end of the winter term 2022/2023.

PhDs and Postdocs in *liv*MatS received training offers in the areas of good scientific practice, scientific argumentation, and post-academic job search skills. Furthermore, a digital Boot Camp in March 2022 focused on data with sessions on open access, research data management, and social media in academia. The boot camp was complemented with one day digital workshops on data visualization and research dissemination via social media. The Writer's Studio developed a new workshop in conjunction with the Freiburg University Open Access Officer detailing the process of publishing in Open Access. This year the Writer's Studio focused on support for those reaching the end of their Phd thesis by offering regular 'Golden Day' sessions (20), which center on focused writing. In addition, the studio gave a workshop aimed at resume and cover letter writing.

In 2021, *liv*MatS implemented the positions of a Data Steward and an Intellectual Property Manager to appropriately address these topics within the cluster setting. Intellectual Property Management offered a workshop on "Intellectual property basics, dealing with patents as a scientist, and tools for creative thinking".

In late 2021, the data steward and volunteering affiliates formed a reaserch data management (RDM) task-force and developed the livMatS RDM policy. This document has been published on the newly created livMatS RDM landing page at on www.livmats.uni-freiburg.de/rdm after board approval in Septemeber 2022. Since early 2022, the data steward provides, maintains and extends a basic interface to Baden-Württemberg data storage infrastructures (bwSFS) [2]. Both in the RDM workshop within the boot camp in March 2022 for new livMatS PhDs and postdocs as well as in another iteration in November 2022, fundamental concepts of good data management practices such as documentation by metadata and provenance tracking were illustrated on the example of this bwSFS interface and the dtool RDM ecosystem. The

data steward participated in numerous university-internal digitalization and RDM strategy events and represented livMatS at April‘s NFDI-MatWerk meeting in Siegburg and at October‘s „Datastewardship goes Germany“ workshop in Braunschweig with poster contributions or talks [3].

In 2022, Intellectual Property Management began creating a knowledge mapping of the cluster based on the *liv*MatS publications listed in the Web of Science database. Knowledge mapping was performed according to the general categories of the Web of Science and according to the citation topics that cluster relationships of citing and being cited between these publications. The top 10 categories of both knowledge mapping strategies were also used for scientific benchmarking in terms of citation impact for the period between 2019 and 2022. A comparative benchmark value is obtained by evaluating the same category or topic in the same time period for all Web of Science publications or for DFG-funded publications only. Intellectual Property Management also evaluated and supported the first invention disclosure resulting from *liv*MatS cluster findings.

Fig. 2: Roofing ceremony for the livMatS Biomimetic Shell @ FIT (Photo: ICD/ITKE/IntCDC University of Stuttgart)

After completion of the *liv*MatS Pavilion in the Botanic Garden in 2021, the cluster’s second pavilion project has gained momentum in 2022. The *liv*MatS Biomimetic Shell @ FIT is a building demonstrator designed and realized by researchers from the Cluster of Excellence "Integrative Computational Design and Construction for Architecture" (IntCDC) at the University of Stuttgart. Scientists from the Stuttgart cluster and *liv*MatS will develop and research sustainable materials and alternative construction methods using the building in the future. The team celebrated the completion of the building shell of the *liv*MatS Biomimetic Shell @ FIT with a roofing ceremony on December 8, 2022. Located in close proximity to the FIT, the biomimetic building shell measures 345-square-meter and is designed as a lightweight construction. The shell's 127 hollow cassettes made of wood are robotically manufactured and inspired by the modular skeleton of the sea urchin.

*liv*MatS has also been involved in several outreach events, such as the “Science Days” at Europapark Rust from October 20 to 22, 2022. At the *liv*MatS booth, around 10.000 visitors of Germany’s biggest science festival were able to experiment with shape-memory polymers, try out for themselves how hydrophobic surfaces or metamaterials behave, learn why thermoresponsive plastics change color, and how soft robot elements work. *liv*MatS participated in the Science Days for the third time. In addition, the cluster offered guided tours of the Botanic Garden of the University of Freiburg for school groups, teachers and professionals, implementing the *liv*MatS outreach concept “Learning from Nature in Nature”. In these tours, the groups gained insight in the idea behind the *liv*MatS Pavilion and the cluster's biomimetic research. The cluster also welcomed students from the “Schüler-Ingenieur-Akademie” program of the Faculty of Engineering for the second time in a row. Together with the group of *liv*MatS Principal Investigator Céline Calvino, the students explored polymers, their production, possible applications and properties.

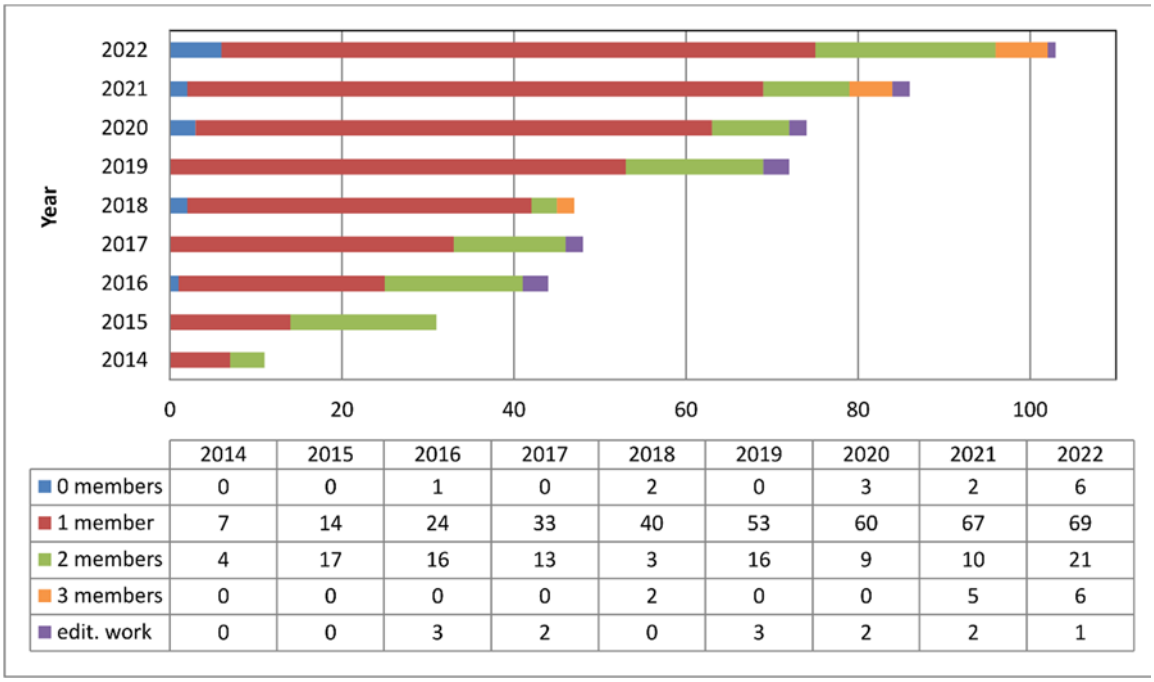
References:

[1] Speck, T., Schulz, M.E., Fischer, A., Rühe, J. (2023). Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS). In: K. Dröder & T. Vietor (eds.), Future Automotive Production Conference 2022, Zukunftstechnologien für den multifunktionalen Leichtbau. Springer-Vieweg. (in press). DOI.org/10.1007/978-3-658-39928-3_18.

[2] Baden-Württemberg Storage for Science, https://rdmg.uni-freiburg.de/posts/2021/06/bwsfs-storage-for-science/

[3] Hörmann, J., livMatS Research Data Management Concept with a focus on the didactic use of dtool. Presented at the Data Stewardship Workshop 2022, Braunschweig, October 13th, 2022. https://doi.org/10.24355/dbbs.084-202211091503-0.

PUBLICATIONS



	2014	2015	2016	2017	2018	2019	2020	2021	2022
0 members	0	0	1	0	2	0	3	2	6
1 member	7	14	24	33	40	53	60	67	69
2 members	4	17	16	13	3	16	9	10	21
3 members	0	0	0	0	2	0	0	5	6
edit. work	0	0	3	2	0	3	2	2	1

Fig. 1: Peer-reviewed publications and editorial work from 2014 until 2022

PEER-REVIEWED PUBLICATIONS

Ates, Hatice Ceren; Mohsenin, Hasti; Wenzel, Christin […], Dincer, Can: Biosensor-enabled multiplexed on-site therapeutic drug monitoring of antibiotics. In: Advanced materials, 34, 2, 2104555. 2022. https://doi.org/10.1002/adma.202104555

Badorrek, Jan; Walter, Michael: Computational study on noncovalent interactions between (n, n) single-walled carbon nanotubes and simple lignin model-compounds. In: Journal of Computational Chemistry, 43, 5, 340-348. 2022. https://doi.org/10.1002/jcc.26794

Barthélemy, Antoine, Glootz, Kim; […]; Krossing, Ingo: Ga+-catalyzed hydrosilylation? About the surprising system Ga+/HSiR3/olefin, proof of oxidation with subvalent Ga+ and silylium catalysis with perfluoroalkoxy-aluminate anions. In: Chemical Science, 13, 2, 439-453. 2022. https://doi.org/10.1039/D1SC05331K

Barthélemy, Antoine; Dabringhaus, Philipp; Jacob, Eike […], Krossing, Ingo: Chemistry with weakly coordinating aluminates [Al(ORF)4]− and borates [B(ORF)4]−: From fundamentals to application. Online first. 2022. https://doi.org/10.1016/b978-0-12-823144-9.00194-1

Barthélemy, Antoine; Scherer, Harald; Krossing, Ingo: Direct comparison of subvalent, polycationic group 13 cluster compounds: lessons learned on isoelectronic DMPE substituted gallium and indium tetracation salts. In: Chemistry – a European journal, 28, 53, e202201369. 2022. https://doi.org/10.1002/chem.202201369

Batista Rodrigues, Edson Silvio; Mello e Silva, Giovanna Nascimento de; Macêdo, Isaac Yves Lopes de […], Dincer, Can […]: Impedimetric immunosensor for on-site measurement of Rituximab from invasive and non-invasive samples. In: Journal of The Electrochemical Society, 169, 5, 057529. 2022. https://doi.org/10.1149/1945-7111/ac725b

Becker, Jing; Speck, Olga; Göppert, Timo; Speck, Thomas, Müller, Claas: Learning from self-sealing deformations of plant leaves: the biomimetic multilayer actuator. In: Advanced Intelligent Systems, 4, 12, 2200215. 2022. https://doi.org/10.1002/aisy.202200215

Beichel, Witali; Skrotzki, Julian; Klose, Petra […], Krossing, Ingo: An artificial SEI layer based on an inorganic coordination polymer with self-healing ability for long-lived rechargeable lithium-metal batteries. In: Batteries & supercaps, 5, 2, e202100347. 2022. https://doi.org/10.1002/batt.202100347

Bentley, Flor Estefany; Passieux, Renaud; David, Laurent, Osorio-Madrazo, Anayancy: Pure chitosan biomedical textile fibers from mixtures of low- and high-molecular weight bidisperse polymer solutions: processing and understanding of microstructure–mechanical properties' relationship. In: International Journal of Molecular Sciences, 23, 9, 4767. 2022. https://doi.org/10.3390/ijms23094767

Berestok, Taisiia; Diestel, Christian; Ortlieb, Niklas, Glunz, Stefan W., Fischer, Anna: A monolithic silicon-mesoporous carbon photosupercapacitor with high overall photoconversion efficiency. In: Advanced Materials Technologies, 7, 11, 2200237. 2022. https://doi.org/10.1002/admt.202200237

Bhagwat, Sagar; O'Brien, Ciarán; Hamza, Ahmed; Sharma, Shatakshi; Rein, Christof; Sanjaya,Mario; Helmer, Dorothea; Kotz-Helmer, Frederik; Pezeshkpour, Pegah; Rapp, Bastian E.: An on-chip liquid metal plug generator. In: Advanced Materials, 34, 23, 2201469. 2022. https://doi.org/10.1002/adma.202201469

Bleiziffer, Alexander; Kost, Jonas; Rühe, Jürgen: Thermal structuring of surface-attached polymer networks by C,H insertion reactions. In: Macromolecular Materials and Engineering, 307, 11, 2200345. 2022. https://doi.org/10.1002/mame.202200345

Bohn, Luca; Holst, Miriam von; Cruz Ortiz, Edgar; Breitwieser, Matthias; Vierrath, Severin; Klose, Carolin: Methods - a simple method to measure in-plane electrical resistance of PEM fuel cell and electrolyzer catalyst layers. In: Journal of the Electrochemical Society, 169, 5, 054518. 2022. https://doi.org/10.1149/1945-7111/ac6e09

Bopda, Aurelien; Mafo, Sandrale Grace Mokue; Ndongmo, Josiane Nguimatsia; […]; Kamdem Tamo, Arnaud […]: Ferromagnetic biochar prepared from hydrothermally modified calcined mango seeds for fenton-like degradation of indigo carmine. In: C: Journal of Carbon Research, 8, 4, 81. 2022. https://doi.org/10.3390/c8040081

Bürger, Jasmin-Clara; Lee, Serin; Penn, Aubrey […]; Fischer, Anna; […]: Size effect in SnO2/Al2O3 core/shell nanowires after battery cycling. In: Advanced Energy and Sustainability Research, 3, 11, 2200098. 2022. https://doi.org/10.1002/aesr.202200098

Büttner, Jan; Berestok, Taisiia; Burger, Stephan […]; Krossing, Ingo; Fischer, Anna: Are halide-perovskites suitable materials for battery and solar-battery applications–fundamental reconsiderations on solubility, lithium intercalation, and photo-corrosion. In: Advanced Functional Materials, 32, 49, 2206958. 2022. https://doi.org/10.1002/adfm.202206958

Cai, Wanhao; Bullerjahn, Jakob T.; Lallemang, Max […]; Hugel, Thorsten: Angle-dependent strength of a single chemical bond by stereographic force spectroscopy. In: Chemical Science, 13, 19, 5734-5740. 2022. https://doi.org/10.1039/D2SC01077A

Conrad, Stefan; Speck, Thomas; Tauber, Falk J.: Multi-material FDM 3D printed arm with integrated pneumatic actuator. In: Biomimetic and Biohybrid Systems. Springer International Publishing, Cham, 27-31. 2022. https://doi.org/10.1007/978-3-031-20470-8_3

Dabringhaus, Philipp; Krossing, Ingo: From mixed group 13 cations [M(AlCp*)3]+ (M = Ga/In/Tl) to an Al4+ cluster. In: Chemical Science, 13, 41, 12078-12086. 2022. https://doi.org/10.1039/d2sc04637g

Dabringhaus, Philipp; Willrett, Julie; Krossing, Ingo: Synthesis of a low-valent Al4+ cluster cation salt. In: Nature Chemistry, 14, 10, 1151-1157. 2022. https://doi.org/10.1038/s41557-022-01000-4

Daub, Michael; Natalukha, Daria; Hillebrecht, Harald: Crystal structures of the Perovskite-related system A /Rb/Cu(II)/Br (A =BA, Gu, PEA, 5-AVA, H2en) with winners, losers and compromises – versatility from 0D to 3D on different levels. In: European Journal of Inorganic Chemistry, 18, e202200136. 2022. https://doi.org/10.1002/ejic.202200136

Delgado Andrés, Rodrigo; Berestok, Taisiia; Shchyrba, Kateryna; Fischer, Anna; Würfel, Uli: A new figure of merit for solar charging systems: case study for monolithically integrated photosupercapacitors composed of a large-area organic solar cell and a carbon double-layer capacitor. In: Solar RRL, 6, 10, 2200614. 2022. https://doi.org/10.1002/solr.202200614

Disch, Joey; Bohn, Luca; Koch, Susann […]; Vierrath, Severin: High-resolution neutron imaging of salt precipitation and water transport in zero-gap CO2 electrolysis. In: Nature Communications, 13, 1, 6099. 2022. https://doi.org/10.1038/s41467-022-33694-y

Djouonkep, Lesly Dasilva Wandji; Kamdem Tamo, Arnaud; Dönch, Ingo […]; Osorio-Madrazo, Anayancy: Synthesis of high performance thiophene–aromatic polyesters from bio-sourced organic acids and polysaccharide-derived diol: characterization and degradability studies. In: Molecules, 27, 1, 325. 2022. https://doi.org/10.3390/molecules27010325

Djouonkep, Lesly Dasilva Wandji; Tchameni, Alain Pierre; Selabi, Naomie Beolle Songwe […]; Osorio-Madrazo, Anayancy: Bio-based degradable poly(ether-ester)s from melt-polymerization of aromatic ester and ether diols. In: International Journal of Molecular Sciences, 23, 16, 8967. 2022. https://doi.org/10.3390/ijms23168967

Durak, Grażyna; Speck, Thomas; Poppinga, Simon: Shapeshifting in the Venus flytrap (*Dionaea muscipula*): Morphological and biomechanical adaptations and the potential costs of a failed hunting cycle. In: Frontiers in Plant Science, 13, 970320. 2022. https://doi.org/10.3389/fpls.2022.970320

Durak, Grażyna; Thierer, Rebecca; Sachse, Renate; Bischoff, Manfred; Speck, Thomas; Poppinga, Simon: Smooth or with a Snap! Biomechanics of trap reopening in the venus flytrap (Dionaea muscipula). In: Advanced Science, 9, 22, 2201362. 2022. https://doi.org/10.1002/advs.202201362

Ebunang, Delmas Vidal Tabe; Tajeu, Kevin Yemele; Pecheu, Chancellin Nkepdep […]; Osorio-Madrazo, Anayancy, […]: Amino-functionalized laponite clay material as a sensor modifier for the electrochemical detection of quercetin. In: Sensors, 22, 16, 6173. 2022. https://doi.org/10.3390/s22166173

Eger, Carmen J.; Horstmann, Martin; Poppinga, Simon […], Speck, Thomas […], Rühe, Jürgen: The structural and mechanical basis for passive-hydraulic pine cone actuation. In: Advanced Science, 9, 20, 2200458. 2022. https://doi.org/10.1002/advs.202200458

Egorov, Artem; Riedel, Bianca; Vinke, Johannes, Schmal, Hagen; Thomann, Ralf; Thomann, Yi, Seidenstuecker, Micael: The mineralization of various 3D-printed PCL composites. In: Journal of Functional Biomaterials, 13, 4, 238. 2022. https://doi.org/10.3390/jfb13040238

Eickenscheidt, Alice; Lavaux, Valentine; Paschke, Stefan […]; Lienkamp, Karen; […]: Effect of poly(oxanorbonene)- and poly(methacrylate)-based polyzwitterionic surface coatings on cell adhesion and gene expression of human keratinocytes. In: Macromolecular Bioscience, 22, 11, 2200225. 2022. https://doi.org/10.1002/mabi.202200225

Flores-González, Nicolás; López, Martí; Minafra, Nicolò […]; Krossing, Ingo; […]: Understanding the effect of lattice polarisability on the electrochemical properties of lithium tetrahaloaluminates, LiAlX4 (X = Cl, Br, I). In: Journal of Materials Chemistry. A, Materials for energy and sustainability, 10, 25, 13467-13475. 2022. https://doi.org/10.1039/d2ta02821b

Franco Corredor, Santiago; Mayoussi, Fadoua; Luitz, Manuel […]; Helmer, Dorothea; Kotz-Helmer, Frederik; Rapp, Bastian E.: A polystyrene photoresin for direct lithography of microfluidic chips. In: Advanced Materials Technologies, 7, 10, 2200084. 2022. https://doi.org/10.1002/admt.202200084

Frötschel-Rittmeyer, Julia; Holthausen, Michael; Friedmann, Christian […]; Krossing, Ingo; […]: Homoatomic cations: from [P5]+ to [P9]+. In: Science Advances, 8, 36, eabq8613. 2022. https://doi.org/10.1126/sciadv.abq8613

Gebhardt, Julian; Elsässer, Christian: The electronic structure of Cs2AgBiBr6 at room temperature. In: Physica status solidi. B, Basic Research, 259, 8, 2200124. 2022. https://doi.org/10.1002/pssb.202200124

Glatz, Regina T.; Ates, Hatice Ceren; Mohsenin, Hast, Weber, Wilfried; Dincer, Can: Designing electrochemical microfluidic multiplexed biosensors for on-site applications. In: Analytical and Bioanalytical Chemistry, 414, 22, 6531-6540. 2022. https://doi.org/10.1007/s00216-022-04210-4

Goralczyk, Andreas; Bhagwat, Sagar; Mayoussi, Fadoua […]; Helmer, Dorothea, Rapp, Bastain E.: Application of micro/nanoporous fluoropolymers with reduced bioadhesion in digital microfluidics. In: Nanomaterials, 12, 13, 2201. 2022. https://doi.org/10.3390/nano12132201

Goralczyk, Andreas; Savicheva, Sofya; Montazeri, Ramin […]; Helmer, Dorothea, Rapp, Bastain E.: Spray-coating of superhydrophobic coatings for advanced applications. Online first. In: Advanced Engineering Materials. 2022. https://doi.org/10.1002/adem.202201314

Goralczyk, Andreas; Zhu, Mingshen; Mayoussi, Fadoua […]; Helmer, Dorothea, Rapp, Bastain E.: Study of repellence on polymeric surfaces with two individually adjustable pore hierarchies. In: The Chemical Engineering Journal, 437, 135287. 2022. https://doi.org/10.1016/j.cej.2022.135287

Grenz, David; Rose, Daniel; Wössner, Jan S. […]; Esser, Birgit: Spiroconjugated tetraaminospirenes as donors in color-tunable charge-transfer emitters with donor-acceptor structure. In: Chemistry – A European Journal, 28, 6, e202104150. 2022. https://doi.org/10.1002/chem.202104150

Gröer, Saskia; Garni, Martina; Samanta, Walther, Andreas: Insertion of 3D DNA origami nanopores into block copolymer vesicles. In: ChemSystemsChem, 4, 6, e202200009. 2022. https://doi.org/10.1002/syst.202200009

Hartley, Jennifer M.; Allen, Jack; Meierl, Juli […]; Krossing, Ingo; […]: Calcium chloride-based systems for metal electrodeposition. In: Electrochimica Acta, 402, 139560. 2022. https://doi.org/10.1016/j.electacta.2021.139560

Huber, Matthias C.; Jonas, Uwe; Schiller, Stefan: An autonomous chemically fueled artificial protein muscle. In: Advanced Intelligent Systems, 4, 4, 2100189. 2022. https://doi.org/10.1002/aisy.202100189

Jentzsch, Maximilian; Badstöber, Marie-Christin; Umlas, Franziska; Speck, Thomas: Damage protection in fruits: Comparative analysis of the functional morphology of the fruit peels of five *Citrus* species via quasi-static compression tests. In: Frontiers in Materials, 9, 979151. 2022. https://doi.org/10.3389/fmats.2022.979151

Jentzsch, Maximilian; Becker, Sarah; Thielen, Marc; Speck, Thomas: Functional anatomy, impact behavior and energy dissipation of the peel of *Citrus* x limon: a comparison of *Citrus* x limon and *Citrus maxima*. In: Plants, 11, 7, 991. 2022. https://doi.org/10.3390/plants11070991

Johnston, Midori; Ates, Hatice Ceren; Glatz, Regina T. […]; Dincer, Can: Multiplexed biosensor for point-of-care COVID-19 monitoring: CRISPR-powered unamplified RNA diagnostics and protein-based therapeutic drug management. In: Materials Today, 61, 129-138. 2022. https://doi.org/10.1016/j.mattod.2022.11.001

Kabay, Gozde; DeCastro, Jonalyn; Altay, Alara […]; Dincer, Can: Emerging biosensing technologies for the diagnostics of viral infectious diseases. In: Advanced Materials, 34, 30, 2201085. 2022. https://doi.org/10.1002/adma.202201085

Kamdem Tamo, Arnaud; Tran, Tuan Anh; Dönch, Ingo […]; Walther, Andreas; Osorio-Madrazo, Anayancy: 3D printing of cellulase-laden cellulose nanofiber/chitosan hydrogel composites: towards tissue engineering functional biomaterials with enzyme-mediated biodegradation. In: Materials, 15, 17, 6039. 2022. https://doi.org/10.3390/ma15176039

Kappel, Heinrich Peter; Kramp, Corinna; Speck, Thomas, Tauber, Falk: Application-oriented comparison of two 3D printing processes for the manufacture of pneumatic bending actuators for bioinspired macroscopic soft gripper systems. In: Biomimetic and Biohybrid Systems. Springer International Publishing, Cham, 54-67. 2022. https://doi.org/10.1007/978-3-031-20470-8_6

Khodayeki, Samaneh; Maftuhin, Wafa; Walter, Michael: Force dependent barriers from analytic potentials within elastic environments. In: ChemPhysChem, 23, 19, e202200237. 2022. https://doi.org/10.1002/cphc.202200237

Klimm, Frederike; Schmier, Stefanie; Bohn, Holger F. […]; Speck, Thomas: Biomechanics of tendrils and adhesive pads of the climbing passion flower Passiflora discophora. In: The journal of Experimental Botany, 73, 4, 1190-1203. 2022. https://doi.org/10.1093/jxb/erab456

Kluck, Sebastian; Hambitzer, Leonhard Roland; Luitz, Manuel […]; Rapp, Bastian, E.: Replicative manufacturing of metal moulds for low surface roughness polymer replication. In: Nature Communications, 13, 1, 5048. 2022. https://doi.org/10.1038/s41467-022-32767-2

Koch, Fritz; Thaden, Ole; Conrad, Stefan […]; Zengerle, Roland; […]; Koltay, Peter: Mechanical properties of polycaprolactone (PCL) scaffolds for hybrid 3D-bioprinting with alginate-gelatin hydrogel. In: Journal of the Mechanical Behavior of Biomedical Materials, 130, 105219. 2022. https://doi.org/10.1016/j.jmbbm.2022.105219

Koch, Susanne; Disch, Joey; Kilian, Sophia K. […]; Vierrath, Severin: Water management in anion-exchange membrane water electrolyzers under dry cathode operation. In: RSC Advances, 12, 32, 20778-20784. 2022. https://doi.org/10.1039/D2RA03846C

Kögel, Julius F.; Sorokin, Denis A.; Scott, Martin […]; Krossing, Ingo; […]: Lewis acid–base adducts of Al(N(C6F5)2)3 and Ga(N(C6F5)2)3 – structural features and dissociation enthalpies. In: Dalton Transactions, 51, 12, 4829-4835. 2022. https://doi.org/10.1039/d2dt00003b

Kozgunova, Elena; Yoshida, Mari W.; Reski, Ralf; […]: Spindle motility skews division site determination during asymmetric cell division in *Physcomitrella*. In: Nature Communications, 13, 1, 2488. 2022. https://doi.org/10.1038/s41467-022-30239-1

Krummer, Michael Christian; Daub, Michael; Hillebrecht, Harald: New Pb(II)-Ammine complexes as intermediates from the interaction of CH3NH2 with PbX2 and CH3NH3PbX3 (X=Cl, Br). In: Zeitschrift für Anorganische und Allgemeine Chemie, 648, 10, e202100176. 2022. https://doi.org/10.1002/zaac.202100176

Kruppert, Sebastian; Horstmann, Martin; Weiss, Linda C. […]; Speck, Thomas; […]: Facing the green threat: a water flea's defenses against a carnivorous plant. In: International journal of molecular sciences, 23, 12, 6474. 2022. https://doi.org/10.3390/ijms23126474

Lallemang, Max; Yu, Leixiao; Cai, Wanhao […]; Hugel, Thorsten; […]: Multivalent non-covalent interactions lead to strongest polymer adhesion. In: Nanoscale, 14, 10, 3768-3776. 2022. https://doi.org/10.1039/D1NR08338D

Langer, Max; Hegge, Elena; Speck, Thomas; Speck, Olga: Acclimation to wind loads and/or contact stimuli? A biomechanical study of peltate leaves of *Pilea peperomioides*. In: The Journal of Experimental Botany, 73, 4, 1236–1252. 2022. https://doi.org/10.1093/jxb/erab541

Leute, Richard; Ladecký, Martin; Falsafi, Ali […]; Pastewka, Lars: Elimination of ringing artifacts by finite-element projection in FFT-based homogenization. In: Journal of Computational Physics, 453, 110931. 2022. https://doi.org/10.1016/j.jcp.2021.110931

Mader, Markus; Prediger, Richard; Schell, Karl G. […]; Rapp, Bastian E.; […]: Injection molding of magnesium aluminate spinel nanocomposites for high-throughput manufacturing of transparent ceramics. In: Advanced Science, 9, 31, 2204385. 2022. https://doi.org/10.1002/advs.202204385

Mayoussi, Fadoua; Chen, Yunong; Mössner, Daniela […]; Helmer, Dorothea; Rapp, Bastian E.: Smooth transparent omniphobic coatings with remarkable Liquid repellence. In: Advanced Materials Interfaces, 9, 28, 2201080. 2022. https://doi.org/10.1002/admi.202201080

Mayoussi, Fadoua; Usama, Ali; Karimi, Kiana […]; Helmer, Dorothea; Rapp, Bastian E.: Superrepellent porous polymer surfaces by replication from wrinkled polydimethylsiloxane/parylene F. In: Materials, 15, 22, 7903. 2022. https://doi.org/10.3390/ma15227903

Mazzolai, Barbara; Speck, Thomas; Lendlein, Andreas: Roadmap on soft robotics: multifunctionality, adaptability and growth without borders. In: Multifunctional Materials, 5, 3, 032001. 2022. https://doi.org/10.1088/2399-7532/ac4c95

Mercer, Christopher; Speck, Thomas; Lee, Junyi et al.: Effects of geometry and boundary constraint on the stiffness and negative Poisson's ratio behaviour of auxetic metamaterials under quasi-static and impact loading. In: International Journal of Impact Engineering, 169, 104315. 2022. https://doi.org/10.1016/j.ijimpeng.2022.104315

Möller, Martin; Grießhammer, Rainer: Prospective technology assessment in the Anthropocene: A transition toward a culture of sustainability. In: The Anthropocene Review, 9, 2, 257-275. 2022. https://doi.org/10.1177/20530196221095700

Monti, Joseph; Pastewka, Lars; Robbins, Mark O.: Fractal geometry of contacting patches in rough elastic contacts. In: Journal of the mechanics and physics of solids, 160, 104797. 2022. https://doi.org/10.1016/j.jmps.2022.104797

Müllers, Stefan; Florea-Hüring, Mara; Vacano, Bernhard von; Rühe, Jürgen: Hairy surfaces by cold drawing leading to dense lawns of high aspect ratio hairs. In: Scientific Reports, 12, 1, 9952. 2022. https://doi.org/10.1038/s41598-022-13419-3

Mylo, Max David; Hoppe, Anna; Pastewka, Lars, Speck, Thomas; Speck, Olga: Elastic property and fracture mechanics of lateral branch-branch junctions in cacti: a case study of *Opuntia ficus-indica* and *Cylindropuntia bigelovii*. In: Frontiers in Plant Science, 13, 950860. 2022. https://doi.org/10.3389/fpls.2022.950860

Nagel, Julian; Hanemann, Thomas; Rapp, Bastian E. et al.: Enhanced PTC effect in polyamide/carbon black composites. In: Materials, 15, 15, 5400. 2022. https://doi.org/10.3390/ma15155400

Ngouoko, Jimmy Julio Kouanang; Tajeu, Kevin Yemele; Fotsop, Cyrille Ghislain; Kamdem Tamo, Arnaud et al.: Calcium carbonate originating from snail shells for synthesis of hydroxyapatite/L-Lysine composite: characterization and application to the electroanalysis of toluidine blue. In: Crystals, 12, 9, 1189. 2022. https://doi.org/10.3390/cryst12091189

Ngouoko, Jimmy Julio Kouanang; Tajeu, Kevin Yemele; Temgoua, Ranil Clément Tonleu […]; Osorio-Madrazo, Anayancy; […]: Hydroxyapatite/L-Lysine composite coating as glassy carbon electrode modifier for the analysis and detection of nile blue A. In: Materials, 15, 12, 4262. 2022. https://doi.org/10.3390/ma15124262

Nguyen, Hien; Klose, Carolin; Metzler, Lukas; Vierrath, Severin; Breitwieser, Matthias: Fully hydrocarbon membrane electrode assemblies for proton exchange membrane fuel cells and electrolyzers: an engineering perspective. In: Advanced Energy Materials, 12, 12, 2103559. 2022. https://doi.org/10.1002/aenm.202103559

Nguyen, Hien; Sultanova, Dilara; Heizmann, Philipp A.; Vierrath, Severin; Breitwieser, Matthias: Improving the efficiency of fully hydrocarbon-based proton-exchange membrane fuel cells by ionomer content gradients in cathode catalyst layers. In: Materials Advances, 3, 23, 8460-8468. 2022. https://doi.org/10.1039/d2ma00761d

Nindjio, Gaël Ferdinand Kazé; Tagne, Rufis Fregue Tiegam; Jiokeng, Sherman Lesly Zambou; […] Osorio-Madrazo, Anayancy […]: Lignocellulosic-based materials from bean and pistachio pod wastes for dye-contaminated water treatment: optimization and modeling of indigo carmine sorption. In: Polymers, 14, 18, 3776. 2022. https://doi.org/10.3390/polym14183776

Pecheu, Chancellin Nkepdep; Jiokeng, Sherman Lesly Zambou; Kamdem Tamo, Arnaud; […] Osorio-Madrazo, Anayancy […]: Fabrication of an organofunctionalized talc-like magnesium phyllosilicate for the electrochemical sensing of lead ions in water samples. In: Nanomaterials, 12, 17, 2928. 2022. https://doi.org/10.3390/nano12172928

Pezeshkpour, Pegah; Sachsenheimer, Kai; Goralczyk, Andreas […]; Helmer, Dorothea; Rapp, Bastian E.: A real-time capacitive sensor to detect the stability of *Salvinia* layers on porous superhydrophobic polymers under shear. In: Advanced Materials Technologies, 7, 11, 2200287. 2022. https://doi.org/10.1002/admt.202200287

Phan, Quynh Anh; Truong, Linh B.; Medina-Cruz, David; Dincer, Can; […]: CRISPR/Cas-powered nanobiosensors for diagnostics. In: Biosensors and Bioelectronics, 197, 113732. 2022. https://doi.org/10.1016/j.bios.2021.113732

Radtke, Valentin; Gebel, Niklas; Priester, Denis […]; Krossing, Ingo: Measurements and utilization of consistent Gibbs energies of transfer of single ions: towards a unified redox potential scale for all solvents. In: Chemistry – A European Journal, 28, 40, e202200509. 2022. https://doi.org/10.1002/chem.202200509

Rajak, Anil; Rühe, Jürgen: High hysteresis suspended wetting state: a wetting regime for controlled trapping of drops on micro-trench covered surfaces. In: Advanced Materials Interfaces, 9, 28, 2201018. 2022. https://doi.org/10.1002/admi.202201018

Rall, Jan M.; Schorpp, Marcel; Keilwerth, Martin […]; Krossing, Ingo: Synthesis and characterization of stable iron pentacarbonyl radical cation salts. In: Angewandte Chemie. International Edition, 61, 32, e202204080. 2022. https://doi.org/10.1002/anie.202204080

Ramezaniaghdam, Maryam; Nahdi, Nadia D.; Reski, Ralf: Recombinant spider silk: promises and bottlenecks. In: Frontiers in Bioengineering and Biotechnology, 10, 835637. 2022. https://doi.org/10.3389/fbioe.2022.835637

Sanner, Antoine; Nöhring, Wolfram G.; Thimons, Luke A. […]; Pastewka, Lars: Scale-dependent roughness parameters for topography analysis. In: Applied Surface Science Advances, 7, 100190. 2022. https://doi.org/10.1016/j.apsadv.2021.100190

Sanner, Antoine; Pastewka, Lars: Crack-front model for adhesion of soft elastic spheres with chemical heterogeneity. In: Journal of the Mechanics and Physics of Solids, 160, 104781. 2022. https://doi.org/10.1016/j.jmps.2022.104781

Schmidt, Alexei; Koger, Hendrik; Barthélemy, Antoine […]; Esser, Birgit; Krossing, Ingo: Is one of the least coordinating anions suitable to serve as electrolyte salt for magnesium-ion batteries?. In: Batteries & Supercaps, 5, 12, e202200340. 2022. https://doi.org/10.1002/batt.202200340

Schmitt, Manuel; Mayländer, Maximilian; Heizmann, Tim […]; Krossing, Ingo: Isolation and characterization of the homoleptic nii and niii bis-benzene sandwich cations. In: Angewandte Chemie. International Edition, 61, 50, e202211555. 2022. https://doi.org/10.1002/anie.202211555

Schneider, Rebecca; Engesser, Tobias Adrian; Näther, Christian; Krossing, Ingo […]: Copper-catalyzed monooxygenation of phenols: evidence for a mononuclear reaction mechanism. In: Angewandte Chemie. International Edition, 61, 25. 2022. https://doi.org/10.1002/anie.202202562

Sellin, Malte; Friedmann, Christian; Mayländer, Maximilian […]; Krossing, Ingo: Towards clustered carbonyl cations [M3(CO)14]2+ (M = Ru, Os): the need for innocent deelectronation. In: Chemical Science, 13, 32, 9147-9158. 2022. https://doi.org/10.1039/d2sc02358j

Sherbaz, Ahmad; Konak, Büşra M. K.; Pezeshkpour, Pegah […]; Rapp, Bastian E.: Deterministic lateral displacement microfluidic chip for minicell purification. In: Micromachines, 13, 3, 365. 2022. https://doi.org/10.3390/mi13030365

Sherkat, Negin; Kattiparambil Sivaprasad, Athira; Pelz, Uwe Martin; Woias, Peter: Fabrication and simulation study for vertical micro-TEGs based on printed circuit board manufacturing processes. In: Smart Materials and Structures, 31, 10, 104003. 2022. https://doi.org/10.1088/1361-665X/ac8dcd

Speck, Olga; Möller, Martin; Grießhammer, Rainer; Speck, Thomas: Biological concepts as a source of inspiration for efficiency, consistency, and sufficiency. In: Sustainability, 14, 14, 8892. 2022. https://doi.org/10.3390/su14148892

Speck, Thomas; Poppinga, Simon; Speck, Olga et al.: Bio-inspired life-like motile materials systems: changing the boundaries between living and technical systems in the anthropocene. In: The Anthropocene Review, 9, 2, 237-256. 2022. https://doi.org/10.1177/20530196211039275

Stegerer, Dominik; Pracht, Martin; Günther, Florian […]; Walter, Michael; […]: Organogels from diketopyrrolopyrrole copolymer ionene/polythiophene blends exhibit ground-state single electron transfer in the solid state. In: Macromolecules, 55, 12, 4979-4994. 2022. https://doi.org/10.1021/acs.macromol.2c00655

Tauber, Falk J.; Riechert, Laura; Teichmann, Joscha […], Speck, Thomas: Unit cell based artificial venus flytrap. In: Biomimetic and Biohybrid systems. Springer, Berlin; Heidelberg, 1-12. 2022. https://doi.org/10.1007/978-3-031-20470-8_1

Tauber, Falk; Auth, Phillip; Teichmann, Joscha; Scherag, Frank D.; Speck, Thomas; Novel motion sequences in plant-inspired robotics: combining inspirations from snap-trapping in two plant species into an artificial Venus Flytrap demonstrator. In: Biomimetics, 7, 3, 99. 2022. https://doi.org/10.3390/biomimetics7030099

Toombs, Joseph T.; Luitz, Manuel; Cook, Caitlyn C. […]; Rapp, Bastian E.; […]: Volumetric additive manufacturing of silica glass with microscale computed axial lithography. In: Science, 376, 6590, 308-312. 2022. https://doi.org/10.1126/science.abm6459

Tschaikowsky, Mathäus; Brander, Sofia; Barth, Vanessa […]; Hugel, Thorsten: The articular cartilage surface is impaired by a loss of thick collagen fibers and formation of type I collagen in early osteoarthritis. In: Acta Biomaterialia, 146, 274-283. 2022. https://doi.org/10.1016/j.actbio.2022.04.036

Wessling, Robin; Delgado Andrés, Rodrigo; Morhenn, Isabel […]; Walter, Michael; Würfel, Uli; Esser, Birgit: Phenothiazine-based donor–acceptor polymers as multifunctional materials for charge storage and solar energy conversion. Online first. In: Macromolecular rapid Ccommunications, 2200699. 2022. https://doi.org/10.1002/marc.202200699

Wolff-Vorbeck, Steve; Speck, Olga; Langer, Max; Speck, Thomas; Dondl, Patrick W.: Charting the twist-to-bend ratio of plant axes. In: Journal of The Royal Society Interface, 19, 191, 20220131. 2022. https://doi.org/10.1098/rsif.2022.0131

Zippel, Sabrina; Dilger, Nadine; Chatterjee, Chandralekh […]; Rapp, Bastian E.; […]: A parallelized, perfused 3D triculture model of leukemia for in vitro drug testing of chemotherapeutics. In: Biofabrication, 14, 3, 035011. 2022. https://doi.org/10.1088/1758-5090/ac6a7e

Zober, Maria; Lienkamp, Karen: “Just antimicrobial is not enough” revisited - from antimicrobial polymers to microstructured dual-functional surfaces, self-regenerating polymer surfaces, and polymer materials with switchable bioactivity. In: Macromolecular Chemistry and Physics, 223, 19, 2200051. 2022. https://doi.org/10.1002/macp.202200051

Conference Proceedings

Koch, Susanne; Kilian, Sophia K.; Disch, Joey]…]; Vierrath, Severin: Water management in anion-exchange membrane water electrolyzers under dry cathode operation. 2022. https://learn.mines.edu/wp-content/uploads/sites/355/2022/06/ICE2021_ProgramComplete01.with-links.6.17.22.pdf

Editorials

Dincer, Can; Chandra, Pranjal; Morales-Narváez, Eden: Editorial: Integrated biosensors towards clinical and point-of-care diagnostics. In: Frontiers in Bioengineering and Biotechnology, 10, 1008603. 2022. https://doi.org/10.3389/fbioe.2022.1008603

Tauber, Falk; Vouloutsi, Vasiliki; Mura, Anna; Speck, Thomas: Editorial: Living machines: from biological models to soft machines. In: Bioinspiration & Biomimetics, 17, 3, 030201. 2022. https://doi.org/10.1088/1748-3190/ac5e81

Editorial Work

Speck, Olga; Taylor; David; Speck, Thomas (eds.): Damage Control of Plants—From the Molecule to the Entire Plant. 2022, Special Topic in Frontiers in Plant Sciences. https://www.frontiersin.org/research-topics/33322/damage-control-of-plants---from-the-molecule-to-the-entire-plant

THESES

PHD THESES

Langer, Max: Blattstiel und Übergangszone von Blattstiel zu Blattspreite in krautigen Pflanzen – Vergleichend morphologisch-anatomische und biomechanische Untersuchungen. — PhD thesis, 2022; Universitity of Freiburg; supervisors: Prof. Dr. Thomas Speck, Dr. Olga Speck.

Mylo, Max: Damage control in the plant kingdom: A case study on the morphology, anatomy, and biomechanics of the European mistletoe (*Viscum album*) and selected cacti species. — PhD thesis, 2022; Universitity of Freiburg; supervisors: Prof. Dr. Thomas Speck, Dr. Olga Speck.

Reuter, L. Bridging Over the Troubled Waters of Quantitative and Qualitative Methods: Exploring Cognitive-Affective Maps in Empirical Research. Doctoral thesis, 2022.

DIPLOMA, MASTER, BACHELOR AND STATE EXAMINATION THESES

Altay, Alara: Design and development of a paper-based electrochemical sensor for wearable exhaled breath monitoring of glucose. — M.Sc. Thesis, Universitity of Freiburg; 25.05.2022; supervisor: Dr.-Ing. Can Dincer.

Bellin, Daniel: Development and characterization of a 3D-printed biomimetic peristaltic pump (3BPP) for fluids and solids. — Master thesis, University of Freiburg, 2022; supervisors: Prof. Dr. Frank Balle (INATECH), Dr. Falk Esser, Prof. Dr. Thomas Speck.

Chaverra Ordoñez, William Felipe: Phase change materials with enhanced thermal conductivity for applications at room and human body temperature. — M.Sc. Biomedical Sciences Thesis – IMBS; 15.04.2022; Uni Freiburg and Universidad de Buenos Aires.

Dubois, Amy (2022): Wachstum, funktionelle Morphologie und Biomechanik der Luftwurzeln von *Ficus elastica* Roxb. Ex Hornem und *Ficus natalensis* Hochst. — Bachelor thesis, Universitity of Freiburg; 2022; supervisors: Dr. Frederike Gallenmüller, Prof. Dr. Thomas Speck.

Khodayeki, Samaneh: Modelling mechanochemistry of PDMS, TASN and DFSN. — M.Sc. Thesis, Universitity of Freiburg; 31.03.2022; supervisor: PD Dr. Michael Walter.

Knorr, Noah: Bionische Optimierung eines Sprechventils. — Master thesis, University of Freiburg, 2022; supervisors: Dr. Falk Esser, Prof. Dr. Thomas Speck.

Kulse, Daniel: Lebens-ähnlich? – eine Problematisierung. — Master thesis, Universitity of Freiburg, 2022; supervisors: Prof. Dr. Thomas Speck, Prof. Dr. Lore Hühn.

Mauß, Jonathan: Manganese Oxides for redox-flow-batteries and supercapacitors. — M.Sc. Thesis, Universitity of Freiburg; March – September 2022; supervisors: Prof. Dr. Anna Fischer, Prof. Dr. Kurz, Dr. Taisiia Berestok.

Petitdemange, Eliot: NiMo/MPNC-Katalysatoren für die alkalische Wasserstoffoxidation. — B.Sc. Thesis, Universitity of Freiburg; Mai 2022 – August 2022; supervisors: Prof. Dr. Anna Fischer and Patrick Elsässer.

Rothmann, W. Cognitive-Affective Maps - Verständnis für Konzeptzusammenhänge in Abhängigkeit der Valenzen. — Masterthesis, Universitity of Freiburg; in German, 2022.

Scheckenbach, Fabian: Entwicklung einer thermisch aktuierbaren, artifiziellen Venus Fliegenfalle. — Master thesis, University of Freiburg, 2022; supervisors: Dr. Falk Esser, Prof. Dr. Thomas Speck.

Scheckenbach, Fabian: Entwicklung einer thermisch aktuierbaren, artifiziellen Venus Fliegenfalle. — Master thesis, University of Freiburg, 2022; supervisors: Dr. Falk Esser, Prof. Dr. Thomas Speck.

Teichmann, Joscha: 3D-gedruckte pneumatische Logikbausteine zur Steuerung von Aktuatoren in der Soft-Robotik. — Master thesis, Universitity of Freiburg, 2022; supervisors: Dr. Falk Esser, Stefan Conrad, Prof. Dr. Thomas Speck.

Wang, Yu: $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) Symmetric Lithium-Ion Cell for photo(-assisted) rechargeable Lithium-Ion Battery. — M.Sc. Thesis, Universitity of Freiburg; August 2022 – February 2022; supervisors: Prof. Dr. Anna Fischer and Jan Büttner.

FIT COLLOQUIUM 2022

9TH FIT COLLOQUIUM
11.10. – 12.10.2022
HYBRID EVENT

PROGRAM

Venue: Hotel Maritim, Titisee and Internet

TUESDAY, 11 OCTOBER 2022

Session 1 (Chairperson: Jürgen Rühe)
14:00 **Paula Straub** "Mechanism of phototropic actuation in azo LCN with long thermal half-lives"
14:15 **Patrick Elsässer** "NiMo/MPNC Anode catalysts for clkaline membrane fuel cells"
14:30 **Wafa Maftuhin** "Mechanochromic torsional springs: Insights from theory and simulations"
14:45 **Joey Disch** "Challenges of electrochemical CO_2 reduction in flow cells"

15:00 Coffee break

Session 2 (Chairperson: Michael Walter)
15:30 **Kun Dai** "A systems chemistry approach towards living materials"
15:45 **Fiona Pescher** "Novel catalyst materials for polymer electrolyte fuel cells via fluidized bed atomic layer deposition"
16:00 **Dennis Rusitov** "Tunable thermal and photochemical crosslinking of CHic-able diazo-groups containing polymers"

16:15 End of first day

19:00 Dinner

WEDNESDAY, 12 OCTOBER 2022

Session 3 (Chairperson: Anna Fischer)
09:00 **Peter Kappel** "Comparison of a pneumatic bending actuator fabricated by FDM and PolyJet 3D Printing"
09:15 **Céline Calvino** "From stimuli- responsive systems to renewable materials"
09:30 **Patrick Huber** "Single- and two-photon absorption based C- H-insertion crosslinking (CHic) of anthraquinone containing copolymers"
09:45 **Linnea Hesse** "Identifying new design and manufacturing concepts for technical fiber-reinforced composites in plants"

10:00 Coffee break

Session 4 (Chairperson: Jürgen Rühe)
10:45 **William F. Chaverra Ordoñez** "Buruli ulcer: thermotherapy enhanced using PCM composites"
11:00 **Niloofar Nekoonam** "Photoswitchable substrates with adjustable softness for droplet behavior analysis"
11:15 **Wei Wei** "Influence of interstitial Li on the electronic properties of LixCsPbI3 for photovoltaic and battery applications"
11:30 Jens Leonhardt "Thermo-responsive liquid crystalline network bilayer actuators"

11:45 End of the colloquium

IMPRESSUM

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