

## 10 years of MSE: Energy Research in Bavaria

10<sup>th</sup> Colloquium of the Munich School of Engineering July 30, 2020



### Organizers of the Colloquium:

Felix Fischer Amelia Mohammed Lennart Reb Dr. Petra Liedl Dr. Christoph Wieland

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### Editor:

Prof. Dr. rer. nat. Thomas Hamacher Director Munich School of Engineering

Technische Universität München Munich School of Engineering

Lichtenbergstr. 4a 85748 Garching http://www.mse.tum.de

#### Jurors:

Dr. Peter Tzscheutschler Dr. Maximilian Keim Dr. Sebastian Fendt Dr. Apostolos Vagias Dr. Volker Körstgens Dr. Petra Liedl Dr. Cristina de la Rua Lope Dr. Stephan Herrmann

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#### The end of the oil era

The year 2020 might mark the end of oil. Certainly, oil will play a central role in the coming years and even decades but at a declining rate. Why?

First, a number of new technologies enter the transport sector. Electric cars are already a visible reality and hydrogen might make its route into the transport sectors, too.

Second, the current crisis demonstrates in a very impressive way that also new forms of communication are more efficient than many people expected. It is rather likely that zoom and skype will replace many day trips, conferences and workshops in future - and eventually even our colloquium.

However, which energy carrier will replace oil on the long run? Will it be electricity, or will it be hydrogen or even synthetic fuels. Picking the winner is impossible by now, but a world with electricity as central final energy carrier will certainly look different from a world driven by hydrogen.

In the end, the system, which can best integrate new and clean energy sources and deliver most conveniently energy to costumers, will win the race. For research, it is even more important to keep the system perspective. This requires integrated research, which is looking well above fences and borders.

The MSE, which soon will receive a new name, is certainly the optimal place to catalyze research for such a system transformation.

Thomas Hamacher Director Munich School of Engineering

## **Munich School of Engineering (MSE)**

The **Munich School of Engineering (MSE)** of the Technische Universität München is an open platform for all researchers and students at TUM to combine knowledge and visions for the energy systems of tomorrow. The MSE bundles competencies from TUM's faculties to develop comprehensive research programs tackling as well fundamental as applied questions in the areas of energy production, distribution and storage. To ready upcoming generations of engineers and scientists to respond to the challenges of tomorrow, programs on undergraduate, graduate and postgraduate (PhD) level have been developed and are continuously refined. Exceptionally talented students are equipped with a fundamental scientific tool box and an interdisciplinary mindset to become the future leaders in energy research.

**TUM.Energy** is a cross-departmental research initiative within the MSE, which offers a platform for the so-called "Green Technologies", in particular energy research in the segments Electromobility, Power Plant Technologies, Renewable Energies, and Energy Efficiency. These main topics are represented in networks in which researchers of different departments are working in detail on the challenges within these fields:

 The Center for Combined Smart Energy Systems focuses on modeling the interdependency of electricity distribution, heat, and communication networks and thus sector-coupling. The goal is to develop strategies for integrating extensive distributed energy sources into smart micro grids.

- The network *TUM.PtX* coordinates interdisciplinary research on electricity-based future energy solutions, such as hydrogen or synthetic fuels. The goal is to understand PtX systems in their complete value chain - from fundamental research to marketing.
- The Network for Renewable Energy is doing research in both, fundamental research in the field of new technologies and materials as well as improvements of existing technologies increasing their applicability.
- The network *TUM.Energy and mobility concepts* is working on future mobility concepts, where innovative approaches, such as the DART concept, are investigaated and disseminated for local use cases in Germany.
- The Center for Sustainable Building is dedicating itself to energy efficiency during the use of buildings and its consideration during planning. Thereby not only technical but also socio-ecologic aspects are integrated in urban planning approaches.
- The network **TUM.Battery** supports research on battery technologies. At the Technical University of Munich, more than 100 persons work in this field. Manifold individual projects are carried out in the area of the chairs' and institutes' core competencies, for instance in cooperation with partners from industry, economy, politics and research.



## 10<sup>th</sup> Energy Colloquium of the Munich School of Engineering 1<sup>st</sup> Virtual Edition

## **10 years of MSE: Energy Research in Bavaria**

## July 30, 2020 – 8:30 a.m. to 6:00 p.m.

Please register by July 23rd to get your login information: http://www.mse.tum.de

#### 8:30 - 8:45 a.m.

**Opening: Prof. Dr. Thomas Hamacher** Director, Munich School of Engineering, TUM

#### 8:45 – 9:15 a.m.

Keynote: Hydrogen – Energy and Fuel of the Future or Great White Hope? Dr. Tobias Brunner, Hynergy

9:15 – 11:00 a.m. *Energy Conversion and Storage at the Nanoscale* Session Chair: **Prof. Dr. Peter Müller-Buschbaum** 

Phase Transitions in Ni-rich Cathode Materials for Lithium-Ion Batteries: Boon or Bane? Felix Riewald, BASF SE/Chair of Technical Electrochemistry, TUM

Molecular Insight into the CO<sub>2</sub> and CH<sub>4</sub> Conversion: C-O and C-H Bond Activation and C-C Coupling Nikita Levin, Chair of Physical Chemistry, TUM

In-Situ Identification of Active Electrocatalytic Sites on Metal-Based Catalysts for Oxygen Reduction and Evolution Reaction Regina Kluge, Physics of Energy Conversion and Storage, TUM

**In-Operando Stability Investigation of Biotemplated Photoactive Layers for Solar Cells** Julian Heger, Chair of Functional Materials, TUM

11:00 – 11:15 a.m. Coffee Break

11:15 – 12:00 p.m. *Energy Storage from Cradle to Roll-Out* Session Chair: **Prof. Dr. Andreas Jossen** 

Access Economy for Storage in Energy Communities Niklas Vespermann, Chair of Renewable and Sustainable Energy Systems, TUM

Influence of Battery Energy Storage Systems on the Carbon Footprint of Energy Systems

Anupam Parlikar, Institute for Electrical Energy Storage Technology, TUM

12:00 – 12:30 p.m. Lunch Break 12:30 – 2:00 p.m. Poster Presentation and Q&A-Session

2:00 – 3:15 p.m. *From Energy Efficient to Smart Buildings* Session Chair: **Prof. Dr. Werner Lang** 

Indoor Farming – Optimize Efficiency Sabine Wittmann, Institute of Horticulture, HSWT

**BIM-Based Embedded Energy and Greenhouse Gas Emissions Analysis – A Case Study** Patricia Schneider-Marin, Institute of Energy Efficient and Sustainable Design and Building, TUM

#### Fast Harmonic Estimation Using Real-Time Embedded Controllers in CoSES Smart Grid Anurag Mohapatra, Center for Combined Smart Energy Systems, TUM

3:15 – 3:30 p.m. Coffee Break

3:30 – 4:45 p.m. Building Blocks of a Future Energy Supply Session Chair: Prof. Dr. Hartmut Spliethoff

**Power-to-Heat with Large Scale Thermochemical Energy Storage in Industrial Combined Heat and Power Plants** Gesa Backofen, Chair of Energy Systems, TUM

A Techno-Economic Optimization for Decentralized Waste-Heat Power Generation with a Steam-Rankine-Cycle Florian Raab, Power and Storage Technologies, THN

100% Renewables for Bavaria - Structures, Costs and Benefits of Full Supply in All Sectors Jakob Schweiger, ZAE Bayern - Energy Storage

#### 4:45 – 5:15 p.m.

Keynote: Network TUM.PtX – Tackling the Energy Transition through Collaborative Research Dr. Sebastian Fendt, Munich School of Engineering, TUM

5:15 – 5:30 p.m. Summary and Closing

5:30 – 6:00 p.m. Virtual Social Networking

## Abstracts

## 1. Oral Presentations

1.1	Phase Transitions in Ni-rich Cathode Materials for Lithium Ion Batteries: Boon or Bane?	9
1.2	Molecular insight into the CO2 and CH4 conversion: C–O and C-H bond activation and C–C coupling	10
1.3	In-Situ Identification of Active Electrocatalytic Sites on Metal-Based Catalysts for Oxygen Reduction and Evolution Reaction	11
1.4	Placeholder until find Poster	12
1.5	Access Economy for Storage in Energy Communities	13
1.6	Influence of Battery Energy Storage Systems on the Carbon Footprint of Energy Systems	14
1.7	Indoor Farming - optimize efficiency	15
1.8	BIM-based embedded energy and greenhouse gas emissions analysis – a case study	16
1.9	Fast harmonic estimation using real-time embedded controllers in CoSES smart grid	17
1.10	Power-to-Heat with Large Scale Thermochemical Energy Storage in Industrial Combined Heat and Power Plants	18
1.11	A techno-economic optimization for decentralized waste-heat power generation with a Steam-Rankine-Cvcle	19
1.12	100% Renewables for Bavaria structures, costs, and benefits of full supply in all sectors	20

## 2. Posters

2.1	Micro Hydro Pump Storage with pump as turbine	22
2.2	Syntheses and Impedance Spectroscopic Investigation of Lithium and Sodium Phosphidoindates	23
2.3	Fast Lithium Ion Conduction in Lithium Phosphidoaluminates	24
2.4	A holistic model for the solid electrolyte/electrode interface	25
2.5	The Effect of Iso- and Aliovalent Substitution on the Ionic Conductivity in Lithium Phosphido Tetrelates	26
2.6	Increasing the Ionic Conductivity of Lithium Phosphido Tetrelates by Spark Plasma Sintering	27
2.7	A force-field based approach towards designing working interfaces in solid-state electrolytes	28
2.8	A surface treatment recipe for significantly enhancing thermoelectric PEDOT: PSS films	29
2.9	Energy supply optimization of the Munich University of Applied Sciences through parametric studies in thermal building simulation	30
2.10	Sputter deposition of Ag on nanostructured PMMA-b-P3HT and PS-b-PMMA copolymer thin films	31
2.11	Development of innovative Nano-CHP using new thermoelectric generators	32
2.12	Photochromic films based on WO3 nanoparticles and cellulose nanocrystals	33
2.13	Switchable thermo-responsive polymer coatings as self-cooling approach for buildings	34

2.14	Climate responsive renovation and densification – An approach to reduce the total energy demand of buildings	35
2 15	Life Cycle-based CO2-neutral Plus Energy Building	36
2.10	Influence of the Building Construction on the Energy Demand	37
2.10	Simulation Recod Analysis of Sustainable Building Services	20
2.17	Simulation based Analysis of Sustainable building Services	30
2.10	Measuring Box for indoor Climate and Thermal Comfort	39
2.19	waterpower Romance: The Cultural Myth of Dying watermills in	40
	German Hydro Narratives around 1900	
2.20	Highly-Ordered Porous GeO2 Thin Film Electrode Materials for Li-	41
	ion Batteries	
2.21	Washing of Ni-Rich CAMs: Mechanistic Understanding	42
2.22	Maximization of solar PV self-consumption using combination of	43
	Ice-battery and Chiller	
2.23	Investigating the growth of copper as contacts for polymer thin film	44
	lithium-ion batteries	
2.24	Contacting of Cylindrical Lithium-Ion Batteries and Copper Bus	45
	Bars Using Green Laser Radiation	
2.25	Machine-Learning Potentials for Battery Materials	46
2.26	A Lithium Ion Battery Cell Design for Operando Neutron Depth	47
	Profiling	
2.27	Heat Transfer: Current Challenges and Future Perspectives of	48
	Hydrogen Storage Technologies	
2.28	The zero step for degrading perovskite solar cells: what	49
	atmosphere should we choose?	
2.29	Printed block copolymer template ZnO photoanodes for	50
	photovoltaic applications	
2 30	Highly ordered titania films incorporated with germanium	51
2.00	nanocrystals used as photoanodes	01
2 31	The effect of crystallization kinetics and properties of perovskite	52
2.01	with SDBS doning	02
2 32	Impact of Cesium on Perovskite Crystallization probed with	53
2.02	GIWAXS	00
2 23	Thin-film printing of pext generation perovskite solar cell materials	54
2.33	Printed Quantum Dot Solids for Ontoelectronic Applications	55
2.34	P2H in widely temperature gliding heat grids; with proper system	56
2.00	integration towards profitability	50
2.26	Metric X A Time Series Processing Application	57
2.30	Integration of flowibility in newer grid planning	57
2.31	Onen aguras Elevibility Estimation Duthen Medel for Dresumer	00 50
2.38	Open-source Flexibility Estimation Python Model for Prosumer	59
0.00	Interaction with LEMS	~~~
2.39	Developing a framework to model energy and emissions impacts of	60
o 40	innovative mobility concepts	
2.40	In-situ Identification of Active Sites Using Electrochemical	61
	Scanning Tunneling Microscopy	
2.41	Determination of the Tortuosity and the Porosity of Microporous	62
	Layers for PEM Fuel Cells	
2.42	Nanostructured PtxM/C (M = Cu, Co, Ni, Ir, Y) Alloy	63
	Electrocatalysts Synthesized via a Novel Top-Down Route	
	Towards the Enhancement of the ORR Activity	
2.43	Searching For Active Catalyst Sites On Pt-Alloys For The Oxygen	64
	Reduction Reaction	

2.44	Experimental and numerical study of conversion of tar	65
2.45	Nitrogen-Functionalized Carbon-Supports for Fuel Cell Catalysts – Effect on Mass Transport Resistances	66
2.46	Modeling Oxygen Diffusion in High Temperature Electrolyzers	67
2.47	Following the morphology formation of printed active layers based on PBDB-T-SF:IT-4F in situ	68
2.48	Germanium-based nanostructure synthesis guided by amphiphilic diblock copolymer templating	69
2.49	Fabrication on plasmonic nanostructures in photovoltaics	70
2.50	Investigating the effects of solvent additives on the stability of organic solar cells	71
2.51	Hybrid Energy Harvester based on Combining Solar Cell and Triboelectric Nanogenerator	72
2.52	Tracking the morphology evolution of active layers for non-fullerene organic solar cells	73
2.53	Drilling risks in the North Alpine Foreland Basin	74
2.54	The impact of different ORC working fluids on the external costs for geothermal power generation	75
2.55	Prosumer in Heat Networks: Is it Worth Trading Heat with Neighbours?	76
2.56	Photocatalytic Alcohol Conversion as Model Reaction for the Hydrogen Economy	77
2.57	A Novel Gas Phase Photoreactor for the Investigation of Planar Substrates	78

## 1. Oral Presentations

## Phase Transitions in Ni-rich Cathode Materials for Lithium Ion Batteries: Boon or Bane?

Felix Riewald<sup>a</sup>, Heino Sommer<sup>b</sup>, Hubert A. Gasteiger<sup>c</sup>

afelix.riewald@tum.de, bheino.sommer@basf.com, chubert.gasteiger@tum.de

Driven by the need of high energy densities at low materials cost, both industry and academia are in a constant strive for improvements in battery materials design. A common approach for the already established materials class of lithium nickel cobalt manganese oxides (NCMs,  $LiNi_xCo_yMn_zO_2$ , x+y+z = 1) as cathode active materials (CAMs) for lithium ion batteries is the use of higher relative nickel contents: The Ni<sup>3+</sup>/Ni<sup>2+</sup> redox couple increases the extractable lithium amount at a given operating voltage whilst coming at a lower cost than the comparably expensive cobalt.



Figure 1: Left panel:  $1^{st}$  cycle voltage profile of LiNiO<sub>2</sub> (LNO) at a C-rate of 0.1 h<sup>-1</sup> in a 3:7 mixture of ethylene carbonate and ethyl methyl carbonate with 1M LiPF<sub>6</sub> at 25 °C. *Right panel:* Differential capacity vs. Voltage plot

Unfortunately, next to its beneficial effects, increasing the nickel content brings a lot of disadvantages, like poor thermal stability in the charged state as well as a severely deteriorated capacity retention over cycle life.<sup>(1)</sup> One of the discussed degradation phenomena is the fracture of the cathode active material particles, induced by a severe change of the crystal lattice parameters during electrochemical (de-)lithiation and the associated inter- and intra-particle mechanical stress.<sup>(2)</sup> This issue is supposedly aggravated by the fact that very nickel-rich CAMs like LiNiO<sub>2</sub> (LNO) undergo several phase transitions during expressed charge/discharge cycling, the by coexistence of two crystallographic phases with a large lattice parameter mismatch.<sup>(3)</sup> Such two-phase regions can be observed as voltage plateaus in voltage vs capacity plots as shown in figure 1.

In the present contribution, the impact of the phase transitions on Ni-rich CAM degradation will be discussed by comparing the charge/discharge cycling performance of different NCM compositions when cycling within a set specific capacity window instead of cycling with a set upper voltage cut-off. It is shown that Ni-rich CAMs which have a poor capacity retention compared to CAMs with low Ni content in the typical cycle-life tests with a set upper voltage cut-off, actually have an essentially identical capacity retention in cycle-life tests with a set capacity window. This indicates that the durability of NCM or LNO materials strongly depends on the degree of delithiation rather than on the Ni-content, and that the negative effect of phase transitions on degradation generally reported in the literature may be overestimated. We furthermore illustrate the advantage of phase transitions as analytical tool, showing exemplary measurements on 100 % nickel materials (LiNiO<sub>2</sub>) that are the end member of the NCM family: (i) a correlation between thermodynamic potential of distinct phase transitions with defects in the LiNiO<sub>2</sub> material is found; (ii) a tilt of the potential plateaus, often interpreted as suppression of a phase transition, can be shown to possibly be rather a sign of material inhomogeneity; (iii) furthermore, degradation phenomena that often are overlooked by merely displaying capacity retention vs cycle-life curves are revealed by in-depth analysis of the change in distinct voltage regions. Strategies to implement these insights into future materials design will be presented.

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- 3. H. Li, N. Zhang, J. Li and J. R. Dahn, *Journal of The Electrochemical Society*, 165, A2985 (2018).

## Molecular insight into the CO<sub>2</sub> and CH<sub>4</sub> conversion: C–O and C-H bond activation and C–C coupling

Nikita Levin<sup>a</sup>, Jozef Lengyel<sup>b</sup>, Martin Tschurl<sup>c</sup>, Ueli Heiz<sup>d</sup>

<sup>a</sup>nikita.levin@tum.de, <sup>b</sup>jozef.lengyel@tum.de, <sup>c</sup>tschurl@tum.de, <sup>d</sup>ulrich.heiz@mytum.de

Carbon dioxide and methane received an increased attention in recent years in the field of catalytic chemistry due to their potential use as a feedstock for production of valuable-added products, such as chemicals and fuels. Methane constitutes the major share in the composition of the natural gas, and its efficient transportation requires its effective liquefaction into, e.g. methanol. Yet, the major part of extracted methane is currently burnt, which represents a great environmental concern, as both methane and CO<sub>2</sub> are known to be the main greenhouse gases. However, despite of significant research efforts, no energy-efficient and selective industrially relevant conversion process has yet been discovered. This is partially due to the high stability of the molecules, but the main limitation is still the poor selectivity of the CO<sub>2</sub> reduction (often leading to formation of methane) and methane oxidation.

Metal clusters serve as conventional catalysts for many industrial processes, as well as for water purification, conversion of harmful substances in car exhausts etc. To enable a detailed understanding of reaction pathways and kinetics for the search of specifically designed catalysts, an in-depth analysis of new prospective candidates must be carried out. Gas-phase studies of reactions between charged metal clusters and small organic molecules proved to be an invaluable tool to reveal chemical properties of investigated systems. Corresponding experimental techniques enable investigation of complex reaction schemes using kinetic modelling in different cluster size regimes, from atomic ions to ionic clusters containing tens of atoms. Coupled with theoretical calculations, this allows for deeper insights into reaction kinetics on the molecular level.

In our experiment, gas-phase studies are performed in a ring-electrode ion trap coupled with a laser-vaporization cluster source. We discovered a unique reactivity of  $Ta_n^+$  clusters and their oxides towards activation of methane and carbon dioxide molecules. In particular, we found strong size-dependence of methane dehydrogenation and CO<sub>2</sub> decarbonylation. Particularly interesting is the reaction of  $Ta_8O_2^+$  with CH<sub>4</sub>, which enables coupling of two methane molecules into ethane. In addition, atomic Ta<sup>+</sup> cation exhibits a remarkable reactivity in a mixture of CO<sub>2</sub> and CH<sub>4</sub>, enabling the C–C coupling of both molecules with a subsequent formation of H<sub>2</sub>C=C=O species. In the present contribution, these peculiar reaction properties will be illustrated in more details.

## In-Situ Identification of Active Electrocatalytic Sites on Metal-Based Catalysts for Oxygen Reduction and Evolution Reaction

R.M. Kluge<sup>a</sup>, R.W. Haid<sup>b</sup>, E. Psaltis<sup>c</sup>, A.S. Bandarenka<sup>d</sup>

<sup>a</sup>regina.kluge@ph.tum.de, <sup>b</sup>richard.haid@tum.de, <sup>c</sup>eleftheriospsaltis@gmail.com, <sup>d</sup>bandarenka@ph.tum.de

In order to economize the resources of our world, research should focus on the use of sustainable materials and techniques. Hydrogen as a fuel can contribute to zero-emission energy systems, if produced from renewable energy sources *via* water splitting. However, for such a "hydrogen economy" to become competitive, suitable catalysts have to be developed. The performance of such a heterogeneous catalyst is highly dependent on the electronic structure of specific surface sites, so-called active sites that offer optimal binding of reaction intermediates. Commonly, Sabatier-type volcano plots are used to predict the geometric structure of optimal active sites. Combining theoretical predictions with a technique that is able to in-situ identify and monitor these sites is a powerful tool to advance the performance and rational design of catalysts.

Here we demonstrate the potential of a conventional scanning tunneling microscope (STM) to spatially map and in-situ identify active sites on a catalyst's surface with resolutions down to the nanometer or even atomic scale. In the course of a reaction, reactants and products ad- and desorbing on and from the surface, change the composition of the tunneling medium, and thus have an influence on the tunneling current. By monitoring relative changes in the tunneling current, an increased noise level was detected over active centers, confirming "noise" electrochemical STM (n-EC-STM) as a powerful tool to determine the position of active sites (Figure 1 a,b).

We have successfully applied n-EC-STM to catalytic systems based on Platinum and its alloys for the oxygen reduction reaction and Iridium oxide for the oxygen evolution reaction. Figure 1c shows an exemplary measurement for the latter, where active sites have been predominantly located on the terraces.



Figure 1: a,b) Principle of n-EC-STM. Turning the reaction on (b) will lead to an increase in fluctuations of the recorded signal compared to reaction off (a). The reason for that is the influence of surface reactions on the tunneling barrier. Since these noise features are particularly distinct if the tip is placed over an active site (colored in gold), "noise measurements" constitute a powerful tool in the in-situ identification of active sites. c) n-EC-STM measurement on Iridium oxide for the OER showing a mono-atomic step edge (marked with black dotted line). When the reaction is turned on, a considerable increase in noise can be observed over the terraces of the crystal. This can also be depicted in the line scans in the in-set (reaction off: black, reaction on: yellow). This measurement leads to the conclusion that active sites are located predominantly on the terraces for this system.

# In operando stability investigation of biotemplated photoactive layers for solar cells

J. E. Heger<sup>a</sup>, N. Li, A.-L. Oechsle, S. Yin, S. Bernstorff, P. Müller-Buschbaum<sup>b</sup>

#### <sup>a</sup>julian.heger@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

The supply of renewable, clean and safe energy is an essential task to overcome related economic and environmental problems. For the benefit of this, enabling energy consumers to satisfy their own demand based on renewable energy sources is of reasonable interest. The possibility of large scaled and cheap roll-to-roll fabrication of solar cells based on organic materials is an important step towards this selfsufficient and environment friendly energy supply. These solar cells have the potential of flexible, semi-transparent and lightweight properties and therefore open new paths of design and application, for example integrated in architecture, clothing and all day accessories. However, enhancement of organic based solar cell's lifetime and efficiency is a key challenge. Photoactive systems consisting of inorganic and organic materials combine advantages of both classes. This includes long-term stability and solution processability, e.g. by industrial relevant spray coating [1]. Furthermore, these systems can be implemented in hybrid solar cells. A designed morphology is crucial for the device performance. It can be achieved by templating a porous inorganic phase and filling with the organic counterpart. Besides



Figure 1: Scanning electron microscope image of TiO2:P3HT layer

well-established templating techniques based on diblock copolymers, there is an interesting approach to substitute these with water soluble biopolymers, thereby making the entire processing more environmental friendly.

In this work, the denatured bovine whey protein ß-lactoglobulin is used as a biotemplate [2] to achieve the nanoporous titania scaffolds. The deposition is water based using spray coating. Figure 1 shows the example of the achieved nanostructure as seen with scanning electron microscopy. We investigate the stability of biotemplated photoactive layers and probe the correlation between performance losses and morphology of the organic and inorganic parts. Changes in conductance of the active layer are investigated during heating and at elevated temperature.

#### **References:**

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## Access Economy for Storage in Energy Communities

Niklas Vespermann<sup>a</sup>, Jalal Kazempour<sup>b</sup>, Thomas Hamacher<sup>c</sup>

#### aniklas.vespermann@tum.de, bseykaz@elektro.dtu.dk, cthomas.hamacher@tum.de

In the last 20 years a significant increase in the installment of roof-top solar photovoltaic (PV) systems in residential areas has been observed [1]. This trend is mainly driven by the aim of decarbonizing the energy sector. Support schemes, such as fixed feed-in tariffs, are the driving force for the increased deployment of PV systems. However, as governments start to cut back fixed feed-in-tariffs, new regulatory frameworks and business models must be developed, such that investments in renewable energy sources by pro-active end-customers, the so-called *prosumers*, remain economical.

One widely discussed approach is the notion of energy communities, which allows prosumers to maximize local usage of PV power generation by local energy exchange, which is exempt from network and other surcharges [2]. However, the intermittent and volatile injection by PV systems necessitates the deployment of energy storage units to alleviate renewable energy curtailment and efficiently deal with the fluctuating power generation. Nevertheless, it is rather likely that within an energy community one energy storage is capable to serve the needs of multiple prosumers.

To this end, we are interested in an *access economy*<sup>1</sup> for energy storage in energy communities, i.e., enabling prosumers to pay for access to the benefits of an energy storage without its direct ownership [3]. In this regard, we assess different paradigms of access economy for energy storage: On the one hand, we explore the case, where a prosumer, who owns an energy storage, provides storage rights, either physical or financial, to other energy community members rather than participating as an arbitrageur in a local energy-only market. On the other hand, we analyze the case, where community members agree on a total system cost allocation rule, while the energy storage is optimally controlled by a system operator.

We consider an energy community that comprises prosumers, who potentially have an energy storage, PV system and a fixed load, as well as an energy community manager, who acts as a non-profit oriented system operator. We represent uncertain PV power generation by a finite set of discrete scenarios. We start with a benchmark case of a non-cooperative market design, where the prosumer, who owns an energy storage, participates as an arbitrageur in local energy-only markets. We continue with the case, where the prosumer, who owns an energy storage, offers physical storage rights in a storage right auction, which clears once in advance to energy-only markets. The energy storage is then scheduled in energy-only markets according to the underlying objective of physical storage right holders. Similarly, we consider the case of financial storage rights. However, under this paradigm the energy storage is socially optimal operated by the energy community manager. We move beyond non-cooperative market designs and consider the case of a cooperative market design, where energy community members agree on a total system cost allocation rule among all prosumers, while the energy storage as well as PV systems are socially optimal operated by the energy community manager. We study implications of different system cost allocation rules such as the well-known Shapley value as well as the nucleolus.

As our main contribution we offer a thorough study, including various local market designs and gametheoretic analyses ranging from non-cooperative to cooperative setups, with a special focus on the economic access to energy storage, and derive regulatory implications.

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- [3] D. Kalathil, C. Wu, K. Poolla and P. Varaiya, "The sharing economy for the electricity storage," IEEE Transactions on Smart Grid, 2017.
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<sup>1</sup> Access economy describes a market-mediated access practice in contrast to a *sharing economy*, which is based on a non-market-mediated form of access [4].

## Influence of Battery Energy Storage Systems on the Carbon Footprint of Energy Systems

Anupam Parlikar<sup>a</sup>, Holger C. Hesse<sup>b</sup>, Andreas Jossen<sup>c</sup>

<sup>a</sup>anupam.parlikar@tum.de, <sup>b</sup>holger.hesse@tum.de, <sup>c</sup>andreas.jossen@tum.de

Rising concerns about global warming and the proven role of anthropological greenhouse gas emissions in this phenomenon - a large part of which emanates from the energy sector, are driving a transition to renewable energy generators such as photovoltaic solar and wind energy turbines. Electrical energy storage systems are key to integration of power generation from intermittent renewable energy sources (RES). Lithium-ion Battery Energy Storage Systems (BESS) have been found to be techno-economically feasible in a number of use-case scenarios. Installed BESS capacities are set to soar to handle the increasing RES generation capacities and corresponding displacement of conventional power generation technologies. Carrying out techno-economic analyses of BESSs is the norm at present. It is of great importance, that the environmental impacts of BESSs in each use-case be positive. To this end, the impacts for each case must also be quantifiable to provide actionable insights for system planners.



Figure 1: Schematic representation of considered energy system with installed BESS.

A methodology which fixes an emission cost, represented by a new metric - the levelized emissions of energy supply (LEES), for each unit of useful energy supplied by a given energy system is introduced in this work. A life cycle analysis (LCA) of an exemplary utility-scale BESS is subsequently presented. The proposed methodology, together with the LCA numbers, is then applied to a use-case scenario - the island grid energy system to ascertain how the emissions cost for each unit of useful energy (LEES) supplied by the system varies with BESS dimensions. It is found that the positive impact of incorporation of each additional unit BESS capacity into the island grid system diminishes up to a certain BESS capacity, beyond which each additional unit of BESS capacity results in a higher emissions value per unit of energy as compared to the minimum possible value. This methodology can hence also identify capacity ranges where the greatest impact on the net system lifetime greenhouse gas emissions in comparison to incumbent solutions can be obtained for the given material and monetary investments. The authors wish to encourage the adoption and inclusion of such methodologies in mainstream project planning and sizing exercises for installation of energy storage systems.

## Indoor Farming – optimize efficiency

Sabine Wittmann<sup>a</sup>, Ivonne Jüttner<sup>b</sup>, Heike Mempel<sup>c</sup>

<sup>a</sup> sabine.wittmann@hswt.de, <sup>b</sup> lvonne.juettner@hswt.de <sup>c</sup> heike.mempel@hswt.de

Indoor Farming can be next to several other strategies one innovative solution for our future food production. Especially in areas with poor agricultural value, like arid regions or areas with a high ground contamination a closed production system with a high yield efficiency footprint, could be beneficial. But multi-layer cultivation systems are already today of increasing interest for producers, since Indoor Farming offers high quality production of horticultural products at the point of sale all year. Furthermore, with the possibility to precisely control all growing conditions, a targeted increase of economically valuable ingredients by a deliberate change in the interaction between the plant and its environment can be obtained. Therefore, Indoor Farming can also serve as a production unit for valuable raw materials for the manufacturing industry, offering new possibilities for today's supply chains. Especially since further automatization makes an industrial production system feasible. Up to today the major disadvantage of Indoor Farming systems remain on the high investment and running costs, which are among others, driven by the high energy consumption. In order to increase profitability and competitiveness, optimized cultivation strategies and systems have to be developed and valuable cultivars introduced.

At the University of Applied Sciences Weihenstephan-Triesdorf the material flows of several plant cultivation trials with different growing conditions were documented. The results showed a possible increase in the Water Use Efficiency (WUE) of 97 % for closed production systems, compared to a greenhouse production (Fig. 1).

		Practice	Publicat	ions cited	Results at the HSWT			
Parameter		Salat Asien PF <sup>1</sup>	Pak Choi Greenh. <sup>2</sup>	Salat EDEN ISS <sup>3</sup>	Pak Choi <b>Greenh.</b>	Pak Choi <b>Growth ch</b> .	Pak Choi . Indoor Farm	
Optimization	Cultivation time (d)	42-45	49	28	21	35	32	32
	Temperature (°C)	18-25	12	19-21	23,0 ± 5,2	16,0 ± 1,7	18	18
	Illumination time (h)	12-14	8	17	16	12	16	12
Material flow	Yield (kg <sub>FM</sub> /(m²*d))	0,08 - 0,13	0,02	0,13	0,11 ± 0,00	0,05 ± 0,00	0,07 ± 0,02	0,06 ± 0,00
	Electrical Energy Consumption (kWh/(m²*d))	n.A.	n.A.	19,24	n.A.	n.A.	3,0	2,2
	Water Consumption (I/(m <sup>2*</sup> d))	n.A.	n.A.	n.A.	3,82 ± 0,25	0,06 ± 0,00	0,42	0,16
Effiziency	Water Use Efficiency (WUE) (kg <sub>FM</sub> /I)	n.A.	n.A.	n.A.	0,03	0,99	0,17	0,38
	Light Use Efficiency (LUE) (kg <sub>FM</sub> /mol)	n.A.	n.A.	n.A.	0,006	0,007	0,008	0,009
	Electrical Energy Efficiency (kWh/kg <sub>FM</sub> )	n.A.	n.A.	147,7	n.A.	n.A.	45,7	36,7

<sup>1</sup>own data from survey <sup>2</sup>Barbosa et al. (2015)

<sup>3</sup>Schubert (2017) <sup>4</sup> DLR.de (assessed on 13.02.2020)

Figure 1: Example of several key figures for the further adjustment and optimization process

While first trials inside the Indoor Farm documented a low WUE, the reuse of condensate improved the water consumption significantly. A running trial even showed the potential to gain a surplus of fresh water (data not shown). Simulations on different lighting strategies showed the potential to reduce the electrical energy consumption further. First measurements proved an overall reduction of energy consumption by 0.8 kWh\*m<sup>-2</sup>s<sup>-1</sup>, resulting in a 20 % reduced energy consumption per kg fresh plant mass. Further tests will show the influence of pulsed LED on the energy consumption and a running plant experiment with tomato will compare the material consumption, efficiency and rentability of fruiting vegetables inside a closed production system compared to a greenhouse cultivation.



Figure 2: Adjusting the spectrum to improve tomato production

Ongoing adjustments to the growing conditions based on plant physiological measurements increase the Light Use Efficiency (LUE), which is directly linked to the growth of the plants.

## **BIM-based embedded energy and greenhouse gas** emissions analysis – a case study

Patricia Schneider-Marin<sup>a</sup>, Manav Mahan Singh<sup>b</sup>, Hannes Harter<sup>c</sup>, Werner Lang<sup>d</sup>, Philipp Geyer<sup>e</sup>

<sup>a</sup>patricia.schneider@tum.de, <sup>b</sup>manavmahan.singh@kuleuven.be, <sup>c</sup>hannes.harter@tum.de, <sup>d</sup>w.lang@tum.de



Figure 1: Life Cycle Energy Assessment (Harter, H., Singh, M. M., Schneider-Marin, P., Lang, W., & Geyer, P. (2019). Uncertainty Analysis of Life Cycle Energy Assessment in Early Stages of Design. Energy and **Buildings**, 109635)

buildina sector offers The valid opportunities for energy savings and the reduction of greenhouse gas (GHG) emissions. The chances to arrive most cost-efficiently at significant savings are typically greatest in early design stages. However, in these stages, the information about the building and its systems is incomplete and vague. BIM (building information modeling) helps to close this gap by offering possibilities to estimate information required for energy simulations embedded and energy calculations and include design uncertainties.

To provide a sound basis for early design decisions, we developed a BIM-based tool for probabilistic estimation of energy demand and GHG emissions taking into account the full life cycle of buildings (Figure 1). In a first step, the tool extracts geometric information from an early design-stage model and enhances it with additional semantic information for the calculations. The calculation is a two-layered process with a module for energy simulation and a parallel module for the calculation of material use and the resulting embedded energy. These results are merged using impact assessment data provided by the database Ökobaudat. The results show a probabilistic primary energy demand for embedded and operational impacts, split into renewable and non-renewable, and probabilistic GHG emissions.

We apply this tool to a real-life design case, a residential building in Berlin (Figure 2). For this building, early-stage design questions are investigated. These include different energy standards and different structural materials, concrete and wood.

Results show a wide range of embedded versus operational GHG emissions depending on the energy standard, energy generation and construction material. Changing the construction material has the potential to reverse the embedded GHG emissions of the structure to show a GHG emissions credit for Figure 2: Material choices for the case-study project



storing carbon in the wood structure. Changing the energy generation technology can save a significant amount of GHG emissions in the operation phase. We conclude that the tool provides valid design information for use in early design stages, which is complementary to other design criteria such as cost or fire safety considerations.

## Fast harmonic estimation using real-time embedded controllers in CoSES

Erhan Sezgin<sup>a</sup>, Anurag Mohapatra<sup>b</sup>

<sup>a</sup>sezginerhan@gazi.edu.tr, <sup>b</sup>anurag.mohapatra@tum.de

Microgrid architectures are an aggregation of end user producer and consumer (Prosumers) interfaced through power electronics converters to the distribution grid. They suffer higher inconsistencies in generation and load schedules due to weather dependent renewable resources and flexible demands such as e-mobility and smart devices. The participants in a microgrid would thus operate in a highly unbalanced grid and introduce electrical harmonics inherent to such mode of operations. There is a need to quickly detect and minimize these harmonics to prevent equipment damage in long term and compliance at the point of coupling with the transmission grid.

The Center for Combined Smart Energy Systems (CoSES) is a low inertia sector-coupled microgrid containing prosumer test benches to research and validate operation strategies. The control system hardware for each of the five prosumers in CoSES, also known as a Real Time (RT) target, is primarily a National Instruments (NI) PXIe 8880 embedded controller, which interfaces with current and voltage transducers in the CoSES electrical grid. We wish to perform continuous harmonic detection over all of the measurements, for 5 selected harmonics, upto the 20th order of the fundamental. These RT targets have a fixed cycle rate of 10kHz. The harmonic estimation exercise should leave enough processing time for the RT target to run other models within one cycle and thus



Fig 1: CoSES control and comms hardware



ensure jitter-free real time operation.

Sliding Discrete Fourier Transform (SDFT), modulated SDFT (mSDFT) and Second Order Generalized Integrators (SOGIs) are deemed suitable as they can be applied to measurements sample by sample to avoid the delays caused by windowing and have easy implementation in the CoSES control system framework. A synthetic signal with five harmonic order and Gaussian noise is used as a reference to test the various algorithms. To mimic worst-case scenarios, maximum signal burden from each prosumer, with individual signal resolved to 5 orders of harmonics, is taken into consideration.

Fig 2: First three harmonics after ampltitude step change

main criteria - settling time on amplitude step changes, presence of unexpected harmonics in reference signal, deviation from the grid frequency and computational burden on the control hardware. A modified version of the mSDFT with variable buffer length is determined to be the best fit for CoSES. It is also appreciated that the number of signals within CoSES is too large for any single RT target to continuously resolve into five orders. Therefore, compromise is reached in separating the signals into the fundamental component, processed at 10kHz and every other harmonics, down sampled to 2kHz.



The

over

## Power-to-Heat with Large Scale Thermochemical Energy Storage in Industrial Combined Heat and Power Plants

Gesa Backofen<sup>a</sup>, Michael Angerer<sup>b</sup>, Manuel Würth<sup>c</sup>, Dr.-Ing Annelies Vandersickel<sup>d</sup>, Dr.-Ing. Stephan Gleis<sup>e</sup> Prof. Dr.-Ing Hartmut Spliethoff<sup>f</sup>

<sup>a</sup>gesa.backofen@tum.de, <sup>b</sup>michael.angerer@tum.de, <sup>c</sup>manuel.wuerth@tum.de, <sup>d</sup>annelies.vandersickel@tum.de, <sup>e</sup>gleis@es.mw.tum.de, <sup>f</sup>spliethoff@tum.de

In order to facilitate the decarbonization of energy systems, multiple methods of energy storage are needed to support renewable energies. More than 20 % of energy consumption in Germany is used to produce process heat at temperature levels above 150 °C. To increase the flexibility of heat producing systems such as CHP systems, large scale high temperature storage systems are needed.

The Chair of Energy Systems of the Technical University of Munich is developing a fluidized bed high temperature storage based on the reversible reaction CaO + H2O  $\leftrightarrow$  CaOH2. The material system is very promising because of its high energy density and low costs. Because of the use of steam as reaction partner, the system was found to be well suited for integration in industrial sites with high steam demand, in particular for Power-to-Process-Heat applications.

For charging, electrical energy generated from renewables is used to drive the endothermic decomposition of Ca(OH)2 to CaO and steam at temperatures of 550 °C – 600 °C. Depending on the operating conditions, about 50% of the energy is stored in the formed CaO. When operated at pressures of ca. 5-10 bar, the generated reaction steam can be simultaneously used as process steam. During discharging, the CaO is recombined with steam in an atmospherically operated reactor. The heat released in this exothermic reaction at temperatures of 510 °C can be used for high pressure steam generation. In an integrated CHP system,

this steam can be used as process steam or for electricity generation in existing steam turbines.

Using process optimization, this study assesses different integra-tion options for the above Power-to-Process-Heat system with respect to increased flexibility and cost efficiency. Based on projec-tions for fuel and electricity prices in the upcoming 30 years and a comparison with different storage methods recommendations for investments into flexibility improvements for industry parks can be made.



Figure 1: Cut out of the storage system model in TOP Energy

## A techno-economic optimization for decentralized waste-heat power generation with a Steam-Rankine-Cycle

Florian Raab<sup>a</sup>, Paris Chatzitakis<sup>b</sup>, Frank Opferkuch<sup>c</sup>

<sup>a</sup>florian.raab@th-nuernberg.de, <sup>b</sup>paris.chatzitakis@th-nuernberg.de, <sup>c</sup>frank.opferkuch@th-nuernberg.de

Waste-heat recovery (WHR) is one of the fundamental CO2-free energy sources that still has a significantly untapped potential. Coal-fired power plants are increasingly being replaced by decentralized combined heat and power (CHP) stations that use internal combustion engines (ICE) to convert the chemical energy of liquid or gaseous fuels such as natural gas, biogas or hydrogen into electrical and thermal energy simultaneously. The electrical efficiency of this process is about 40 %, while the remaining 60 %, the "waste" thermal energy, often remains unused because of the low return on investment (ROI) rates of conventional technologies. State of the art for the conversion of waste heat into electricity in small power plants are Organic Rankine Cy-



cle (ORC) processes, which use an organic liquid as a working fluid, whereas in large power plants the Steam Rankine Cycle (SRC) process is preferred. ORC working fluids are more efficient at lower process temperatures whereas water shows its potential at higher temperatures. However, ORC working fluids are prone to thermal decomposition and SRC plants become prohibitively expensive in smaller scales. Additional disadvantages of organic working mediums, which are becoming increasingly important in the current debate on sustainability, are their climate concerns and safety issues. For this reason, the "KompACT" research project focuses on a techno-economic optimization of a decentralized SRC based technology to convert high temperature waste heat into electrical power. The SRC technology presented here for the conversion of waste heat into electrical energy is intended to offer plant operators a safe, environmentally friendly and cost-comparable alternative to ORC systems at higher waste gas temperatures.

In a collaborative research project, two universities of applied sciences together with five companies, specialists in steam turbines, steam generators and power-cycle architecture, attempt to redevelop a SRC based technology as a CHP bottoming cycle with improved performance, simplified and maintenance-free design and reduced cost. In detail, an ultra-compact steam generator is expected to reduce the mass of the entire plant by up to 60 %. Different designs of this steam generator are being investigated in a downscaled test rig for evaporator quality and stability. The steam turbine will include a high-speed rotor that can be manufactured modularly in a wide range of performance classes. With the help of a predictive control system, dynamic fluctuations in the load are to be efficiently compensated in order to be able to operate the plant at peak load and still achieve a maximum operation life. All developed apparatuses of the target SRC plant will be evaluated in a test facility of the Nuremberg Institute of Technology, under real process parameters and optimized during operation. The variation of operating parameters, their effect on efficiency, material, costs and operation, first measurement results and the next steps are presented.

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## 100% Renewables for Bavariastructures, costs and benefits of full supply in all sectors

Andreas Hanel<sup>a</sup>, Sebastian Miehling<sup>b</sup>, Benedikt Schweiger<sup>c</sup>, Jakob Schweiger<sup>d</sup>, Wolf Wedel<sup>e</sup>, Rene Schwermer<sup>f</sup>, Maximilian Blume<sup>g</sup>, Hartmut Spliethoff<sup>h</sup>

<sup>a</sup>andreas.hanel@tum.de, <sup>b</sup>sebastian.miehling@tum.de, <sup>c</sup>benedikt.schweiger@tum.de, <sup>d</sup>Jakob.Schweiger@zae-bayern.de <sup>e</sup>wolf.wedel@tum.de, <sup>f</sup>Rene.Schwermer@zae-bayern.de, <sup>g</sup>Maximilian.Blume@zae-bayern.de, <sup>h</sup>spliethoff@tum.de

The aim of the presented work of the KITS team, a cooperation between the Institute for Energy Systems and ZAE Bayern, is to optimize a bavarian energy system based on CO<sub>2</sub>-neutrality for the year 2040. In particular, the interactions between the electricity, heat and transport sectors will be identified. The analysis of the optimisation results should finally identify the required structures and the associated costs.

Therefore Bavaria has a number of usable potentials to build a CO<sub>2</sub>-neutral energy system. At the beginning of the study, detailed potential analyses are carried out with regard to the availability of individual renewable energies. Finally, taking into account possible restrictions, technologies based on solar radiation, wind and biomass, as well as geothermal and hydropower are transferred to the energy system optimizer.

First results regarding cost-optimal power generation, as shown in Figure 1, indicate the need of more than 30 GW of wind power, which would be impossible under current regulations, and aproximately 55 GW of installed PV power. For the heat supply analysis the area of Bavaria is divided into several regions with characteristic demand curves by a GIS data based approach, as well as different temperature levels are considered. Figure 2 shows the cost-optimal heat supply ratios of a selection of considered consumer structures. For example, the industrial heat demands are covered by two technologies. During the day the supply is provided by power-to-heat from sustainable power generation plants, whereas biomass plants are used at night. Finally, the transport sector is taken into account by using characteristic demand curves. Scenarios with a fully electrified transport sector as well as variants with liquefied gas driven cargo transport are considered.



## 2. Posters

## Micro Hydro Pump Storage with pump as turbine

Florian Lugauer<sup>a</sup> M.Sc., Prof. Dr. Josef Kainz<sup>b</sup>

### <sup>a</sup>florian.lugauer@hswt.de, <sup>b</sup>josef.kainz@hswt.de

Energy storage technologies are becoming increasingly important in order to continue the needed expansion of renewable energy production, not only in Germany but in the whole world. To reduce the grid load and to be able to use renewable electricity flexibly, different storage technologies will gain more and more interest in the near future. Therefore, a micro-hydro pump storage system could be a promising extension for an existing PV system, which has exceeded the maximum remuneration period of the EEG and should now participate in the electricity market. In this way, the generated electrical energy can be stored and used more flexibly.

To lower the specific costs of the micro-hydro pump storage, a standardized centrifugal pump, which enables both, turbine and pump operation, will be used along with other standardized components. This makes it possible to save expenditure on components that would otherwise have to be realized through cost-intensive individual production.

Since characteristic maps for turbine operation of a centrifugal pump are often not available from manufacturers, a test bench for the measurement of characteristic turbine maps of various centrifugal pumps has been set up. There, a pump creates a controllable pressure increase with which different heads can be simulated. The water flows through a penstock from the feed pump into the centrifugal pump which now works in turbine mode. The use of various measuring instruments makes it possible to record important parameters such as rotation speed, torque or flow rate. With this information, it is possible to create the entire turbine map of the centrifugal pump. Using similarity relationships, maps for pumps with other dimensions will be calculated to increase the available number.

With the help of the determined characteristic maps, the optimal operation of the pump as a turbine in combination with an existing PV system will be simulated by a specially created tool. The program, which is based on the programming language MATLAB, offers the possibility to vary all important system parameters. Through various optimization processes, e.g. the most suitable conditions for the economic efficiency of the system are being calculated. Once this optimization has been completed, the program simulates the operation of a micro pump storage power plant over a period of one year. The result is an exact calculation of the stored energy quantities, efficiency, and many other key values. This is followed by a profitability calculation in accordance with VDI 2067, with which the economic performance indicators are determined over the entire life cycle of the power plant. This allows also a comparison with alternative storage technologies, such as a battery storage. With the help of the simulation results, potential plant sites can be examined and a pilot system can be projected.

## Syntheses and Impedance Spectroscopic Investigation of Lithium and Sodium Phosphidoindates

Jan Meyer<sup>a</sup>, Tassilo M. F. Restle, Thomas F. Fässler

<sup>a</sup>ga84hiz@mytum.de

The development of all-solid-state batteries (ASSB) is currently attracting lots of interests. Solid electrolytes need to be non-flammable and need a high ionic conductivity to utilize them in ASSBs. Therefore, intensive research for the synthesis of new compounds owing these properties is ongoing. Nowadays, the ionic conductivity of solid electrolytes reaches the level of organic-based electrolytes ( $\sim 10^{-2}$  S cm<sup>-1</sup>).<sup>[1]</sup>

Recently our group investigated lithiumphosphidosilicates and germanates, which are moderate ion conductors. The highest reached ionic conductivity accounts 1.1×10<sup>-3</sup> S cm<sup>-1</sup>.<sup>[2-4]</sup> Restle et al. investigated the

Li–Al–P and Li–Ga–P phase systems and discovered the compound  $\beta$ -Li<sub>9</sub>AlP<sub>4</sub>, which has the highest ionic conductivity of all phosphide-based compounds ( $\sigma_{ion} = 3.0 \times 10^{-3} \text{ S cm}^{-1}$ ).<sup>[5]</sup> Now we present here two new compounds of the phosphidotriels, named Li<sub>3</sub>lnP<sub>2</sub> and Na<sub>3</sub>ln<sub>2</sub>P<sub>3</sub>. The lithium compound Li<sub>3</sub>lnP<sub>2</sub> was synthesised phase-pure via a ball mill synthesis and subsequent quenching. The crystal structure was determined by single crystal X-ray diffraction method. The compound consists of corner-sharing lnP<sub>4</sub> tetrahedra, which build up T2-supertetrahedra (Figure 1). The supertetrahedra are connected forming two interpenetrating adamantane-like networks. The ionic conductivity of the compound accounts 2.8×10<sup>-9</sup> S cm<sup>-1</sup>.

The second compound  $Na_3In_2P_3$ , was also synthesised with the aid of the ball mill from the stoichiometric amounts of the elements followed by a moderate thermal treatment. The structure consists of corner-sharing  $InP_4$ tetrahedrons building up six-membered pores, which are possible ion pathways (Figure 2a). However, the ionic conductivity of  $Na_3In_2P_3$ accounts only  $3.6 \times 10^{-7}$  S cm<sup>-1</sup> (Figure 2b).



Figure 1: Crystal structure of Li<sub>3</sub>lnP<sub>2</sub> with lnP<sub>4</sub> tetrahedrons (blue) and T2-supertetrahedrons (red).



Figure 2: a) Crystal structure of Na<sub>3</sub>In<sub>2</sub>P<sub>3</sub> with InP<sub>4</sub> tetrahedrons (blue) b) Impedance spectrum of Na<sub>3</sub>In<sub>2</sub>P<sub>3</sub>.

The new phosphidoindates  $Li_3InP_2$  and (bite) b) impedance spectrum of Na<sub>3</sub>In<sub>2</sub>P<sub>3</sub>.Na<sub>3</sub>In<sub>2</sub>P<sub>3</sub> show a huge structural variability. Even both compounds have a low ionic conductivity, the contribute to the understanding of ionic conductivity and present the starting point for the discovery of new compounds in this phase systems.

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## Fast Lithium Ion Conduction in Lithium Phosphidoaluminates

Tassilo M. F. Restle<sup>a</sup>, Christian Sedlmeier, Holger Kirchhain, Wilhelm Klein, Gabriele Raudaschl-Sieber, Volker L. Deringer, Leo van Wüllen, Hubert A. Gasteiger, and Thomas F. Fässler<sup>b</sup>

#### atassilo.restle@tum.de, bthomas.faessler@lrz.tum.de

Solid electrolyte materials are crucial for the development of high-energy-density all solid-state batteries (ASSB) using a non-flammable electrolyte. In order to retain a low lithium-ion transfer resistance, fast lithium ion conducting solid electrolytes are required.<sup>[1]</sup> So far the highest ionic conductivity was achieved by the lithium thiophosphate  $Li_{10}GeP_2S_{12}$  (1.2  $10^{-2}$  S cm<sup>-1</sup>).<sup>[2]</sup> Recently our group discovered with

lithiumphosphidosilicates and germanates new phosphide-based materials for lithium ion which proved to be moderate lithium ion conductors with conductivities up to 8.6 10<sup>-5</sup> Scm<sup>-1</sup> at RT.<sup>[3-4]</sup> Just now we expand this material class with the novel superionic conductor Li<sub>9</sub>AIP<sub>4</sub>.<sup>[5]</sup> Li<sub>9</sub>AIP<sub>4</sub> is easily obtained via ball milling synthesis of the elements and subsequent annealing at moderate temperatures. Its structure is characterized by single crystal and powder X-ray diffraction and featured isolated highly charged [AIP<sub>4</sub>]<sup>9-</sup> tetrahedra (Fig. 1). This first representative of a novel compound class of lithium phosphidoaluminates has as an undoped material a remarkable fast ionic conductivity of ~ 3 mS cm<sup>-1</sup> and a low activation energy of ~ 29 kJ mol<sup>-1</sup> as determined by impedance spectroscopy (Fig. 2). Temperature- dependent <sup>7</sup>Li NMR spectroscopy supports the fast lithium motion. In addition, Li<sub>9</sub>AIP<sub>4</sub> combines a very high lithium content with a very low theoretical density of 1.703 g cm<sup>-3</sup>. The distribution of the Li atoms over the diverse crystallographic positions between the [AIP<sub>4</sub>]<sup>9-</sup> tetrahedra is analysed by means of DFT calculations.



Figure 1. Crystal structure of Li<sub>9</sub>AIP<sub>4</sub>. Isolated [AIP<sub>4</sub>]<sup>9-</sup> tetrahedra are highlighted in blue.



Figure 2. a) Nyquist plot of  $Li_9AIP_4$  measured under blocking conditions. b) Arrhenius plot of the product of conductivity and temperature.

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# A holistic model for the solid electrolyte/electrode interface

Leon Katzenmeier<sup>a</sup>, Aliaksandr Bandarenka<sup>c</sup>

<sup>a</sup>leon.katzenmeier@tum.de, <sup>c</sup>bandarenka@ph.tum.de

Energy storage is one of the most essential problems in solving the energy challenges humanity faces. Renewable energies in the form of electricity need to be stored for all applications. The traditional Lithium Ion battery (LiB) technology has approached its maximum in energy and power density in the last years, but emerging new material systems and technologies such as All-Solid-State Batteries (ASSB) have been proposed. The traditional liquid electrolytes of LiB are flammable, as they are based on organic solvents and do not provide mechanical strength to inhibit the growth of Lithium metal dendrites, which is the most



important reason why the holy grail of battery technology, namely lithium metal anodes, have not been implemented in commercial systems. Pure lithium metal anodes have the highest theoretical energy density (3860mAh/g) and lowest negative electrochemical potential of 3.04V (against standard hydrogen).

While stand-alone solid electrolytes, such as LATP and LAGP are stable in air, even with humidity and against metallic lithium, a variety of problems occur at the interface to the electrode materials. These phenomena are either within the solid electrolyte (such as space-charge occurrence) or happening



Figure 2: Energy dispersive X-Ray Spectroscopy for different acceleration voltages.

Figure 1: Theory and Experimental Work on Solid Electrolytes.

right at the interface, such as a material decomposition. In this work, we combine different experimental and theoretical approaches (Fig.1) to build a holistic model of the interface.

As every electrochemical system, the impedance response of the interface is characteristic for the electrochemical processes. Therefore, electrochemical impedance spectroscopy, together with modelling via equivalent circuits can yield many insights into the charge accumulation at this interface under different bias conditions.

In addition, a variety of spectroscopic techniques is to elucidate the exact material composition at the interface, such as the elemental distribution (EDX) and oxidation states (XPS).

## The Effect of Iso- and Aliovalent Substitution on the Ionic Conductivity in Lithium Phosphido Tetrelates

Moritz Bohn<sup>a</sup>, David Müller<sup>b</sup>, Thomas F. Fässler<sup>c</sup>

<sup>a</sup>moritz.bohn@tum.de, <sup>b</sup>david.mueller@tum.de, <sup>c</sup>thomas.faessler@lrz.tum.de

In the future, solid-state ion conductors will replace conventional liquid electrolytes ion lithium ion batteries. In order to reach marketability, demands in terms of energy density, cycle stability and safety must be met. This requires research to develop and optimize new materials. The lithium phosphidotetrelates and trielates represent a group of solid-state ionic conductors with promising properties showing ionic conductivities of  $8.6 \cdot 10^{-5}$  S cm<sup>-1</sup> for Li<sub>8</sub>GeP<sub>4</sub><sup>[1]</sup> and  $3 \cdot 10^{-3}$  S cm<sup>-1</sup> for Li<sub>9</sub>AlP<sub>4</sub>.<sup>[2]</sup> Investigations have shown that substitution with heavier homologues can lead to reduced energy barriers for lithium ion migration and aliovalent substitution can increase conductivity by altering the charge carrier concentration.<sup>[3]</sup>

In this work we present the quaternary solid solutions  $Li_8Ge_{1-x}Sn_xP_4$  and  $Li_{9-x}AI_{1-x}Sn_xP_4$ . The goal of this work is to picture



Figure 2: Vegard plot of Li<sub>8</sub>Ge<sub>1-x</sub>Sn<sub>x</sub>P<sub>4</sub>.



Figure 1: Crystal Structure of  $Li_8Ge_{1-x}Sn_xP_4$ . The phosphorus atoms form a fcc structure where germanium and tin occupy 1/8 of the tetrahedral voids.

the effect of changes in the lattice parameter and charge carrier concentration on the lithium-ion transfer resistance. For the synthesis, the starting materials are first activated via ball mill synthesis and then annealed with appropriate thermal treatments. The samples are analyzed by powder X-ray diffractometry and Rietveld refinement. All mixed compounds crystallize in the cubic space group  $P\bar{4}$ 3n (no 218). The mixing ratios show a behavior according to Vegard's law, where the lattice parameter systematically increases with increasing tin content. The ionic conductivities are determined via Impedance spectroscopy in a custom-made setup where the samples are pressed and pelletized inside the measurement cell.

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## Increasing the Ionic Conductivity of Lithium Phosphido Tetrelates by Spark Plasma Sintering

David Müller<sup>a</sup>, Thomas F. Fässler<sup>b</sup>

<sup>a</sup>david.mueller@tum.de, <sup>b</sup>thomas.faessler@lrz.tum.de

Spark Plasma Sintering (SPS) is a powerful technique to produce pellets with up to 100% of a material's theoretical density. A SPS device consist of a DC generator and a hydraulic press inside a vacuum chamber

(Figure 1). The sample is placed in an electrically conducting graphite die. During sintering the sample is heated by applying a high ampere DC pulse. Depending on the electrical conductivity, the current flows not only through the graphite mold, but also directly through the sample, producing energy via resistive heating. This leads to fast heating rates and allows for short sintering times and low total temperatures compared to conventional techniques sintering are Thereby grain coarsening achieved. is suppressed and the nanostructure of the sample particles stays intact.<sup>[1]</sup> The Joule heating is associated with electric current and field effects like electromigration, the Peltier effect and the generation of spark discharges



Figure 1:a) Schematic setup of a SPS furnace. b) Graphite die inside sintering chamber.

with plasma formation between two adjacent particles, releasing locally high energy which leads to melting and evaporation at the particle surface, resulting in neck formation and closing of the gaps.<sup>[2]</sup>

Lithium phosphido tetrelates<sup>[3,4]</sup> and – trielates<sup>[5]</sup> represent a new phosphide based class of solid state lithium ion conductors with conductivities of up to 3\* 10<sup>-3</sup> Scm<sup>-1</sup>.<sup>[5]</sup> The measured capacities reveal that the limiting factor for the conductivity is not the intrinsic conductivity of the bulk material, but the contact resistance at grain boundaries in the sample. We apply spark plasma sintering to increase the density of the pellets for impedance measurements to reduce the influence of the grain boundary resistance and address the ionic conductivity of the bulk material.

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## A force-field based approach towards designing working interfaces in solid-state electrolytes

S. Stegmaier<sup>a</sup>, Roland Schierholz<sup>b</sup>, Christoph Scheurer<sup>c</sup>, Karsten Reuter<sup>d</sup>

<sup>a</sup>sina.stegmaier@tum.de

Secondary batteries are a key component for intermittent energy storage and e-mobility in the current energy transition. The state-of-the-art technology is based on Li-ion cells containing liquid electrolytes. All-solid-state batteries (ASSB) present a potential next-generation technology, promising increased operation safety and lifetime. The performance of solid-state electrolytes (SSE) in ASSBs, though, is severely limited by poorly understood interfacial processes [1]. Atomistic insight into the structure, transport, and degradation processes at working SSE grain boundaries (GB) [2] is thus required to enable insight-driven progress.

We apply molecular dynamics simulations (MD) with a systematically first-principles derived force field to study GBs in the SSE LATP ( $Li_{(1+x)}Al_xTi_{(2-x)}(PO_4)_3$ , x=0.3). An experimentally guided simulation protocol is established to model the formation of GBs during sintering. Anisotropic compression at high pressure and temperature leads to the loss of periodic structure. The obtained semi-amorphous domain is in agreement with findings from experimental TEM studies [3]. Structural scoring of simulated [4] and experimental TEM images confirms the co-existence of bulk-like with metastable interphase regions in the GB. Extensive sampling is reduced to the truly glassy regions of the GB. The resulting GB structural models enable the investigation of anisotropic lateral and transverse ion transport and the comparison to macroscopically measurable properties.

With this approach, we leverage experimental input for modeling realistic solid-solid working interfaces [3] and explore the vast glassy configuration space by accelerated statistical sampling of structural ensembles through computational means.

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# A surface treatment recipe for significantly enhancing thermoelectric PEDOT: PSS films

Suo Tu<sup>a</sup>, Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>suo.tu@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Organic semiconductors have attracted intense attention because of their potential use in mechanically flexible. liahtweiaht. and inexpensive electronic devices. Especially. poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) is the most studied conducting polymer system due to their intrinsically high electrical conductivity, low thermal conductivity, and high mechanical flexibility [1,2]. These factors render PEDOT:PSS a promising candidate for thermoelectric (TE) generators based on organic materials operating at moderate temperatures. The energy conversion efficiency of a TE material is evaluated by a dimensionless figure of merit ZT. Here,  $\sigma$  represents the electrical conductivity, S the socalled Seebeck coefficient,  $\kappa$  the thermal conductivity, and T the absolute temperature [3,4]. However, pristine PEDOT:PSS thin films show low electrical conductivities of around 1 S cm<sup>-1</sup> and Seebeck coefficient of about 15 µV K<sup>-1</sup>. Therefore PEDOT:PSS is not viable for many applications. Moreover, it is generally considered that it is difficult to obtain a high ZT value of TE materials, due to the fact that the parameters are interdepending as function of carrier concentration and hard to be optimized simultaneously. Mostly methods employing film treatment or both film treatment and additives in the solution show better conductivity than the mere additives in the PEDOT:PSS aqueous solution. Herein, a facile multi-step surface treatment was applied to enhance TE properties of pristine PEDOT:PSS thin films. Subsequently, the surface morphology and the inner morphology were probed using atomic force microscopy and grazing-incidence wide/small-angle X-ray scattering [5], respectively. Additionally, UV-Vis spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy were employed to investigate the mechanism behind for TE performance improvement.



Figure 1: Schematic diagram representing the morphology of PEDOT:PSS in a film geometry.

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## Energy supply optimization of the Munich University of Applied Sciences through parametric studies in thermal building simulation

Nico Ehlers<sup>a</sup>, Daniel Kierdorf<sup>b</sup>, Farzan Banihashemi<sup>c</sup>, Werner Lang<sup>d</sup>

<sup>a</sup>ge29duf@mytum.de, <sup>b</sup>daniel.kierdorf@tum.de, <sup>c</sup>farzan.banihashemi@tum.de, <sup>d</sup>w.lang@tum.de



Figure 1: Detailed Model of the University of Applied Science Munich

Within the research project "NuData Campus" of the Federal Ministry for Economic Affairs and Energy, an attempt is being made to create a  $CO_2$  – neutral usage of a university. The University of Applied Science Munich serves as an object of investigation. To get detailed information about the current thermal situation of the building fabric and technical facilities, a digital model is built to perform thermal simulations. The goal of these simulations is to find the best refurbishment strategies to minimize the energy-use and maximize the indoor thermal comfort. The main advantage

of a building energy simulation is the possibility to analyze the object in detail and perform parametric simulations. Depending on the number of parameters and the given size of the building, the simulation can take several weeks. In order to simulate a necessary number of parameters, it is required to reduce the simulation time. Therefore, the given detailed model of the campus building must be simplified. Different cluster analysis methods will be performed and compared, to identify rooms of the detailed simulation model with similar thermal responses, to group them and discover reference rooms which best represent the thermal behavior. The resulting reference rooms are then used for the parametric thermal simulation.

This investigation deals with the building energy simulation, the simplification of the model and the parametric simulation of the technical facilities. The methodical procedure is shown in figure 2. The following research questions are examined during the investigation:

- How can the heating and cooling supply of the University of Applied Science Munich be as climate neutral as possible without compromising thermal comfort?
- How much can the simulation time be reduced by the reduction of the detailed model?
- How can the energy supply of the reference rooms be optimized?



## Sputter deposition of Ag on nanostructured PMMA-b-P3HT and PS-b-PMMA copolymer thin films

Marc Gensch<sup>a</sup>, Peter Müller-Buschbaum<sup>b</sup>, Stephan V. Roth<sup>c</sup>

amarc.gensch@desy.de, bmuellerb@ph.tum.de, cstephan.roth@desy.de

Tailoring the polymer-metal-interface on the nanoscale and designing its optical and electronic properties is the prerequisite for the efficient fabrication of organic electronics [1] and photovoltaics [2]. Yet, on the nanoscale, it becomes necessary to extend well-established lithographic methods as advanced fabrication techniques to produce devices with improved control. This is due to the boundary conditions of traditional lithography, namely being the large-scale nanostructure fabrication and the production costs for real-world applications. On macroscopic scale, bottom-up routines to fabricate nanostructures with desired properties have attracted much interest in science and industry [3].

On the nanoscale, one makes readily use of selfassembly to nanostructure polymer-metalcomposites: It offers an excellent perspective by combining the wealth of polymer materials and morphologies with the size- and shape-dependent optical and electronic properties of metals. The deposition of thin metal layers on microphaseseparated copolymer thin films is one important example of using nano-structured polymer templates to guide the nanogranular metal layer growth [4]. The metal nanoparticles grow preferentially and thus more selectively on one polymer domain. This socalled selective wetting describes the preferred growth of metal nanoparticles on one polymer block. Figure 1: General growth of Ag on PS-b-PMMA

Three prominent driving forces are responsible for different this phenomenon: surface energies



copolymer templates with five distinct growth regimes. From 5.

changing the mobility of the clusters on the polymer; embedding; chemical interaction. We hence studied the silver cluster morphology during the growth on a block copolymer template by grazing incidence smallangle X-ray scattering (GISAXS). Our study reveals the selective wetting of silver on one of the polymer blocks and the influence of the template on the percolation behavior of the nanogranular silver layer. We correlate our nanostructural studies with macroscopic resistivity measurements during the sputter deposition [5].

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# Development of innovative Nano-CHP using new thermoelectric generators

Prof. Dr. Thomas Metz<sup>a</sup>, Arne Stumpf<sup>b</sup>

<sup>a</sup>thomas.metz@th-nuernberg.de , <sup>b</sup>arne.stumpf@th-nuernberg.de,



The presentation shows the actual stand of the project "development of innovative Nano-CHP using new thermoelectric generators based on Skutterudite Bismuth Telluride - semiconductors and for application as decentral power supply in single-family Bundeswirtschaftsministerium houses." The is financing this project the Zentrale by Innovationsprogramm Mittelstand (ZIM). Project aim is the development of a combined heat and power plant (CHP) for converting waste heat generated in the heating operation in single-family electrical energy. In contrast houses in to conventional CHP-concepts, which are using conventional combustion engines, this new concept

#### Figure 1: concept of Nano-CHP

is using thermoelectrically modules (TEM) as power generator and a common condensing boiler to thermal energy generation. Skutterudites and Bismuth Telluride – semiconductors are the base for these thermoelectric elements. The temperature gradient between the hot combustion gas and cooling water is the driving force and responsible for electric energy production.

The great advantage of the newly developed technology is in contrast to the previously available system based on internal combustion engines, it also provides electrical energy on low load ranges below 5 kW thermal output. The aim is a thermally controlled Nano-CHP to generate a small amount of electricity. The amount of electricity is based on the typically power consumption of single-family houses.

Condensing boilers usually use modulating surface burners. The modulating mode of operation guarantees a burner output which is adapted to the thermal requirements. This makes it difficult to design precisely the generator for a specific operating point. In order to keep the wiring effort of the generator low, the aim is to generate the single TEM voltages as homogeny as possible. This requires homogeneous thermal utilization of the TEM. A homogeneous, effective utilization initially contradicts a modulating mode of operation of the burner. The modulation causes a fluctuating heat flow, which causes to a fluctuating and therefore not optimal

utilization and use of the TEM. The resolution of this contradiction by constructive and control elements is a central component of the project.

The presentation will give an overview and some results of the project and the preliminary works. Ideas and questions according to described above will be discussed.



Figure 2: operation mode of TEM

## Photochromic films based on WO<sub>3</sub> nanoparticles and cellulose nanocrystals

•S. Hasegawa<sup>a</sup>, V. Körstgens<sup>b</sup>, P. Müller-Buschbaum<sup>c</sup>

<sup>a</sup>shu.hasegawa@tum.de, <sup>b</sup> volker.koerstgens@ph.tum.de, <sup>c</sup> muellerb@ph.tum.de

In the emerging field of printable electronics there is a growing demand for transparent, flexible substrate and coating materials [1]. Films based on cellulose nanofibrils are a promising sustainable alternative to fully synthetic polymers [2]. Transparent films can be obtained of cellulose nanofibrils (CNFs) or even more downsized particles, cellulose nanocrystals (CNCs). These cellulose materials can be extracted out of soft wood with an oxidative process with 2,2,6,6-tetramethyl-piperidine-1-oxyl radicals [3].



Figure 1: Oxidation process of cellulose

The TEMPO-oxidation converts hydroxyl-groups into carboxyl functional groups on the surface of fibrils and nanocrystals, respectively as shown in figure 1. This procedure leads to a much better dispersion in water. In this investigation we demonstrate how photochromic thin films can be produced out of such CNCs in combination with inorganic nanoparticles. Photochromism is defined as the light induced, reversible transformation of a chemical species between two forms with different absorption spectra. A well-known example to exhibit this behavior is  $WO_3$  whose photochromic mechanism especially in combination with the

cellulose polymer shall be further explained in the following: In a CNC-WO<sub>3</sub> composite the oxygen atoms of the tungsten trioxide can form Hbonds with the six OH-groups of the monomer units of the cellulose polymer as shown in figure 2. To explain the photochromic behavior of tungsten(VI) oxide and cellulose nanocrystals, Adachi et al. concluded that the WO<sub>3</sub> colloids responsible for the change in color are mainly WO<sub>3</sub>·2 H<sub>2</sub>O crystallites [3, 4]. If these particles are radiated with UV light electron-hole pairs can be generated in the conduction and valence band which can weaken the O-H bonds of the water molecules of WO<sub>3</sub>·2 H<sub>2</sub>O causing the H<sub>2</sub>O to decompose into H<sup>+</sup>, O<sub>2</sub> and free electrons. While the oxygen molecules are released in the ambient air, the protons subsequently bind with remaining oxygen atoms, again forming H<sub>2</sub>O. The change of color due to the UV radiation can now be explained through the reduction of colorless W<sup>6+</sup> into colored W<sup>5+</sup> ions [4]. We investigated composite films of cellulose nanocrystals and  $WO_3$ nanoparticles. Different ratios of the two components have been applied with a number of coating techniques ranging from simple drop casting, blade coating and spray deposition.



crystallites and cellulose

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# Switchable thermo-responsive polymer coatings as self-cooling approach for buildings

Lucas P. Kreuzer<sup>a</sup>, Tobias Widmann, Nuri Hohn, Kun Wang, Jean-Francois Moulin, Viet Hildebrand, André Laschewsky, Christine M. Papadakis, and Peter Müller-Buschbaum<sup>b</sup>



#### <sup>a</sup>lucas.kreuzer@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Over half of humankind's population already lives in urban areas and this trend is expected to even increase to 70 % by 2050. [1] In order to keep these urban hot spots sustainable, a well-balanced energy management is necessary. Today, for example the United States, already uses approximately 40 % of their energy consumption to heat up or cool down buildings. [1] Novel concepts, such as vegetation on roofs and facades of buildings, have been proposed to support the selfcooling of buildings. However, these systems demand autonomous adaption to fulfill the short-period need for

cooling. Wet and/or cool conditions appear at least once per day in most latitude areas and therefore, cooling is only required between noon and midnight. One new, promising approach to self-cooling buildings is sweating [2]. For example, mammals are able to life under environmental conditions of more than 25°C above their body temperature since they have the ability to sweat. With the transformation of this capability towards buildings, an environmental friendly way of autonomous cooling can be achieved.

By using thermo-responsive polymer thin films as smart surface coatings, buildings are able to sweat. The polymer coating undergoes a phase transition either upon cooling (upper critical solution temperature -UCST) or heating (lower critical solution temperature - LCST). Above the UCST and below the LCST, polymer-solvent interactions are favored and H<sub>2</sub>O molecules from the surrounding atmosphere diffuse into the polymer coating. However, once the UCST is undershoot or the LCST is exceeded, respectively the polymer - polymer interactions are favored and water molecules are pushed out of the polymer film. The released water molecules evaporate and the building is cooled down by the effect of evaporative cooling. By combining selected types of thermo-responsive polymers (UCST and LCST) a diblock copolymer (DBC) with both, UCST and LCST is generated. Since both transition temperatures are tunable, the behavior of such DBCs can be adapted. Hence, this concept works in different climate zones. Still, a fundamental understanding in the switching kinetics as well as proof of reproducibility is needed. Therefore, we investigate in-situ the temperature-dependent behavior as well as the reversible (in total 3 cycles) water storage/release ability of a poly(sulfobetaine)-based DBC with neutron reflectometry in time-of-flight mode. With this sophisticated measurement technique, mesoscopic parameters, such as film thickness and water content are determined. In addition, FTIR spectroscopy is used to complement the results with information about the role of the SO<sub>3</sub><sup>-</sup> group (PSPP block) and the amide groups (both blocks) upon hydration and de-hydration.

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## Climate responsive renovation and densification: An approach to reduce the total energy demand of buildings

Hannah Wittmann<sup>a</sup>, Farzan Banihashemi<sup>b</sup>, Werner Lang<sup>c</sup>

<sup>a</sup>hannah.wittmann@tum.de, <sup>b</sup>farzan.banihashemi@tum.de, <sup>c</sup>w.ang@tum.de

The purpose of the paper is to investigate the impact of different building materials on the energy balance of buildings. In doing so, not only the energy demand during the operational time is considered, but also the energy needed for the construction itself.

To facilitate this, a multi-storey residential building in Munich is modeled in the program IDA ICE (IDA Simulation EQUA 2013). The performance of biogenic and non-biogenic construction materials is compared with consideration to the building's heating and cooling energy performance. For the simulations, the regional climate model REMO scenario A1B is used for the years 2052 and 2073, where various scenarios are implemented. In doing so, different methods of renovation and densification in the urban contexts are reflected. These scenarios are simulated with different energy standards based on EnEV 2016 (Energy Saving Ordinance), KfW 55 and KfW 40 standards (efficiency house standards). In addition, the impact of different building materials is compared through a Life Cycle Assessment. Through these calculations, the embodied energy of the construction methods is analyzed. Thus, the question of whether biogenic building materials can improve a building's total energy demand is investigated.

Furthermore, due to climate change and urbanization, sustainable building methods are becoming increasingly necessary. This is due to great potential for resource-saving and therefore climate-friendly development (Püschen and Teller 2013). The paper presents ideas of how sustainable construction methods can counteract the influence of the climate. Concurrently, construction methods which aim to reduce their impact on the climate through the use of sustainable materials are compared. Through analyzing varying methods in a holistic way at an early stage of development well informed decisions can be made from the beginning. This can have a positive effect on the environment.

Global warming prompts a rethink of building design – therefore not only the energy balance during the operation requires consideration, but also the energy used for the construction. This approach could help to achieve the climate policy target.

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## Life Cycle-based CO<sub>2</sub>-neutral Plus Energy Building

Hannes Harter<sup>a</sup>, Michael Vollmer<sup>b</sup>, Christina Meier-Dotzler<sup>c</sup>, Werner Lang<sup>d</sup>

<sup>a</sup>hannes.harter@tum.de <sup>b</sup>michael.vollmer@tum.de <sup>c</sup>christina.dotzler@tum.de <sup>d</sup>sekretariat.enpb.bgu@tum.de

For planning and realising a life cycle based greenhouse gas neutral plus energy building the research project 'Eco+Office AS-Bau' was carried out in cooperation between the Insitute for Energy Efficient and Sustainable Design and Building of the Technical University of Munich, AS-Bau Hof GmbH and the Bavarian Construction Industry Association. The case study of this project was the office and administration building of AS-Bau Hof GmbH where scientific and innovative methods were developed and applied in practice to reach the overall project objective. The main topics of investigation were the life cycle-based ecological (Life Cycle Assessment (LCA)) and economic assessment (Life Cycle Costing (LCC)) as well as the investigation on the influence of the construction elements on the load management of the building. This abstract is focusing on the LCC and LCA topics. In both main topics, different design variants were investigated, looking detailed on structural elements as well as on elements of the technical building services. These considerations resulted in recommendations for action to achieve the overall objective of planning and realising a life cycle based greenhouse gas neutral plus energy building. The recommendations for action flew directly into the planning process and contributed significantly to the decision-making process.

With regard to the overall project objective, the assessments included the examination of whether the existing building can be reused/rehabilitated in an ecologically manner and can be linked to an extension, or whether the existing building were to be demolished and a new replacement building was to be constructed. Existing building structures should continue to be used as far as possible. The LCA and LCC revealed that the office and administration building of AS-Bau Hof GmbH, built in 1977/78, is better to be renovated and extended then to be completely renewed. For this concept, the ground floor is realised as massive construction made of reinforced concrete with external thermal insulation of mineral wool. The upper floor is dominated by solid wooden interior walls. The facade consists of a post and beam construction made of oak wood with an aluminium cover shell as well as a triple pane sun protection glazing. The new roof is also constructed in solid wood. The heat supply is provided by an air/ water heat pump. The results of the LCA prodive information about the life cycle-based primary energy demand from non-renewable ressources (PENRT [MJ]) and emissions (GWP – Global Warming Potenzial [kg CO<sub>2</sub>-eq.]) of the described realised building concept, which have be compensated in a next step.



Figure 1: Compensation of the life cycle based PENRT and GWP of the refurbishment variant + Extension with air-water WP, over 50 years of building use

The compensation of the lifecycle-based GWP and PENRT is realized by means of a photovoltaic (PV) system with a panel area of 868m<sup>2</sup>. It is assumed that the generation and feed-in of renewable electricity from the PV plant of AS-Bau Hof GmbH will 'displace' or 'compensate' the PENRT and GWP arising from the electricity production of the German electricity mix in the grid. The result of the compensation calculation can be seen in Figure 1. The leaps in the curve progressions refer to the replacement of the PV modules after every 20 years, according to the 'Bewertungssystem Nachhaltiges Bauen (BNB)'. However, it can be seen that the compensation of PENRT and GWP is

possible over a life cycle of 50 years, but only in combination with the already mentioned size of the PV system, whose surface area is realizable in the context of this project. For projects in more urban contexts, this solution might be not be very practical. With a self-use rate of the electricity of 30%, the LCC revealed that the life cycle-based costs of the PV system are also amortized over the life cycle of 50 years. In future research it is important to focus on realizing sustainable ecosystem specific compensation measures (of e.g. co<sub>2</sub>-emissions) and to therefore reduce, besides others, the danger of biodiversity loss.
## Influence of the Building Construction On the Energy Demand

Michael Vollmer<sup>a</sup>, Hannes Harter<sup>b</sup>, Werner Lang<sup>c</sup>

<sup>a</sup>michael.vollmer@tum.de, <sup>b</sup>hannes.harter@tum.de, <sup>c</sup>sekretariat.enpb.bgu@tum.de

The research project "Eco+Office AS-Bau" aims to develop a life cycle-based greenhouse gas-neutral plus energy building. As a case study an office and administration building of the AS-Bau Hof GmbH in Hof, Germany built in 1977/78 was used. The building will be renovated and extended with further space for offices and seminar rooms. In Cooperation between the Institute of Energy Efficient and Sustainable Design and Building of the Technical University of Munich, AS-Bau Hof GmbH and the Bavarian Construction Industry Association, scientific and innovative methods are developed and applied in practice. The main topics are the ecological Life Cycle Assessment (LCA) and economic Life Cycle Costing (LCC) and the influence of the building construction on the load management of the building. In all three main topics, different design variants regarding the building construction as well as the building services are investigated. The recommendations for action flow directly into the planning process and contribute significantly to the decision-making process. To determine the influence of the building construction on load management and the indoor climate, thermal building simulations were carried out. Dynamic thermal building simulations offer, in contrast to static calculations, the decisive advantage that the influences of the outdoor climate, the user and and control of the plant technology can be estimated in a more precise way. In the first step two critical zones (office rooms) were identified and examined. Critical zones are rooms or areas, which have particularly critical properties: e.g. large proportion of window area high internal loads or high solar loads, due to orientation. The influences of the building construction type in the two offices were determined by parametric simulations. For each zone the effective heat storage capacity was thereby systematically varied from light construction ( $c_{wirk} \le 50 Wh/m^2 K$ ) to heavy construction ( $c_{wirk} \ge 130Wh/m^2K$ ) and simulated over a timespan of one year. The effective heat storage capacity was calculated according to [1]. In order to achieve the widest possible range of possible combinations of different heat storage capacities, the thickness of the thermally relevant layers of the space boundary surfaces (outer wall, ceiling and inner walls) was varied between 0 cm and 25cm in 2.5cm steps. Furthermore, four different variations regarding night ventilation and active cooling (with and without) were investigated. Considering all possible combinations of the different layer thicknesses and the four variations, regarding cooling and night ventilation, a total of 4,000 individual simulations were carried out.



Figure 1: Annual energy demand for cooling dependent of the effective heat storage capacity

Regarding the peak temperatures, it is shown that an increase of the effective heat storage capacity is only useful in combination with a night ventilation. A peak temperature reduction of 1.8K between a light construction (26.0°C) and (24.2°C) construction heavv was achieved in both zones. Regarding the total annual energy demand for heating it is shown that the influence of the effective heat storage capacity is estimated to be low at  $\pm$  5%. The influence of the effective heat storage capacity on the annual cooling energy demand is significant higher with ± 30%. The investigation of

the influence of the building structure on the load management can thus make a valuable contribution to reduce the energy consumption of the building during its use. This in turn leads to less greenhouse gas emissions and therefore contributes to the achievement of the above-mentioned overall project objective. The overall project results show practical and realizable strategies for planning and realization of a life cycle-based greenhouse gas neutral plus energy building.

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# Simulation Based Analysis of Sustainable Building Services

Asgeir Björn Eliasson

abje31@gmail.com

The goal of the German Federal Government is to realize an almost climate-neutral building stock by 2050 and to consume about 80 percent less energy than in 2008. Because buildings account for about one third of the total German energy consumption and  $CO_2$  emissions, buildings and quarters will play a key role in the realization of the energy transition [1]. The design of climate neutral building operations is realizable thanks to modern technical possibilities, but the practical implementation is difficult due to user specification, user influence [2]. Due to their structure and size, cities and neighbourhoods usually appear too complex to adequately capture the structural and energetic challenges. By contrast, the building stock of a university is easier to capture as a quarter, because of its manageable size and user specification. Its heterogeneity in terms of existing buildings, technologies used and user influence makes it possible to transfer the results obtained to other quarters [3].

The main goal of the master's thesis will be to simulate the energy consumption of the campus of the Munich University of Applied Sciences in Karlstraße. The ongoing simulation of the energy consumptions will be carried out in IDA ICE using two models with different level of detail and finally compered. IDA ICE is a simulation program for the study of the thermal indoor climate as well as the energy consumption of the building stock [5]. The first model of the building stock will be simulated in full detail and will be used as a reference for the energy consumption. The second model will be simulated using the reference room method that minimizes the calculation effort. The reference room method defines reference rooms with typical usage profiles and distributions and extrapolates their energetic and thermal behaviour on the entire building stock. With the use of the models the potential of increasing energy efficiency and decreasing energy demand of the building stock can be examined in regards to energetic refurbishments of building physics and building services [4].Additionally, the photovoltaic potential of the whole building stock of the Munich University of Applied Sciences will be analysed with PV\*SOL, which is a photovoltaic planning program [6]. The photovoltaic installations will be designed with regards to the load profile of the specific building location with the goal of maximizing the own consumption and minimizing the amortization period. Deeply connected to the utilization of photovoltaic energy is the implementation of an energy storage system in the facilities of the university. Because of the limited operating hours of the university during summer break, the potential for peak-shaving and atypical grid usage is to be examined from an economical and sustainable perspective. After the simulations and analysis of the building stock, the interpretation of the results will follow. Recommendations for actions will be developed in order to achieve the climate protection targets by 2050. The findings of the master's thesis and the superior research project "NuData Campus" will be incorporated into the masterplan of energetic refurbishment of the building stock of the Munich University of Applied Sciences. The masterplan will include the implementation potential on the thermal indoor climate and energy consumption as well as the utilization potential of photovoltaic energy and energy storage system [3].

Will the Munich University of Applied Sciences be able succeed in reducing energy demand and increasing efficiencies to become a climate neutral university?

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# Measuring Box for Indoor Climate and Thermal Comfort

Saskia Pinter<sup>a</sup>, Daniel Kierdorf<sup>b</sup>, Michael Vollmer<sup>c</sup>, Farzan Banihashemi<sup>d</sup>, Hannes Harter<sup>e</sup>, Werner Lang<sup>f</sup>

<sup>a</sup>saskia.pinter@tum.de, <sup>b</sup>daniel.kierdorf@tum.de, <sup>c</sup>michael.vollmer@tum.de, <sup>d</sup>farzan.banihashemi@tum.de, <sup>e</sup>hannes.harter@tum.de, <sup>f</sup>w.lang@tum.de

With today's technical possibilities a climate-neutral building operation can be certainly planned and realized. A challenging task during the planning stages of a building however is to deal with uncertainties regarding the energy performance gap between predicted energy demand and operational energy consumption. Also user-specific requirements and influences are making implementation and operation difficult. Besides thermal building simulations, based on technical building parameters, user-related data of the building occupants are required to determine the energy demand and furthermore to reduce the building's energy consumption during its use. While energy efficiency is increasing on the one hand, the demand for thermal comfort in the interior is rising on the other. In order to ground both sides equally, indoor climate and potential energy relevant user behavior needs to be investigated and assessed. Regarding to indoor climate and user behavior monitoring, the following main problems were identified:

- Indoor climate has to be measured in close distance to the relevant occupants
- The measurement system has to be mobile in order to react to certain changes in the room(s). The measurement system has to be modular in a sense that sensors can be added during later stages
- It has to be a cost-effective system e.g. sensors and components must to be reusable after the project To meet these needs, a mobile measuring box (see Fig. 1) was developed at the Institute of Energy Efficient and Sustainable Design and Building at the Technical University of Munich. The box will be used in two research projects named "NuData Campus" and "NuOpt Office" to monitor indoor thermal comfort and energy



Figure 1: Measuring Box

relevant user behavior. The box is equipped with necessary sensory devices from Tinkerforge [1] in order to record air temperature, mean radiant temperature, relative humidity, CO<sub>2</sub>-concentration, sound pressure, ambient light, air velocity, indoor air quality. Connecting the measuring box to a singleboard computer (SBC), which is executing a python script. The measured data by the sensory devices is saved within defined intervals on a specific database. Hence, the measured parameters are easily accessible for subsequent data processing. By having all named sensors installed in one device, its big variety of recorded parameters at the same time, as well as its flexibility caused by its compactness and the simple usage, the box differs from other products that are already used for climate measuring in several studies on thermal comfort [2].

In a test phase, the box is first validated in the solar station of the Technical University of Munich to ensure

that it is measuring correctly before it is tested in the field afterwards. The device will be located in an office room where indoor climate parameters are recorded (see Fig. 2), which represent the status quo of the thermal environment. At the same time surveys are carried out investigating the thermal well-being of the occupants. Therefore, information about the impacts of the climatic ambient and user-specific requirements for the indoor climate is provided. Analyzing and evaluating the data enables user-specific adaptation of the indoor climate and the provision of a high level of comfort, optimizing the required amount of energy at the same time.



Figure 2: Field of investigation

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# Waterpower Romance The Cultural Myth of Dying Watermills in German Hydro Narratives around 1900

Agnes Limmer<sup>a</sup>, Christian Zumbrägel<sup>b</sup>,

alimmer@zv.tum.de

Even in the 21st century, myths of a preindustrial form of energy utilization are woven around watermills with waterwheels. However, alongside German watercourses many grinding shops and hammer mills held on to waterwheels and delivered mechanical rather than electric power until the interwar period. This "old technologies" (David Edgerton) did not become redundant but remained in good use despite electrification and scientific development of hydraulic turbines. When analyzing the dominating contemporaneous discourses around hydropower, these historical circumstances are easily overlooked. This is not surprising, considering that scientific, literary, and conservationist narratives around 1900—actively and subtly—propagated and spread the myth of dying watermills (*Mühlensterben*) that has been rehearsed over and over again in reflections on hydropower history in the 20th century.

In this article, we challenge the popular imaginaries of "old" and "outmoded" watermills in a two-step approach. Firstly, we construct a data foundation using statistics and stories from small creeks alongside German hydro landscapes. Secondly, we deconstruct the romantic bias towards the preindustrial symbolism of the waterwheel by analyzing different levels of arguments in professional journals as well as romanticizing and nostalgic literature. Therefore, we combine approaches and empirical material of both historical and literary sciences to provide new perspectives on small-scale hydropower history, asking, if and how different narratives reinforced the image of waterwheels being outdated.

# Highly-Ordered Porous GeO<sub>2</sub> Thin Film Electrode Materials for Li-ion Batteries

Suzhe Liang<sup>a</sup>, Shanshan Yin<sup>b</sup> Peter Müller-Buschbaum<sup>c</sup>

<sup>a</sup>suzhe.laing@ph.tum.de, <sup>b</sup>shanshan.yin@ph.tum.de, <sup>c</sup>muellerb@ph.tum.de

In recent years, germanium oxide (GeO<sub>2</sub>), is regarded as a promising alternative anode material for lithiumion batteries due to its high theoretical capacity (2152 mAh  $g^{-1}$ ) [1]. However, GeO<sub>2</sub> suffer from volume expansion during charge and discharge, leading to a rapid capacity fading. Creating hollow or porous structure is an effective strategy to improve cycling stability because it can provide enough void space to accommodate volume changes of germanium oxide. Creating hollow or porous structure is an effective strategy to improve cycling stability of GeO<sub>2</sub> anodes, because it can provide enough void space to accommodate volume changes of GeO<sub>2</sub>.

Herein, we propose a novel method to synthesize highly regular mesoporous germanium oxide tin film anode materials assisted with block copolymer. Amphiphilic block copolymers (ABC) have been widely utilized as surface modification agents by constructing nanoscale architectures on various substrates through evaporation induced self-assembly processes [2]. Polymer/inorganic nanocomposites can be obtained via a microphase separation process in mixture solution of mixing block copolymer and precursor of metal oxide. In this work, PS-b-PEO, 1,4-dioxane, and germanium ethoxide are selected as the block copolymer template, solvent, and Ge precursor, respectively. Additionally, concentrated HCI solution acts as a poor solvent for the PS block, leading to the formation of micelles in solution because of increased interfacial energy between the PS block and the solvent. Firstly, PS-b-PEO was dissolved into 1,4-dioxane under continuous stirring. Then, germanium ethoxide and HCI solution were added into the solution successively. After sufficient, hybrid GeO<sub>2</sub>/polymer composite thin films were prepared by spinning coating the stock solution on silicon wafer. After removing the block copolymer by calcination, mesoporous GeO<sub>2</sub> thin films were obtained. In order to investigate the effect of copolymer concentration on the final morphology, we fabricated four parallel samples with different concentration of PS-b-PEO in 1,4-dioxane. The surface morphologies of as-prepared mesoporous GeO<sub>2</sub> thin films are presented in the Figure 1. Additionally, inner and large-scale morphology of these samples are characterized by grazing incidence small angle X-ray scattering (GISAXS) technique [3].



Figure 1: SEM images of the GeO<sub>2</sub> thin films with different concentration of PS-b-PEO in 1,4-dioxane, corresponding to a) 0.125 wt%, b) 0.167 wt%, c) 0.250 wt%, and d) 0.500 wt%, respectively. The up-right insets of the images refer to the corresponding FFT patterns.

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# Washing of Ni-Rich CAMs: Mechanistic Understanding

Louis Hartmann<sup>a</sup>, Stefan Oswald, Maximilian Graf, Daniel Pritzl, and Hubert A. Gasteiger

<sup>a</sup>louis.hartmann@tum.de

Ni-rich cathode active materials (CAMs), like NCM851005 ( $Li_{1+x}(Ni_{0.85}Co_{0.10}Mn_{0.05})_{1-x}O_2$ ), are promising candidates for achieving the energy density target needed for battery electric vehicles.[1] However, these materials are susceptible to the formation of surface impurities and, for this reason, an additional washing step is needed to remove the surface groups.[2,3] It was shown that this washing step results in a H<sup>+</sup>/Li<sup>+</sup> exchange in the near-surface region of the CAM and a metal oxohydroxide-like structure is formed.[4] During the consequent heating step these protons are evolved in the form of water and a metastable spinel-like shell is formed. The resulting structure decomposes evolving oxygen at 250 °C and finally a rocksalt layer can be obtained.

In this work, we investigate the mechanism behind the formation of surface groups on Ni-rich CAMs during washing using TGA-MS, on-line mass spectrometry (O-MS) and NEXAFS. In addition, we synthesized and characterized the model materials,  $LiNiO_2$ ,  $HNiO_2$  and  $Li_xH_{1-x}NiO_2$  to deconvolute the different effects playing a role during the drying step after washing.

At first, we washed the pristine material with an excess of water (CAM:H<sub>2</sub>O-ratio: 1:5), to observe its drastic effect. The model material HNiO<sub>2</sub> (Nickel oxohydroxide) was also synthesized from a simple water-based synthesis. Afterwards, TGA-MS analysis is performed in order to deconvolute the release of physisorbed water from the evolution of water and  $O_2$  produced by the thermal decomposition of the surface protonated species on the washed material. The protocol contains a temperature hold phase at 25 °C, then a heat ramp (10 K/min) to 120 °C with a hold at this temperature for 30 minutes, followed by a second temperature ramp to 450 °C and a final hold at this temperature (see upper panel, Figure 1). In Figure 1 (upper panel), the weight loss of the measured samples is shown. When a washed sample is analyzed a release of water is seen at 180 °C. (m/z = 18 from coupled MS shown in the middle panel). At higher temperatures (>250 °C) an oxygen evolution (m/z=32 shown in lower panel) is visible. The weight loss equals to 0.75 wt.%. When the pristine sample is analyzed, only a very small amount of surface contaminants (< 0.1 wt.%) is observed and no gas evolution is visible.

Surprisingly, the model  $HNiO_2$  material does not show the thermal separation of water and oxygen evolution and both gases are evolved simultaneously at  $180^{\circ}C$ . By chemical lithiation of  $HNiO_2$  we were able to move the oxygen evolution to higher temperatures. We will discuss the mechanism behind this and, furthermore, we concomitantly



Figure 2: TGA-MS analysis of LNO pristine (in black) and washed (in blue),  $HNiO_2$  (in red) and  $Li_xH_{1-x}NiO_2$ (in green). The upper panel shows the TGA profile and relative mass change of the different samples. The MS traces of  $H_2O$  (m/z = 18, middle panel) and those of  $O_2$  (m/z=32, lower panel) are plotted.

investigate the surface and bulk using NEXAFS on pristine and washed-and-heated material.

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# Maximization of solar PV self-consumption using combination of Ice-battery and Chiller

Tushar Sharma<sup>a</sup>, Prof.Dr.-Ing.Tobias Plessing<sup>b</sup>, Prof. Dr.-Ing.Robert Honke<sup>c</sup>

<sup>a</sup>tushar.sharma@hof-university.de, <sup>b</sup>tobias.plessing@hof-university.de, <sup>c</sup>robert.honke@hof-university.de

The energy demand for heating and cooling in Europe is around 50 % of the total energy demand. As stated in [1], the energy demand for cooling is around 5 % of the total demand, which although seems less but amounts to around 60 TWh per year. Most of the electricity used to meet this demand comes from non-renewable sources. Thus, by increasing the amount of renewable energy usage in an optimum way will help us in bringing down the global  $CO_2$  levels as well as reduce the dependency on fossil fuels.



Figure 1: System diagram for the yearly simulations in Polysun simulation software

the degree of self-sufficiency (selfconsumption of solar PV energy (kWh) / Total electrical consumption (kWh), is found to be maximum at 45.2 %(marked with arrow) when we select a chiller size of 10 kW and a heat exchanger area of 52 m<sup>2</sup> having a tank volume of around 5 m<sup>3</sup>. This study was focused on a plate heat exchanger based ice storage and the results shown are for a specific industry under certain boundary conditions. The concept, however, can be extended to other industries as well as other types of ice storages.

In the future work, we wish to make a generic automated tool that will apply to any kind of industry with different load profiles and will determine the appropriate size of components based on complex optimization strategies. **References:**  The project aims to develop efficient control strategies to maximize the self-consumption of solar PV energy while using Ice-battery and a chiller to meet cooling demand. Yearly dynamic simulations were performed in Polysun simulation software [2]. As shown in the figure1, Ice-battery is essentially a storage tank, which is used to produce ice using a plate or coil heat exchanger immersed inside the tank. For this project, we chose a typical walk-in cooler in a German bakery having an air volume of 78 m<sup>3</sup> and assumed to be maintained at around 6 °C throughout its operation. Cooling loads have been provided as hourly load values to the building model in the simulation tool with maximum load being 2.4 kW and reduces to 1.2 kW within 4 hours of cooling period. Several parametric studies have been performed in the simulation tool to maximize the utilization of ice-battery as well as the self-consumption of solar PV. As seen in the figure 2,



\*Value in the bracket represents the chiller size in kW at which the maximum value of self-sufficiencv is obtained

Figure 2: Variation in degree of self-sufficiency with heat exchanger area and chiller capacity

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# Investigating the growth of copper as contacts for polymer thin film lithium-ion batteries

Simon J. Schaper<sup>a</sup>, Franziska C. Löhrer, Senlin Xia, Volker Körstgens, Matthias Schwartzkopf, Pallavi Pandit, Alexander Hinz, Oleksandr Polonskyi, Thomas Strunskus, Franz Faupel, Stephan V. Roth, and Peter Müller-Buschbaum<sup>b</sup>

#### <sup>a</sup>simon.schaper@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Understanding the interface between metals, commonly used as current collectors, and ion-conducting polymers used in polymer lithium-ion batteries (LIBs) is crucial to develop highly reproducible, low-cost and reliable devices. To address these issues, sputter deposition is the technique of choice to fabricate scalable, reproducible and controllable nanometer and sub-nanometer metal layers on polymer thin films. The sputter deposition process, being well understood and controlled, offers advantages over chemical methods to tailor metal thin-flim morphologies on the nanoscale and offers a superior adhesion of the deposition atomic force microscopy (AFM) as well as scanning electron microscopy (SEM) to investigate the formation, growth and, self-assembled structuring on polymer thin films and composite anodes used in LIBs.[2]

The growth of gold on silicon and homopolymer substrates was investigated by Schwartzkopf et al. [1],[2]. Continuing these studies having a polymer solid-state LIB in mind, the growth of copper on polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO), a diblock copolymer with a glassy PS block providing mechanical stability and a soft, ion-conducting PEO block, used for polymer electrolytes and composite battery electrodes is investigated. It is found that the sputter deposited copper is a cluster-like growth. Depending on the evolution of the cluster distance D, the growth can be devided into four stages: I nucleation, II diffusion-driven growth, III adsorption-driven growth, IV layer growth (figure 1a). Inspired from a model by Schwartzkopf et al. [3], the growth is described by a model using hemi-spheroidal particles in a local hexagonal arrangement (figure 1b).



Figure 1: a) evolution of polymer's periodic distance *d*, copper cluster distance *D*, and radius *R* with effective copper layer thickness  $\delta_{Cu}$ ; b) sketch of the hemispheroidal model to calculate the cluster radius *R*.

A hierarchical structure guided by the selective agglomeration of copper clusters on the different polymer blocks is revealed by AFM, SEM, and GISAXS measurements. Thus, this work gives valuable insight into understanding the growth mechanism of sputter deposited copper current collectors on polymer composite electrodes for LIBs.

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# Contacting of Cylindrical Lithium-Ion Batteries and Copper Bus Bars Using Green Laser Radiation

Michael K. Kick<sup>a</sup>, Jan Bernd Habedank<sup>b</sup>, Johannes Heilmeier<sup>c</sup>, Michael F. Zäh<sup>d</sup>

To stop the climate change and to reduce  $CO_2$  emissions, lithium-ion cell-based battery storages are indispensable. For this purpose, cylindrical18650 cells are regularly utilized and linked by cell connectors made of nickel-plated steel. Since this setup suffers from high electrical losses and a poor heat removal during operation, copper connectors are demanded more often. Due to its low energy input and high flexibility, laser beam welding reveals a great potential to join the cells and the connector. However, challenges arise, as copper materials show a strong reflectivity for infrared wavelengths.

In this study, experimental investigations for the contacting of 18650 cells and copper connectors using a spike pulse welding strategy and green laser radiation are presented. Furthermore, the influence of the individual parameters on the weld seam quality, electrical resistance and mechanical strength, will be discussed.

# **Machine-Learning Potentials for Battery Materials**

C. Staacke<sup>a</sup>, Johannes Margraf<sup>b</sup>, Christoph Scheurer<sup>c</sup>, Gabor Csanyi<sup>d</sup>, Karsten Reuter<sup>e</sup>

<sup>a</sup>carsten.staacke@tum.de

All-solid-state Li-ion batteries promise gains in safety and durability by combining high Li-ion conductivity and mechanical ductility. In this respect, solid-state electrolytes (SSE) such as the Li7P<sub>3</sub>S<sub>11</sub> glass-ceramic have gained much attention.[1] From a modelling perspective, describing ionic conductivity and the role of crystalline/amorphous interfaces in such SSEs requires an accurate and efficient description of covalent and electrostatic interactions. To this end, we have combined short-ranged machine-learning potentials based on the Gaussian Ap- proximation Potential (GAP) [2] approach with a classical electrostatic model in the long-range. We will present a first-principles validation of both, pure GAP potential and the new electrostatic GAP for the LPS SSE. In particular, the role of Coulomb interactions in SSE simulations will be shown and evaluated.

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## A Lithium Ion Battery Cell Design for Operando Neutron Depth Profiling

Philip Rapp<sup>a</sup>, Fabian Linsenmann<sup>b</sup>, Markus Trunk<sup>c</sup>, Lukas Werner<sup>d</sup>, Roman Gernhäuser<sup>e</sup>, Ralph Gilles<sup>f</sup>, Bastian Märkisch<sup>g</sup>, Zsolt Révay<sup>h</sup>, Hubert A. Gasteiger<sup>i</sup>

<sup>a</sup>p.rapp@tum.de

Neutron depth profiling (NDP) is a non-destructive analytical technique for measuring concentration profiles of several light isotopes through the detection of the decay products upon cold neutron capture.<sup>1</sup> Lithium is especially suitable for this technique because of the high energy of the decay products. Upon neutron capture, the lithium nucleus splits into a *triton* and an *alpha* particle with defined energies. The particles lose kinetic energy as they travel through the host material. This energy loss correlates to the depth in which the nuclear reaction occurred. Because of the high sensitivity for lithium, NDP proved to be a useful tool for the characterization of lithium ion-battery (LIB) materials through various *ex situ* and *operando* studies. However, to the best of our knowledge, none of the *operando* setups for liquid electrolyte-based LIBs reported in the literature, proved that the cell performance is comparable to a standard laboratory cell.



Figure 2. NDP spectra of the graphite electrode obtained during cycling, first charge (blue), first discharge (red), and second charge (yellow).

In this work, we present a novel cell design for liquid electrolytebased LIBs to operando detect the lithium concentration as a function of depth during cycling.<sup>2</sup> This was accomplished through the utilization of a thin Kapton<sup>®</sup> window covered with copper layer serving as current collector which enables the decay products to escape from the cell. The cell was cycled in a helium atmosphere with a pressure higher than the vapor pressure of the electrolyte. To provide adequate compression, we used multiple small holes with a diameter of 500 µm which were evenly distributed on an 8 mm diameter circular area instead of a single large hole. This cell setup shows comparable performance to standard laboratory coin cells when cycled at low C-rates as it is the case during formation. To prove the functionality of the cell, we present operando data of the first three half cycles recorded during formation of a porous graphite electrode using a liquid electrolyte. An electrode thickness of 14 µm was selected to ensure lithium detection across the complete electrode depth

The NDP spectra were recorded with a time resolution of 1 h and visualize the lithium distribution as a function of state-of-charge (SOC). This allows for the distinction between electrochemically active lithium and irreversibly lost lithium, captured in the solid electrolyte interphase (SEI). The depth profile of the graphite electrode after formation at 0 % SOC revealed that a small amount of lithium is electrochemically alloyed into the copper current collector. This was confirmed by additional NDP measurements of the blank current collector without active material as well as *ex situ* X-ray photoelectron spectroscopy (XPS) measurements of the current collector through sputter depth profiling.

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# Heat Transfer: Current Challenges and Future Perspectives of Hydrogen Storage Technologies

Tobias Gschnaidtner<sup>a</sup>, Thomas Ferrand<sup>b</sup>, Victor Voulgaropoulos<sup>c</sup>, Hannah Moran<sup>d</sup>, Christoph Wieland<sup>e</sup>, Christos N. Markides<sup>f</sup>, Hartmut Spliethoff<sup>g</sup>

<sup>a</sup>t.gschnaidtner@tum.de, <sup>b</sup>thomas.ferrand@tum.de, <sup>c</sup>v.voulgaropoulos@imperial.ac.uk, <sup>d</sup>hannah.moran11@imperial.ac.uk, <sup>e</sup>wieland@tum.de <sup>f</sup>c.markides@imperial.ac.uk, <sup>g</sup>spliethoff@tum.de

Energy and environmental aspects are two of today's most crucial global challenges. The supply of energy in the form of fossil fuels is currently governed by dynamic decline, driven by political, economic, and ecological factors. These factors result often in volatile and high energy prices. At the same time, environmental policy welcomes efforts to decrease the dependence on fossil fuels and to reduce greenhouse gases and toxic emissions. To address the energy demand and supply, as well as the environmental and economic aspects of energy provision, a coherent strategy is required: in the near term, higher energy efficiency and an increase in energy supply from renewable sources are desirable; in the longer term hydrogen appears as an appropriate alternative energy vector with which to develop near or zero-carbon energy systems. Hydrogen (H<sub>2</sub>) can be produced from sustainable, renewable sources and can, for example, be used in transportation eliminating environmental problems caused by burning fossil fuels. As an energy carrier, H<sub>2</sub> is also suitable for storing energy by utilizing the surplus electricity of wind and PV farms. Nevertheless, many technical challenges have to be addressed before a H<sub>2</sub>-economy becomes viable.

While previous research has focused on the conversion of  $H_2$  into electricity and *vice versa*, critical issues remain concerning the economics of  $H_2$  distribution and storage. In general,  $H_2$  needs to be stored for onboard vehicular, portable, stationary, bulk or transport applications. Key technical issues related to these applications are the density, volume, discharge rates, heat requirements, and recharging time. While several studies have addressed various aspects relating to the aforementioned challenges, only a few of these have focused on heat transfer and related energy-efficiency issues of storing  $H_2$ . The most common methods of storing  $H_2$  are "compressed" and "liquid"  $H_2$  storage systems. Because of its low energy density by volume at ambient conditions, compressed storage systems  $H_2$  operate at pressures up to 700 bar; at 700 bar and room temperature the density of  $H_2$  is more than 400 times its density at ambient conditions. Liquid storage systems, in contrast, store  $H_2$  in its liquid phase at cryogenic temperatures and ambient pressure; cryogenic  $H_2$  has a density almost twice as high as compressed  $H_2$  at 700 bar. Both methods face high energy intense processes related to thermal management and heat transfer aspects. Although a compromise of both systems – a cryo-compressed hydrogen storage system – tends to be less demanding, thermal management and heat transfer issues remain.

Motivated by the aforementioned overall opportunity, in this work we will provide a short review of the mentioned  $H_2$  storage technologies and discuss the current challenges and future prospects of relevant solutions focusing on the thermal management and heat transfer issues of  $H_2$  storage systems.

# The zero step for degrading perovskite solar cells: What atmosphere should we choose?

Renjun Guo<sup>a</sup>, Lennart K. Reb, Manuel A. Scheel, Wei Chen, Nian Li, Anna Lena Oechsle, Shambhavi Pratap, Matthias Schwartzkopf, Stephan V. Roth, Peter Müller-Buschbaum<sup>b</sup>

### <sup>a</sup>renjun.guo@ph.tum.de, <sup>b</sup>muellerb@tum.de

The power conversion efficiency (PCE) of perovskite solar cells (PSCs) reached the champion value of 25.2 %, making this technique competitive with commercial silicon solar cells. Despite such advantages, the application of PSCs is currently limited by combining high performance and operational stability because PCE of PSCs can degrade due to the presence of temperature, light, humidity, and oxygen. So far, the degradation research on PSCs is carried out without having an established standard protocol. Therefore, it is necessary to establish a standard protocol for the long-term degradation of PSCs. In this respect, we investigate degradation processes of PSCs under both, AM 1.5G and different atmosphere conditions with in-situ grazing incidence wide-angle X-ray scattering (GIWAXS) and grazing incidence small-angle X-ray scattering (GISAXS). With these approaches, we can follow the evolution of characteristic structures and of the inner morphology under the respective operational conditions. After understanding the degradation mechanisms upon different atmospheres (nitrogen and vacuum), we can suggest a reasonable atmosphere which enters the protocol for the standard aging routine to guide future industrial development.

# Printed block copolymer template ZnO photoanodes for photovoltaic applications

Ting Tian<sup>a</sup>, Shanshan Yin, Stephan V. Roth, Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>ting.tian@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

ZnO has received much attention over the past few years because it has a wide range of properties including a range of conductivity from metallic to insulating (including n-type and p-type conductivity), high transparency, piezoelectricity, wide-bandgap semiconductivity, room-temperature ferromagnetism, and chemical-sensing effects [1]. As an n-type semiconductor, ZnO, has several potential advantages over  $TiO_2$ such as a better electron mobility and a low crystallization temperature. To improve the photovoltaic performance of ZnO-based devices, an interconnected mesoporous inorganic nanostructure is favorable, which can provide a high surface-to-volume ratio for exciton separation within their lifetime and a good pathway for charge carrier transport. To fabricate the mesoporous inorganic ZnO semiconductors, various methods can be employed, such as chemical vapor deposition, wet chemical method and hydrothermal synthesis. Among these methods, the diblock copolymer assisted sol-gel synthesis approach has been corroborated by countless reports to be powerful in its morphology tunability. Typically, block polymers can phase separate into different morphologies including cylindrical, spherical, lamellar, and gyroid domains by controlling the characteristic parameters [2]. In this respect, the deposition methods play an important role in producing nanoporous networks as well. Compared to laboratory-scale techniques such as spin coating, industrial-coating process, in particular printing is more applicable for large-scale production [3]. However, the printing process is essentially different due to its complicated kinetics caused by solvent evaporation induced self-assembly.

In the present work, the amphiphilic diblock copolymer assisted sol-gel synthesis method and suitable printing parameters are used to fabricate nanostructured ZnO films. Grazing-incidence small angle X-ray scattering (GISAXS) is used to probe the inner film morphology without intervening the film formation process or impairing the printed films [4].



Figure 1: a) SEM image and b) 2D GISAXS data of printed mesoporous ZnO film after template removal.

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# Highly ordered titania films incorporated with germanium nanocrystals used as photoanodes

Nian Li<sup>a</sup>, Shanshan Yin, Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>nian.li@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Nanostructured titania films have attracted great attention due to their non-toxicity, low cost and morphology controllability, etc. These advantages enable them to be successfully applied in many fields, such as, photocatalysis, lithium-ion batteries and photovoltaics. Especially, anatase titania with interconnected network structures as well as a high surface-to-volume area is desirable as an electron transport layer in solid-state dye-sensitized solar cells (ssDSSCs) and hybrid solar cells. Until now, ssDSSCs based on interpenetrating titania networks can achieve high performance (up to 11.9%). Also, impressive efficiency of 25.2% has been reported in the hybrid perovskite solar cells. However, these advances all closely depend on the evolution of a superior sensitizer (dye molecules, quantum dots, perovskite-sensitized) or a hole-transporting material. Only a few researches exist targeting whether tailoring the titania could further improve the photovoltaic device performance. For example, Song et al. obtained more efficient titania photoanodes via incorporating with a presyntheised crystalline titania nanoparticles.<sup>[1]</sup> Duan et al. designed TiO<sub>2</sub>/GeO<sub>2</sub> nanocrystallite anodes with an attempt to increase the photogenerated electron density in the conduction band of the titania nanocrystallites and interference light intensity.<sup>[2]</sup> In this study, we introduce dodecyl functionalized germanium nanocrystals (GeNCs) with a size of  $\approx$  7-9 nm into the titania films to obtain TiO<sub>2</sub>/GeNC composite films for a better solar cell efficiency.

Different weight percents of GeNCs are added to the titania sol-gel solution. During thermal annealing in argon at 500 °C, the templating block copolymer is combusted as well as the organic ligands on the surface of GeNCs. Finally, mesoporous TiO<sub>2</sub>/GeNC composite films are obtained. Resulting surface and inner morphology changes are investigated by scanning electron microscopy (SEM) and grazing incidence small-angle X-ray scattering (GISAXS), respectively. The crystalline properties and elemental composition of the TiO<sub>2</sub>/GeNC composite films are observed via X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), respectively. The optical properties are investigated by ultraviolet–visible spectroscopy (UV-Vis). Through the incorporation of GeNCs with varied weight percent, the optimized morphology and properties of TiO<sub>2</sub>/GeNC composite films for solar cell application are studied, providing a promising photoanode candidate.



Figure 1. SEM images of the mesoporous TiO<sub>2</sub>/GeNCs films after thermal annealing in argon at 500 °C: (a) 0 wt%, (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.5 wt% and (e) 5.0 wt%.

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# The Effect of crystallization kinetics and properties of perovskite with SDBS doping

Yuqin Zou<sup>a</sup>, Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>yuqin.zou@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de



Perovskite solar cells have attracted researchers much attention in recent years and have achieved remarkable development due to their excellent optical properties, and the power conversion efficiency has reached 25.2%. However, the efficiency, hysteresis and stability of PSCs are still the main obstacles to their commercial application, and largely attributed to the presence of defect states. Tailoring functional ligands to passivate the defects in perovskite films and interfacial traps is an effective way to improve the performance of PSCs. Herein, a small amount of surfactants (SDBS) was introduced to modify the perovskite interface, then high efficiency and stability PSCs can be obtained by crystallization control and defect passivation. The crystal structure, phase and orientation are studied by grazing incidence wide angle X-ray scattering (GIWAXS).

Figure 1: Crystal structure of cubic crystal perovskite

## Impact of Cesium on Perovskite Crystallization probed with GIWAXS

Lennart K. Reb<sup>a</sup>, Manuel A. Scheel<sup>b</sup>, Renjun Guo<sup>c</sup>, Peter Müller-Buschbaum<sup>d</sup>

alennart.reb@ph.tum.de, bmanuel.scheel@ph.tum.de, crenjun.guo@ph.tum.de, dmuellerb@ph.tum.de

Today, humanity is facing climate warming mainly because of greenhouse gas emissions. Considering the continuously growing global power demand, a quick transition towards clean and renewable energy use is essential. Sunlight harvesting is one of the most promising energy sources and silicon-based solar cells (SCs) produce electric power efficiently. However, their energy-intensive production leads to an energy-payback time of several years. In comparison, novel material based thin-film perovskite SCs are easily produced at low temperatures via up-scalable and low-cost industrial deposition techniques such as printing or spray casting. In addition, they recently surpassed a certified power conversion efficiency of 25 per cent, a value similar to silicon SCs [1]. This enables extremely short energy-payback times of less than one year, which could substantially decrease the production costs for renewably generated electric power [2].



Figure 1: GIWAXS detector pattern for perovskite with increasing cesium content.

The highly variable chemical composition of the perovskite precursor solution can be used to tune the hybrid crystal structure. For example, incorporating the alkali metal cation cesium (Cs) into the perovskite crystal lattice is advantageous for the perovskite SCs: It influences the crystallization of the perovskite layer, which can change the crystallite orientation in thin-films.

To quantify the impact of Cs-incorporation, we apply statistically relevant grazing-incidence wide-angle X-ray scattering (GIWAXS) for perovskite thin-films of different Cs contents (see Fig. 1). A more-detailed analysis of the intensity reflexes comprises an investigation of the crystallite size and their orientation in dependence of Cs content and reveals a change of preferable crystallite orientation for higher Cs contents. We discuss the possible impact of different crystallite orientation for the optoelectronic properties that are crucial for photovoltaic applications. Improving our understanding of the deeper connection between the bulk film morphology and the optoelectronic semiconductor properties will help to optimize the perovskite layer, essential for highly efficient and long-term durable perovskite SCs.

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# Thin-film printing of next generation perovskite solar cell materials

Manuel A. Scheel<sup>a</sup> Lennart K. Reb<sup>b</sup>, Renjun Guo<sup>c</sup>, Peter Müller-Buschbaum<sup>d</sup>

## <sup>a</sup>manuel.scheel@ph.tum.de, <sup>d</sup>muellerb@ph.tum.de

Thin-film organic-inorganic metal halide perovskite based solar cells (PSCs) are currently intensely researched for their potential as cheap, ultrathin and flexible next generation solar cells. Reaching minimodule efficiencies of around 17% in 2018 and 15% on ultrathin flexible substrates commercialization is promising. However, further improvement on upscaling is needed in order to push PSCs to the market. Especially the development of industrial compatible deposition methods without losing efficiency requires further research and development.<sup>[1]</sup> In principle, industrial requirements can be met by roll-to-roll slot-die coating.<sup>[2]</sup> Highly crystalline and uniform films with low defect concentrations are paramount in reaching high power conversion efficiencies in PSCs.<sup>[3]</sup>

GISAXS and GISANS (grazing incidence small angle x-ray and neutron scattering) measurements are well suited to probe the influence of temperature, ambient moisture, printing parameters and precursor composition on crystallization kinetics and crystal film quality by probing stochastically relevant large sample areas.<sup>[4]</sup> In order to better understand morphology evolution and crystallization kinetics during printing deposition in-situ GISAXS and in-situ GIWAXS measurements were done on methyl ammonium lead iodide (MAPI) thin films also covering the wet film stage during the printing process. Printing was carried out at ambient conditions with a self-built slot-die coater equipped with a meniscus guiding blade and temperature-controlled sample stage.

## Resources

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## Printed Quantum Dot Solids for Optoelectronic Applications

Wei Chen<sup>a</sup>, Haodong Tang<sup>b</sup>, K. Wang<sup>c</sup>, Peter Müller-Buschbaum<sup>d</sup>

<sup>a</sup>wei.chen@ph.tum.de, <sup>b</sup>tangh@mail.sustech.edu.cn, <sup>c</sup>wangk@sustech.edu.cn, <sup>d</sup>muellerb@ph.tum.de



Colloidal quantum dots are a promising material for solutionprocessed thin-film optoelectronic applications. Specifically, the wavelength of photon-electron response for PbS QDs can cover and beyond near-infrared (NIR) due to the intrinsic small and tunable band-gap, which enables PbS QDs are attractive in photodetector (PDs) and photovoltaics (PVs). The inter-dot distance of neighboring QDs determines the energy transport and charge extraction properties of the final QD solid, which is mostly acting as the functional layer in related devices. Due to the presence of ligands and the intrinsic shape of the QDs, QD partials demonstrate different stacking behaviors during their self-organization processes (deposition processes or ligand exchange process), resulting in not only different final inter-dot distances, but also different structure induced disorder energy states.

Figure 1: Sketch of printing PbS QD solid via slot die printer.

In this work, the printing deposition with different parameters is used for achieving QD solid films towards high-efficient optoelectronic devices in the NIR region. Besides conventional morphology characterizations, the inner structures, including the inter-dot distance between neighboring QDs, of the solids are investigated by grazing-incidence small-angle X-ray scattering (GISAXS). In association, the time-resolved photoluminescence (TR-PL) with spectral mapping we accordingly evaluate the inner energy state distributions and corresponding charge carrier dynamics in the solids, which well explains the improved device performances.



Figure 2: Schematic of the post ligand exchange treatment.

## P2H in widely Temperature gliding Heat Grids: With proper System Integration towards Profitability

Stefan Adldinger<sup>a</sup>, Dr. Marlene Gruber<sup>b</sup>, Lothar Behringer<sup>c</sup>

<sup>a</sup>stefan.adldinger@stadtwerke-neuburg.de, <sup>b</sup>marlene@emg-projekte.de, <sup>c</sup>lothar.behringer@stadtwerke-neuburg.de

Findings achieved in the preliminary study [1] showed that by operating heat grids in a widely temperature gliding way significant monetary potential savings can be reached. On the one hand capital expenditure declines due to smaller pipe dimensions, on the other hand operating costs decline due to less network losses. Though, sustaining an energy efficient and economic operation of heat grids with wide temperature ranges, system integration of power-to-heat (P2H) plants are essential due to building related requirements. Expanding on these results the present study assesses value added potentials of decentralized P2H plants on demand side in widely temperature gliding heat grids and derives where P2H plants should be installed within such heat supply systems – considering the course of time and growing renovation rates.

Hypothesis of this study is, that due to an aimed use of P2H plants - in particular heating pumps - on demand side, flow temperatures can be reduced on the one hand. On the other hand power transfer can be increased, so that savings potentials of widely temperature gliding heat grids can be fostered. The benchmark case builds a conventional heat grid (operation mode: 363.15/333.15 K) for a typically structured small city with 2,000 connecting points and a needed total connected load of 50 MW (radial network). By a statistical modeling, heating characteristics will be assigned to the building stock in accordance to their specific building classification, year of construction and insulation standards of the relevant Thermal Insulation Act (Wärmeschutzverordnung). As a result, flow temperature of the secondary side can be determined for each building depending on the outdoor temperature. Subsequently the heat amount that is required from down streamed decentralized P2H plants will be calculated. This will be done by a mathematical optimization that approximates the flow temperature of the heat grid gradually towards the widely temperature gliding operation mode. Thereby it can be determined, at what point savings potentials due to the lowered flow temperature of the heat grid are higher than the costs of the decentralized auxiliary heating plants. In particular in the transition period the heat amount can be covered both directly by the heat grid and by the decentralized P2H plants provided by the buildings. Thus, further monetary effects next to the savings potentials can be identified because of the flexibility that results from the interconnection between the power and heat sectors.

Derived of these findings the maximum cost can be showed that can be invested in a heat supply system with decentralized P2H plants considering the reduced capital expenditure for the heat grid, the lowered operating and production costs and the revenue potential due to the provided flexibility on electricity markets. In times the heating sector is increasingly coming to the fore relating to the German Energiewende especially energy supply companies strive for realizing an economic, secure and climate-friendly heating supply system. Therefore, this study discusses system solutions for heat grids that provide approaches for today's conflicting goals. An important approach is the operation of widely temperature gliding heat systems accompanied by decentralized P2H plants on demand side - in particular heating pumps. Using this plant configuration monetary savings both in heat grid investments and in operating costs can be realized. Thus, costs of heat distribution can be reduced significantly. Instead of grid temperatures remaining the same all year seasonal and demand side adjusted temperature levels should foster the integration of efficient heat production technologies as well as renewable heat and waste heat sources. In this way potentials of otherwise not or hardly useable low temperature sources can be leveraged. The included variability of production possibilities realizes a real interconnection between the sectors power and heat, because heat supply can be ensured optionally by using electrical energy (e.g. decentralized PV-systems) or by using thermal hydraulic energy depending on the market conditions. Due to the flexibility of the heat supply the use of a widely temperature gliding heat grid combined with decentralized P2H plants leads to expecting a long-term economic operation of a city's heat supply regardless of the future developments.

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# **MetricX – A Time Series Processing Application**

Marc Hager<sup>a</sup>, Dominikus Bücker<sup>b</sup>

<sup>a</sup>marc.hager@th-rosenheim.de, <sup>b</sup>dominikus.buecker@th-rosenheim.de

Technical University of Applied Sciences Rosenheim and AGFW | Der Energieeffizienzverband für Wärme, Kälte und KWK e.V. are cooperating on a research project "Nemo – Wärmenetze im energetischen Monitoring" to develop a procedure for monitor performance of district heating systems (DHS). Eight different DHS operators with a total of 15 district heating systems are participating in the project. In the course of the project, the web application "MetricX" was developed to enable administration of large numbers of measuring points and processing of time series data. The application is used to centralise, validate and analyse 12,000+ measuring points from the 15 DHS in near realtime. Currently, a total of 16 million metering values are processed daily. Multiple projects can be created on a single server, making MetricX much easier to manage and maintain than local applications. User access to meta and measurement data can be administered to ensure that classified data is only visible and retrievable with matching access authorization. The application offers a stand-alone solution for processing and analysis of time series data. Common tasks such as validation, aggregation, calculation, transformation and visualization are performed via a web interface. MetricX enables interactive user collaboration. The "MetricX Notebook Tool" combines data visualization with a text editor and enables individually created "notebooks" to be saved and shared between users. In order to cover a large variety of use cases, the MetricX backend features parametric RESTful web interfaces to enable data access from external applications.

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## Integration of flexibility in power grid planning

Thomas Sippenauer

thomas.sippenauer@oth-regensburg.de

In the course of the turnaround in energy policy, the German distribution grid will face major challenges due to the installation of renewable energy sources (RES) and the potential development of electric mobility. On



the basis of grid simulations, an analysis can be carried out regarding voltage and current limit violations ( $\Delta U_{Node}$ ,  $\Delta I_{Line}$ ) as well as their potential occurrence times *t* and occurrence durations  $\Delta t$ , see Figure 1. In parallel, sensitivity analyses in the grid calculation software PowerFactory are used to investigate how effectively available flexibility can be used. In principle, it can be noticed that the voltage sensitivities increase if the used flexibility is closer to the critical node which is usually at the end of a line.

Figure 1: Grid analysis regarding voltage limit violations

In addition to the amount of the power deviation, the flexibility requirement is also characterized by the times

and durations of use and by the frequency of the necessary flexibility applications. In this way, it is possible to analyze, for example, how much flexibility energy is required to completely eliminate the voltage limit violation. Another possibility is to remedy only a part of the problem by means of a flexibility application and to use a combination with feed-in management instead. This procedure is particularly useful if the flexibility potential of the plants is not sufficiently large or cannot be used economically to the full extent.

From the results it is possible to derive to what extent the flexible use of consumption systems can be integrated in grid planning methods. The reliability of the flexibility that can be provided is therefore particularly relevant. Depending on the flexibility provider, a very high reliability level of readiness for use may not be possible or may only be guaranteed at very high prices. The suitability of the flexibility provider is therefore

assessed from both a technical and an economical point of view. Since complete reliability cannot be guaranteed anyway (technical faults in a plant, weather influences, etc.), fallback strategies, e.g. peak capping of RES, are also included in the analysis. Figure 2 shows an example how the voltage can be kept within the permissible range (green) or when additional measures have to be taken (red).



A further goal is to minimize the risks of manipulation (commonly known as INC-DEC-Gaming). It means that plant operators cause or aggravate power grid congestions through their operational behaviour in order to be compensated or ultimately even be rewarded with economical advantages for the grid critical procedure. A potential solution is to negotiate the power performance between the grid operators and the flexibility providers – deviations will not be remunerated or in extreme cases even be sanctioned. Also, incentives must be created for providing flexibility to solve or control grid congestions. This might be done by reducing grid fees – knowing well that this would require extensive adaptations of the existing grid fee system.

## Open-source Flexibility Estimation Python Model for Prosumer Interaction with LFMs

Babu Kumaran Nalini<sup>a</sup>, Zhengjie You<sup>b</sup>, Michel Zadé<sup>c</sup>, Peter Tzscheutschler<sup>d</sup>, Ulrich Wagner<sup>e</sup>

<sup>c</sup>babu.kumaran-nalini@tum.de, <sup>b</sup>zhengjie.you@tum.de, <sup>c</sup>michel.zade@tum.de, <sup>d</sup>ptzscheu@tum.de, <sup>e</sup>uwagner@tum.de

The share of renewable energy sources have been increasing consistently in the recent years. Alternative methods are ought to be sort to provide power system ancillary services to ensure stable and secure operation of the electricity grids. Recent researches have inclined their interests towards the aggregation of the small-scale system flexibility potentials to satisfy the grid variations. Studies have shown the requirement of local energy markets that allow prosumers participation by submitting their device flexibility bids. In this context, the concept of "flexibility" comprises the measures that influence the generation and/or consumption of electricity in reaction to an external signal (price signal) and "Prosumer" refers to the electricity consumers who are able to influence their generation or demand pattern actively <sup>[1, 2]</sup>.

In the following approach, a Python based open-source flexibility estimation model is developed. The core of the model is an energy management system (EMS) which controls and optimizes the operation plan of the prosumer's energetic systems. Based on the input data from different energy systems, the EMS generates cost-optimal operation schedules using Mixed Integer Linear Programming (MILP). Any deviation from the optimal operation is considered as the device flexibility and it is computed using an estimator. The flexibility estimator has inbuilt python-based models for PV, battery, CHP, HP and EV and takes into the device parameter, user comfortability and device availability for its calculations. The output of the model are the flexibility bids that can be traded in the local flexibility markets (LFMs).



The figure (top left) represents model workflow and the table (left bottom) shows an excerpt from the flexibility bid table resulted from the open-source model. A flexibility bid includes the scheduled operation and available flexibility in terms of power, energy and price. Alternatively, the flexibility table for a battery system can be represented as a figure (in right) where the black line defines the scheduled cumulative energy exchange of the battery and the red and blue forks define all possible deviations the battery system can make during a flexibility call. The model also offers other features to analyse individual and aggregated flexibility.

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## Developing a framework to model energy and emissions impacts of innovative mobility concepts

M. Qurashi<sup>a</sup>, H. Jiang<sup>b</sup>, C. Antoniou<sup>c</sup>

<sup>a</sup>moeid.qurashi@tum.de, <sup>b</sup>haijiang@tsinghua.edu.cn, <sup>c</sup>c.antoniou@tum.de

Novel shared mobility concepts promise to provide more sustainable, energy efficient and environmentally friendly transport alternatives, such as private resource sharing (like bike, car sharing, and ride hailing), or on demand ride sharing (like taxi ride sharing and dynamic vanpooling). Such on-demand ride sharing services, as a flexible, demand adaptive transport alternative, require a dynamic routing scheduler to reroute vehicles for serving dynamic travel requests. An on-demand ridesharing service, with appropriate routing optimization and penetration rates, can promise economical travel with high level of energy and emission saving, due to lesser total vehicle kilometers travelled.

Due to the dynamic nature of these services, we need to appropriately model them under different scenarios of varying characteristics to better understand their benefits and impacts. Hence, we develop such a modeling

platform to model autonomous dynamic ridesharing services [1], using the traffic simulator SUMO [2] by integrating a dynamic routing scheduler [3,4] required for their dynamic operation. The platform models autonomous vehicle classes, discrete passenger trips with passenger usage preferences model for trip requests and their attributes, and the dynamic vehicle rerouting setup based on the routing algorithm's logical framework. An experimental setup with scenario variables i.e. network type and travel demand, ridesharing service attributes, and dynamic requests, are used to create different simulation scenarios to be executed within the platform. A set of simulation outputs, i.e. passenger waiting, travel times, network emissions, total vehicle kilometers travelled etc., are used to quantify the energy and emission impacts of such ride sharing services with different demand and service penetration rates.

In the first phase of evaluation, we attach the platform with





the network of Munich to model such services with different simulation scenarios either on different subnetwork areas as a feeder service (for having network type/topology as scenario variable) or on a larger scale with lesser meeting/services points (as a hybrid transit/ridesharing service). Based on the set of different scenarios we will further compare the outputs between with and without ridesharing service simulations to evaluate and quantify the energy and emission-based impacts of such services.

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# In-situ Identification of Active Sites Using Electrochemical Scanning Tunneling Microscopy

R. W. Haid<sup>a</sup>, R. M. Kluge<sup>b</sup>, A. S. Bandarenka<sup>c</sup>

<sup>a</sup>richard.haid@tum.de, <sup>b</sup>regina.kluge@ph.tum.de, <sup>c</sup>bandarenka@ph.tum.de

Many electrochemical energy provision devices, most prominently fuel cells, rely on the interplay of solid/liquid interfaces. In order to comprehend the processes at such heterogeneous interfaces on a nanoscopic level, special in-situ investigation techniques are necessary. Recently, Electrochemical Scanning Tunneling Microscopy (EC-STM) has been utilized as a means to observe the behavior of electrode surfaces under reaction conditions<sup>1</sup>. This technique combines the possibility to control the occurrence of reactions on the sample surface with the nanoscale imaging of an STM. In consequence, experimental distinction between non-active and active sites of a catalytic system can be achieved by comparison of the noise level in the recorded signal. If the scanning tip is positioned over a non-active site, the tunneling current will be stable. Over an active site, on the other hand, reactions occurring within the tunneling gap will distort the EC-STM signal. The technique has been successfully employed to differentiate between the activity of steps and terraces on Pt (111) towards the oxygen reduction and hydrogen evolution reaction (ORR, HER)<sup>1</sup>. Further investigated materials include dichalcogenides<sup>2</sup>, graphene, Pt<sub>3</sub>Ni (111), as well as IrO<sub>2</sub>.

Here, we demonstrate one of the most powerful aspects of EC-STM, its capability to obtain information on an atomic level. For the HER on the carbon-based material highly ordered pyrolytic graphite (HOPG), it was possible to identify individual active sites on the 'honeycomb' structure surface, located primarily near steps and defects (Figure 1). Furthermore, we show that the technique can even be used to obtain quantitative information of the local activity. This was done for Pt (111) under ORR conditions, by relating the recorded noise level to its turn-over frequency. Currently, the functionality of the technique for methanol oxidation is being investigated.



Figure 1: Atomic resolution of active sites on HOPG under HER conditions. Bright spots appear in the measurements, indicating active centers. They can be observed predominantly at step edges and defects, while the basal plane (terrace) remains inactive. Images were processed by Fourier transformations (FFT).

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## Determination of the Tortuosity and the Porosity of **Microporous Layers for PEM Fuel Cells**

Anne Berger<sup>a,</sup>, Robert Morasch<sup>b</sup>, Hubert A. Gasteiger<sup>c</sup>

### anne.berger@tum.de

Proton exchange membrane (PEM) fuel cells are expected to play a major role in the electrification of the transportation sector. The fast refueling process along with large driving ranges <sup>[1]</sup> makes them not only suitable for passenger cars, but also for heavy-duty transport<sup>[2]</sup>. To reach their full potential, several obstacles still need to be overcome. One major challenge during the operation of PEM fuel cells is the water



**Figure 1: Scanning electron** microscope images of the microporous layer (MPL) structure: a) carbon black; b) carbon fiber.

management at the air-side of the cell (i.e., at the cathode). If water accumulates, the pathways for oxygen to reach the catalyst layer are blocked. Consequently, an increased oxygen transport resistance that leads to a large overpotential is observed, especially at high current densities <sup>[3]</sup>. To mitigate this effect, a microporous layer (MPL) is placed in between the electrode and the macroporous gas diffusion layer (GDL). The MPL usually consists of a thin carbon black or graphite structure with a hydrophobic binder (typically PTFE), supported on the GDL material <sup>[4]</sup>. The MPL does not only improve the water management, but also reduces the electrical contact resistance to the catalyst layer. However, a better understanding of the effect of the microporous layer properties on the oxygen transport resistance is necessary.

Therefore, this study aims at characterizing the tortuosity ( $\tau$ ) and the porosity ( $\varepsilon$ ) of MPLs based on different carbon materials. Here, carbon fibers are compared to carbon black, as their different structures were shown to lead to a difference in cell performance [3-4]. The scanning electron microscope images in Fig. 1 reveal the morphological differences between a carbon black and a carbon fiber MPL: while a carbon black based MPL exhibits a dense carbon structure, the use of carbon fibers in the MPL creates a loose network with larger pores.

In this study, the  $\frac{\tau}{\varepsilon}$  value is determined *in-situ* via limiting current measurements in an operating PEM fuel cell and ex-situ via impedance spectroscopy. To disentangle the tortuosity from the porosity, the porosity is measured separately using mercury intrusion porosimetry.

The detailed analysis of both parameters can provide a better description of the ideal MPL structure and can therefore lead to an improved MPL design.

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# Nanostructured PtxM/C (M = Cu, Co, Ni, Ir, Y) Alloy Electrocatalysts Synthesized via a Novel Top-Down Route Towards the Enhancement of the ORR Activity

Theophilus Kobina Sarpey

### theok.sarpey@tum.de

Addressing the sluggish kinetics of the oxygen reduction reaction which occurs on the cathodic end of the fuel cell is of peculiar interest for future sustainable energy conversion and storage in the automotive industry to be specific. Continuous search for an optimum catalyst to address this challenge has led to the discovery of Pt-based nanostructured alloys as prominent candidates. As such, alloying nanostructured Pt with 3d transition metals and/or rare-earth elements is an auspicious approach to tune the electrocatalytic activity towards the ORR. Usually, bulk Pt-alloys are used in the synthesis of nanostructured Pt-alloys. With the exception of PtxIr nanoparticles (NPs) that were synthesized from their bulk metal alloys, all the other NPs investigated in this study were synthesized using a different strategy or method. For the first time herein, this study presents the direct dissolution and/or deposition of 3d transition metal/rare-earth element precursor salts into the 1.0 M KOH electrolyte to produce NPs from bulk Pt. By so doing, nanostructured PtxM/C (M = Cu, Co, Ni, Y) alloys were synthesized using a novel top-down nanostructuring technique which is the electrochemical erosion of bulk metal and/or metal alloys. The nanoparticles were characterized using transmission electron microscopy, energy-dispersive x-ray spectroscopy, x-ray diffraction and spectroscopy. The electrocatalytic oxygen reduction activity for the various nanocatalysts were also measured.

All the synthesized samples apart from the leached PtxY/C-15V exhibited specific activities (SAs) higher than the reference Pt/C TKK catalyst. In terms of mass activities (MAs), aside PtxNi/C-10V and PtxY/C-15V that displayed lower MA compared to the reference Pt/C TKK catalyst, all the other investigated nanostructured electrocatalysts outperformed the reference Pt/C TKK catalyst. In particular, PtxCu/C-15V showed a 4 fold enhancement (0.64 A/mgPt at 0.9V vs RHE) in terms of mass activity and ~ 5.5 fold higher specific activity (2.27 mA/cm2 at 0.9V vs RHE) when compared to the reference Pt/C TKK catalyst.

## Searching For Active Catalyst Sites On Pt-Alloys For The Oxygen Reduction Reaction

E. Psaltis<sup>a</sup>, R.M. Kluge<sup>b</sup>, R.W. Haid<sup>c</sup>, A.S. Bandarenka<sup>d</sup>

<sup>a</sup>eleftheriospsaltis@gmail.com, <sup>b</sup>regina.kluge@ph.tum.de, <sup>c</sup>richard.haid@tum.de, <sup>d</sup>bandarenka@ph.tum.de

Heterogeneous catalysis has been a key area of interest as it allows us to improve upon existing production processes with regards to scale, rate and selectivity. Its influence is more pronounced in the chemical industry but also extends into the fields of energy production and storage. The best example would be fuel cells, since their commercial viability and performance competitiveness hinge on catalytic processes. Both performance and cost can be immensely benefited by improving upon kinetics and reducing catalyst material loading, as it is usually scarce. As we gain more insight and discover further principles governing this discipline, the need for a direct correlation between surface structure and catalytic properties in search of optimal catalyst performance becomes evident. Not all of the available surface actively contributes to catalyzing reactions, but only certain sites that offer optimal binding conditions. The identification of these so-called active sites dictates the use of computational approaches, needed due to the sheer abundance of parameters involved. However, experimental screening of the resulting candidates is still necessary.

To serve as a means of identifying active sites we employ scanning tunneling microscopy (STM), a technique capable of even atomic-scale resolution. This mapping practice is based on the tunneling effect and the extreme sensitivity of the resulting current on both the distance and the tunneling barrier between sample and probe. By demanding a constant current the first dependence leads to a profile of surface atomic orbitals. The second comes into play after contemplating the effects of on-going reactions on barrier height and width. These manifest themselves as increased tunneling current. In the context of our work, known as "noise" electrochemical STM (n-EC-STM), this heightened noise level is utilized to determine the position of active sites.

The here presented work concerns the sluggish reaction taking place at the cathode side of fuel cells, namely the oxygen reduction reaction (ORR). In the case of acidic media, Pt-based alloys are viewed as the state-of-the-art materials due to their selectivity towards the desired reaction mechanism and their satisfactory binding of intermediates, thus enhancing the reaction rate and limiting corrosion issues. Alloying is required due to sustainability and cost considerations, as well as the fact that pure Pt binds the reaction intermediates a bit too strongly, possibly leading to poisoning of the catalyst material. A measurement of a Pt<sub>5</sub>Gd alloy is presented in the figure below, clearly indicating that step-like defects show minimal to no noise in stark contrast to flat terraces.



Figure 1. (A, B) Schematic representation of identifying active sites using n-ECSTM. The level of the tunneling current noise is increased when the STM-tip is located over active surface sites. (C,D) n-EC-STM measurement on  $Pt_5Gd$  for the ORR showing several step edges .When the reaction is turned on, a considerable increase in noise can be observed over the terraces of the crystal and not along the steps. This can also be depicted in the corresponding line scans (E).

## Experimental and numerical study of conversion of tar contaminants on SOFC and their impacts on the cell performance

Yixing Li

yixing.li@fau.de

The operation of a SOFC with biomass-derived syngas would provide convincing solutions for combined heat and power production from renewable sources. Depending on the gasification processes, the syngas from the thermochemical conversion of biomass contains various heavier hydrocarbons (summarized as tars). Several studies have demonstrated that operating SOFC fuel cells with unsaturated or aromatic hydrocarbons as fuel gas is in principle possible. The key problem for operating SOFC fuel cells with high hydrocarbon concentrations is the formation of solid carbon, which must be counteracted by excess steam content and increased temperature.

It is shown [1-3] that the higher hydrocarbons are generally reformed at the anode and lead to a voltage increase at the SOFC. Not only the reforming, but also direct electrochemical reaction of hydrocarbons could take place at the SOFC anode [4, 5]. However, the investigation of the effects of tars on the electrochemical processes at the anode is still insufficient. It is uncertain whether and to what extent tars are converted at the anode. The way tars behave depends on the amount and nature of the hydrocarbons as well as on the operating conditions such as temperature, gas composition, moisture, and anodic material [6]. Since the reforming of tars supplies more hydrogen as fuel gas, the temperature-dependent reforming rate of tars can lead to inadmissibly high fuel utilization at lower temperature. The reducing atmosphere at the anode cannot be ensured if the critical fuel cell utilization is exceeded. The nickel catalyst at the anode could be oxidized, which will lead to irreversible damage of SOFCs.

This work represents an experimental and a numerical study of a planar commercially available electrolyte supported solid oxide fuel cell operated with tar-contaminated fuel gas. Single fuel cell was fed with tar model compounds (e.g. benzene, naphthalene) with different concentrations at different temperatures and atmospheric pressure. Polarization curve measurements and gas analysis were used to evaluate the impact of tar contaminants on the cell performance. In addition, a CFD model was developed that takes into account reforming kinetics of different tar species. The CFD model was validated with the experimentally determined data and will support the design of a prospective SOFC stack design.

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## Nitrogen-Functionalized Carbon-Supports for Fuel Cell Catalysts – Effect on Mass Transport Resistances

T. Lazaridis<sup>a</sup>, H. A. Gasteiger<sup>b</sup>

<sup>a</sup>timon.lazaridis@tum.de, <sup>b</sup>hubert.gasteiger@tum.de

The still significant amount of platinum required in current proton exchange membrane (PEM) fuel cell systems presents a major obstacle to achieving cost parity with internal combustion engines. Hence, recent research efforts aim to employ cathodes based on carbon-supported Pt catalyst (Pt/C) with very low Pt loadings (< 0.1 mg<sub>Pt</sub> cm<sup>-2</sup>). When operating PEM fuel cells with such low-loaded cathodes at high current density (HCD, > 2.0 A cm<sup>-2</sup>), the required high reactant fluxes of O<sub>2</sub> and protons to the Pt surface cause high local transport resistances, resulting in large voltage losses.<sup>[1]</sup>

Our group observed improved HCD performance with Pt/C cathode catalysts employing nitrogenfunctionalized carbon-supports.<sup>[2]</sup> For these catalysts, Pt was deposited onto a carbon-support that had been modified *via* oxidation in nitric acid followed by high temperature treatment in ammonia. While the performance improvement was ascribed to a lower O<sub>2</sub> transport resistance, the mechanism by which Nfunctionalization leads to this outcome has not been fully understood. The present study distinguishes the proposed explanations such as (i) a thinner, more homogeneously distributed ionomer film within the Pt/C layer due to coulombic interaction between N<sup>+</sup> moieties and SO<sub>3</sub><sup>-</sup> groups in the ionomer, (ii) Pt nanoparticle deposition in more accessible locations,<sup>[3]</sup> and (iii) increasing the pores in the carbon-support by ammonia etching, which allows for better reactant access of the Pt particles.



(i) Homogeneous ionomer distribution

(ii) Accessible Pt location

(iii) Open pore morphology

Figure 1 Proposed origins of improved  $O_2$  transport in nitrogen-functionalized carbon (gray: carbon, black: Pt nanoparticles, red: ionomer).

Commercially used carbon-supports are nitrogen-functionalized using a wide range of experimental conditions. Treatment effects on pore morphology, amount, and nature of nitrogen-containing functional groups are characterized by N<sub>2</sub> physisorption, elemental analysis, and X-ray photoelectron spectroscopy, respectively. After location-specific Pt nanoparticle deposition onto these modified carbons, catalysts are fabricated into low-loaded membrane electrode assemblies (MEA, < 0.1 mg<sub>Pt,Cathode</sub> cm<sup>-2</sup>). Subsequent single-cell PEM fuel cell testing (5 cm<sup>2</sup> active area) allows for the comparative analysis of catalyst performance and mass transport-related voltage losses for differently functionalized carbons. The understanding of improved mass transport properties within the catalyst layer provides guidelines for novel carbon-support modifications.

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# Oxygen Vacancy Formation and Diffusion in High Temperature Electrolyzers

Hanna Tuerk<sup>a</sup>, Christoph Scheurer<sup>b</sup>, and Karsten Reuter<sup>c</sup>

<sup>a</sup>hanna.tuerk@tum.de

The climate-induced trend to renewable energy technologies bears the problem of their fluctuating energy production. This evokes a demand of systems, that are able to stabilize in the electric grid without local production shutdowns. A promising solution is solid-oxide electolyzer cells (SOECs), which are able to convert excessive energy into hydrogen on demand. The product can then either be reconverted into electricity or used in other processes e.g. as chemical reactant [1]. However, such high temperature electrolyzers are not yet commercialized, as cell performance and lifetime are limited due to degregation of the anode [2]. On this electrode, the oxygen evolution reaction (OER) takes place at the triple phase boundary, where the electrolyte and electrode interface meet the gas phase. As the degregation comes in conjunction with the OER, it is critical to clarify the mechanism of the process. In order to elucidate the reaction mechanism, oxygen vacancy formation and defect mobility of the typical electrode material strontium doped lanthanium manganite (LSM) are theoretically investigated and critically discussed.

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## Following the morphology formation of printed active layers based on PBDB-T-SF:IT-4F in situ

Kerstin S. Wienhold<sup>a</sup>, Volker Körstgens, Sebastian Grott, Xinyu Jiang, Matthias Schwartzkopf, Stephan V. Roth, and Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>kerstin.wienhold@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de



Figure 1: In situ GISAXS during printing of active layers based PBDB-T-SF and IT-4F

Grazing incidence small angle X-ray scattering (GISAXS) allows following the structure formation in situ during printing (Figure 1). This advanced scattering technique provides fundamental knowledge to better understand the drying kinetics and morphology formation mechanism during slot-die coating of active layers for application in organic solar cells. [2]

In situ optical microscopy and in situ UV/Vis spectroscopy (Figure 2) were performed during printing to gain insight into the change of optical properties during drying and to support the findings obtained from the X-Ray scattering experiment.



PBDBT-SF:IT-4F were studied in situ.

to

Figure 2: In situ UV/Vis spectroscopy during drying of a slot-die coated thin film based on PBDB-T-SF:IT-4F

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# Germanium-based nanostructure synthesis guided by amphiphilic diblock copolymer templating

Christian Weindl<sup>a</sup> and Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>christian.weindl@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Latest research in the field of hybrid photovoltaics focuses on the benefits of inorganic and organic materials. Flexibility, low cost and large-scale production are the most valuable properties of organic components whereas the inorganic components add chemical and physical stability. So far thin films based on titanium dioxide are well investigated, whereas less is known about silicon (Si) and germanium (Ge) based compounds. In this work, we analyze thin films with optical, electrical and morphological measurement techniques to understand and control the corresponding properties. An amphiphilic diblock copolymer template with polystrene-b-polyethylene oxide (PS-b-PEO) and a Si-Ge precursor are used to prepare thin films via sol-gel synthesis. The copolymer templating results in nanoporous foam-like thin SiGe films. Their inner structure can be controlled by tuning distinct parameters during the sol-gel syntheses as well as by changing the block lengths of the structure guide.





Figure 1: (a) Sketch of the desired morphology of the hybrid film with the inorganic component shown in red. (b) Scanning electron microscopy image of a SiGe thin film prepaed with the sol-gel approach.

First results show a mesoporous film with randomly distributed domain sizes. To get further information of the inner structure of the mesoporous film, x-ray scattering techniques are applied. As the size of the pores plays a major role in the field of photovoltaics, we aim to find the best ratio of backfilling ability and homogeneity of the thin films.

# Fabrication on Plasmonic Nanostructures in Photovoltaics

Tianfu Guan<sup>a</sup>, Peter Müller-Buschbaum<sup>b</sup>

<sup>a</sup>tianfu.guan@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Photovoltaic technology that can convert sunlight directly into electricity is one of the most promising technologies to harvest solar energy for renewable electricity supply. In recent years, the state-of-the-art power conversion efficiencies (PCEs) of photovoltaics, such as organic solar cells (OSCs) and perovskite solar cells (PSCs), have been rapidly enhanced by interfacial engineering, optimizing device processing and developing new active layer materials. However, to pave the way for their practical application of OSCs and



Figure 1: Schematic diagram of the plasmonic metal nanoparticles enhanced photovoltaics.

In view of this point, to regulate the plasmonic spectra of Au NPs for maximizing the enhancement in light-absorption of active layer, we assembly the metal NPs onto the electron collecting layer to broaden absorption band of photoactive layer of OSCs and PSCs as well as enhance the device performance as is shown in Figure 1. To meet the optimal results, we put effort into the plasmonic structure regulation, since the size, density, and morphology of the Au NPs will influence the crystallinity of the photoactive film and charge transportation of the device. In order to investigate the possible influence of the sizes of Au NPs on subsequent films and device performances, as is shown in Figure 2, we can see that the well-dispersed Au NPs with different sizes were visibly assembled on the silica surface. In addition, grazing incidence wide angle x-ray scattering (GIWAXS) is used to probe the crystalline structure of the polymer/perovskite active layers. Grazing incidence small angle x-ray and neutron scattering (GISAXS and GISANS) is used to study the quality of the interface in terms of contact area between the materials.

PSCs, further enhancements in efficiency and device stability remains urgently required. For photovoltaics, light and electric management are essential issues for achieving higher device efficiencies. On the basis of this concept, various light manipulation methods, such as using tandem device structure, photonic crystals, surface textures, and plasmonic metallic nanostructures have been employed to enhance the light absorption of active layers as well as the device performance. Among plasmonic them, the utilization of metal nanostructures has been demonstrated as a promising approach for enhancing light harvesting. Thus, the development of facile and scalable fabrication methods that enable integrate the highlydispersed plasmonic metal NPs into OSCs and PSCs is highly desirable but yet remains challenging.



Figure 2: SEM images of Au NPs assembled on the sunstrates with different sizes a) 40 nm b) 60 nm c) 80 nm d) 100 nm.

# Investigating the effects of solvent additives on the stability of organic solar cells

Dan Yang<sup>a</sup>, Franziska C. Löhrer, Volker Körstgens, Armin Schreiber, Sigrid Bernstorff, Jillian M. Buriak, Peter Müller-Buschbaum<sup>b</sup>



<sup>a</sup>dan.yang@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

Organic photovoltaics (OPVs) have some outstanding advantages, such as flexibility, low-weight, potentially low-cost fabrication and large-scale production, which make them more comparable to other photovoltaic products. However, efficiency and stability are so far lacking, hampering the commercial application of this technology. Recently, the power conversion efficiency (*PCE*) of single-junction organic solar cells (OSCs) is approaching to 17%, but it is still behind their counterparts, such as silicon and perovskite solar cells. It has been demonstrated that the short exciton diffusion length in OSCs seriously limits the development of efficiency. The morphology of the photovoltaic active layer players a key role in the device performance. Therefore, bulk heterojunction (BHJ) photovoltaics (Figure 1) are proposed, in which donor (D) and acceptor (A)

materials blend to get an interpenetrating network film, thereby providing

approaches are applied to optimize the BHJ morphology as well, such as thermal annealing, solvent annealing and doping with solvent additives. However, concerning future large-scale fabrication, doping with solvent additives is identified as the most effective way to modify the BHJ morphology and to improve the solar cell performance. The solvent additive usually has a higher boiling point than the host solvent, thus, it can extend the film drying time to modify the morphology. However, the question arises whether doped solvent additives will deteriorate the device stability.



Figure 2: Chemical structures of donor and acceptor materials and solvent additives

To figure out the degradation effects of doped solvent additives, the investigation is firstly carried out on PTB7-Th:PC<sub>71</sub>BM (Figure 2) based solar cells, prepared without and with solvent additives (DIO and CBA) (Figure 2). There is no post-treatment involved in the fabrication process, so some high boiling point solvent may remain in the final device. Afterwards, the BHJ morphology and device performance are simultaneously tracked through in-operando GISAXS measurements. The results show that the changes in the IV-characteristics are related to morphological changes caused by the evaporation of solvent additives. To avoid the influence of residual solvent additives on device stability, further study is conducted on PffBT4T-2OD:PC<sub>71</sub>BM (Figure 2) based devices via in-operando GISAXS/GIWAXS measurements. Since the PffBT4T-2OD:PC<sub>71</sub>BM films are assembled by thermal spin-coating and thermal annealing, no solvent additives remains in the final devices. Thus, we don't observe any morphological degradation in this series by in-operando GISAXS measurements. However, we find that the decay of *Voc* depends significantly on the polymer crystallinity according to in-operando GIWAXS measurements. These findings provide an insight into the effect of solvent additives and are an important step to optimize the stability of organic solar cells.

# Hybrid Energy Harvester based on Combining Solar Cell and Triboelectric Nanogenerator

Tianxiao Xiao<sup>a</sup>, Wei Cao, Wei Chen, Stephan V. Roth, Peter Müller-Buschbaum<sup>b</sup>

### atianxiao.xiao@ph.tum.de, bmuellerb@ph.tum.de

Developing clean energy techniques plays a central role in the sustainable development of human society [1], in which collecting solar energy is one of the most promising ways in replacement of conventional used fossil fuels. However, the daily and seasonal fluctuations limit the continuous electricity generation from solar cells. Thus, integrating solar cells with other kinds of energy harvesters in one device is considered as an effective solution to continuously provide an energy source [2]. Triboelectric nanogenerator (TENG) originating from Maxwell's displacement current is a new type of energy harvesters. Due to its advantages of lightweight, low-cost, and easily fabricated, different kinds of TENG devices have been fabricated for harvesting various energies in the past years [3-4].

In the present work, a flexible hybrid energy harvester was designed and fabricated based on PbS quantum dots (QDs). This device consists of a QD solar cell part and a polydimethylsiloxane (PDMS) based TENG part, which can harness both, solar and mechanical energy from ambient environment to generate electricity. The structure of the hybrid energy harvester is schematically shown in Figure 1a. Figure 1b shows a photograph of as-fabricated energy harvester device at initial and bending state. Figure 1c illustrates the working principle of the TENG part. Here, the electricity generation cycle is formed by the periodic movements of the external object. Additionally, GISAXS measurements are used to characterize the bending stability and morphology changes of the mesoscale structure [5]. This work may have great applications in both artificial intelligence and soft robots.



Figure 1: a) Fabricated hybrid energy harvester as sketch and b) in reality. c) The electricity generation cycle of the TENG part.

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### Tracking the morphology evolution of active layers for non-fullerene organic solar cells

Xinyu Jiang<sup>a</sup>, Sebastian Grott, Volker Körstgens, Kerstin S. Wienhold, Matthias Schwartzkopf, Stephan V. Roth, Peter Müller-Buschbaum<sup>b</sup>



Figure 1: Energy level diagram of the materials in an invert organic solar cell devicearchitecture, which contains PffBT4T-2OD:EH-IDTBR as the active layer.

#### <sup>a</sup>xinyu.jiang@ph.tum.de, <sup>b</sup>muellerb@ph.tum.de

In the past few decades, organic solar cells (OSCs) have received significantly progress with novel materials. However, the achieved best efficiencies remain behind than that of traditional silicon solar cells, which demonstrates the need for intensive investigations. Moreover, most highperformance OSCs are fabricated in an inert atmosphere with a spin coating method through labor-intensive testing on a small area, which is not compatible with large-area mass production. Therefore, developing large-area printing techniques is urgent to manufacturing energy-efficient, highthroughput, low-cost, and low carbon-footprint OSCs. Slotdie coating is intensively used as a fully scalable, robust, and reproducible technique in active layer deposition because it can be employed in sheet-to-sheet and roll-to-roll (R2R) large-area solution processing with low solution consumption, high film homogeneity, and good device performance on a flexible substrate.[1]

The performance of OSCs is strongly influenced by the morphology of the active layer. Therefore, to understand the

mechanism of the inner structure as well as the structure forming process of the active layer during drying kinetics is the key for the device optimization. For tracking the mechanism of the structure formation of polymer domains, we use in-situ grazing incidence small angle X-ray scattering (GISAXS). The non-destructive GISAXS technique is capable of providing domain sizes and spatial correlations down to nanometer scales regarding the inner structures of the films, which is desirable for the present work to determine the morphology change during the printing process.[2] In this work, a low bandgap donor polymer (pffBT4T-2OD) and a non-fullerene acceptor (EH-IDTBR) are used as the active layer material due to the advantages of air-stable, thickness insensitive and high device performance. Figure 1 shows the energy

diagram of an invert organic solar cell. During the experiment, the solution, as well as the substrate stage, moves with an optimized rate to get a homogenous thin film. X-rays with a wavelength of 0.096 nm were used to make the outstanding time resolution of GISAXS images during the thin film drying process. For quantitative analysis, figure 2 shows horizontal line cuts are performed on the 2D GISAXS data at the Yoneda peak position of pffBT4T-2OD. From the data simulation, we know that the development of morphology of polymer donor exhibits four stages independent of the drying conditions. The findings give us important information in tailoring the assembly process. In addition, atomic force microscopy (AFM) and scanning electron microscope (SEM) techniques were used to get the surface morphology information of the dried printed active layers.

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Figure 2: Horizontal line cuts extracted from the in-situ GISAXS data. Time in the experiment increases from bottom to top.

## **Drilling risks in the North Alpine Foreland Basin**

Indira Shatyrbayeva

### indira.shatyrbayeva@tum.de

The exploration and exploitation of either oil and gas or geothermal resources by creating boreholes into the deep subsurface often trigger various drilling problems such as borehole instability, stuck pipe, loss of circulation, collapses, leakages, differential stickings, etc. These drilling hazards often result in high non-productive time (NPT) with a drastic increase in well construction cost. Drilling costs are a major investment position of the Bavarian deep drilling operations and it can occupy 40-70 % of the total investment cost. Mitigation of the severity of these drilling challenges is therefore important for safe and economic drilling operations. Planning new wells requires careful screening of the trajectory for possible geo-drilling hazards. Before proceeding with the specific aspects of the process, it is necessary to consider the relevance of the preliminary survey phase, which involves a work program to assess the already available data within a specific area.

Data inventory (Bavarian State Office for the Environment – LfU) indicates that over 800 wells of depth larger than 1000 m have been drilled in the North Alpine Foreland Basin, SE Germany. The drillings were carried out for various fields of applications such as drinking water, oil and gas exploration, geological and raw material investigation using different technical methods.

About 50 deep geothermal wells have been drilled in the last 10 years in the Bavarian Molasse Basin reaching a depth of up to 6000 m. In the coming years, even deeper and more challenging wells are planned to further develop geothermal resources. However, drilling and well completion in this geological setting close to the Alps with high tectonic stresses and overpressured zones is quite challenging.

The objective of this research is to provide an overview of drilling risks and possible risk mitigation measures taking into account formation geology and pore pressures in the North Alpine Foreland Basin. The study focuses primarily on analyzing historic drilling reports, observations on drilling incidents and classification of geo-drilling event types from existing boreholes in the region and properly predicting pore pressure profiles based on log measurements. Ultimate target is to establish a new risk estimation tool on the learnings from the experience on drilling events gathered over the past years

# The impact of different ORC working fluids on the external costs for geothermal power generation

Christopher Schifflechner<sup>a</sup>, Christoph Wieland<sup>b</sup>, Hartmut Spliethoff<sup>c</sup>

#### <sup>a</sup>c.schifflechner@tum.de

Geothermal energy has a tremendous potential for the necessary energy transition within the global power sector [1]. However, in many regions, the achievable temperatures of the utilized geothermal reservoirs are not hot enough for direct power generation. Thus, in these regions, such as the South German Molasse Basin, a binary power plant must be used for power generation. The most common type is the Organic Rankine Cycle, which uses an organic working fluid with a lower boiling temperature than water. There is a broad range of possible ORC working fluids. Thus, the environmental impact caused by the different potential working fluids must be evaluated to ensure an environmentally friendly power generation. This study presents a detailed evaluation of the external costs caused by power generation through geothermally driven Organic Rankine Cycles (ORCs) with different working fluids.

In current operating geothermal applications, ORC working fluids of the hydrocarbons (HC) and hydrofluorocarbons (HFC) groups are dominating [2]. During the last years, new working fluid groups have been developed, which are in the hydrofluoroolefines (HFO) and hydrochlorofluoroolefines (HCFO) group. The HFO R1234yf and R1234ze(E) as well as the HCFO R1233zd(E) and R1224yd(Z) are promising low-GWP alternatives to the HFC R134a and R245fa [3]. Nevertheless, especially the assessment and legal handling of HCFOs with an ODP slightly above zero is controversial. For instance, the German Environment Agency intends to prohibit the application of R1233zd(E), due to its ODP of 0.00024. However, R1233zd(E) has several favorable aspects, such as a very low GWP and no flammability and toxicity. A case study for a hypothetical geothermal system with a brine temperature of 138°C and a flow rate of 122 kg/s is carried out. The external costs caused by the high-GWP refrigerants R245fa and R134a are 0.69 €ct/kWh<sub>el,net</sub> and 0.83 €ct/kWh<sub>el,net</sub> respectively. All derived external costs for the investigated low-GWP working fluids are



significantly lower and are in a range between 0.29 and 0.30 €ct/kWh<sub>el,net</sub>. This proves, that the very small ODP by R1233zd(E) and R1224yd lead to no significant increase of the external costs. A more detailed discussion is presented in [4].

Figure 1: External costs of one kWh produced net electricity for the investigated working fluids.

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# Prosumer in Heat Networks: Is it Worth Trading Heat with Neighbors?

Daniel Zinsmeister<sup>a</sup>

<sup>a</sup>d.zinsmeister@tum.de

The reduction of CO2 emissions by 80 to 95 % until 2050, as planned by the German government, requires a joint approach within all sectors. In the heat sector, district heating grids can help to reach these goals.



District heating technologies are commonly divided into four generations. All of these have relied on centralized heating stations.

Opening district heating grids to prosumers, similar to electric grids as shown in Figure 1, could allow a reduction of CO2 emissions, by integrating renewable and efficient technologies, such as solar thermal, heat pumps and combined heat and power plants into the system. However, this new approach with decentralized heat suppliers and prosumers brings several new challenges, for instance complex control strategies, technical requirements concerning temperature and pressure and a new billing system.

Figure 1: District heating grid with prosumers

These challenges will be investigated in the new laboratory of the Center for Combined Smart Energy Systems (CoSES, Figure 2). The laboratory emulates a small electric and heat microgrid consisting of five houses with controllable electric and heat demand and real producers. Each house is equipped with a heat transfer unit that allows exchange of heat within the thermal grid.

This work investigates promising use cases of prosumer integration in thermal networks. Therefore, I use *urbs*, a linear optimization model for distributed energy systems, to model several houses. *urbs* can plan system expansion and/or schedule resources by finding the minimum costs to satisfy given demand time series for commodities such as



Figure 2: CoSES laboratory [Stefan Hobmaier / TUM]

electricity and heat. Most analyses consider heat as merely another form of energy, neglecting the influence of temperature levels. In many cases, this is a tolerable simplification, but since it is my aim to analyze the heat sector in detail, heat is considered at different temperature levels within *urbs*.

To identify the use cases best suited for district heating prosumer units, different scenarios are analyzed. Regarding buildings and infrastructure, different consumption rates, heat generators, distances between buildings and topologies of district heating grids are considered. On the financial side, the influence of energy and technology prizes is regarded. The aim is to determine, which are the best suiting technologies for the different use cases: District Heating grid or decentralized heat generation – Centralized feed in or heat prosumers – which technologies should be installed.

The most promising use cases will then be tested experimentally within the CoSES laboratory.

## Photocatalytic Alcohol Conversion as Model Reaction for the Hydrogen Economy

Moritz Eder<sup>a</sup>, Carla Courtois<sup>b</sup>, Martin Tschurl<sup>c</sup>, and Ueli Heiz<sup>d</sup>

<sup>a</sup>moritz.eder@tum.de, <sup>b</sup>carla.courtois@tum.de, <sup>c</sup>tschurl@tum.de, <sup>d</sup>ulrich.heiz@mytum.de

Sustainable and eco-friendly energy production is a major challenge of the future, as the impact of global warming is aggravated by the dependence on fossil fuels. This accounts not only for the consumption, but also their production. For example, while hydrogen is economically friendly in consumption, its generation by the steam reforming process of natural gas is environmentally harmful. Thus, alternative pathways and technologies have to be developed for the generation of renewables.



A very promising approach is photocatalysis, whose aim is to utilize (sun)light for the generation of high-value chemicals, biomass conversion and renewable fuels. The natural role model is photosynthesis, where carbon dioxide is activated and upgraded to high-value chemicals, i.e. the energy from sunlight is stored in chemical bonds. Photocatalysis is particularly interesting for the hydrogen economy, as it has been shown that applied systems are indeed capable of generating hydrogen from water or organic compounds, such as alcohols.

Figure 1: Photocatalytic reactions on a semiconductor

Our group investigates phenomena in heterogeneous photocatalysis, where semiconductors are used as catalyst material. They are usually optimized by loading metal particles as co-catalysts onto their surface, as e.g. in a three-way catalytic converter. As co-catalyst material, noble metals (in particular platinum) were found to be suitable for hydrogen evolution reactions. Whereas the role of semiconductors is quite well understood, a lack of insights into the properties and role of cluster co-catalysts remains. For this reason, current state-of-the-art systems are difficult to improve in a strategic manner.

We investigate the role of these co-catalysts during the photocatalytic conversion of alcohols. The latter are perfect model substrates, since they serve as biomass precursors and hydrogen carriers. Since we want to understand fundamental chemical mechanisms, our reactions are carried out under ideal conditions on single crystals in ultra-high vacuum.

By combining surface science and cluster research, our research goals are targeted toward the used of welldefined metal clusters in catalytic applications.

## A Novel Gas Phase Photoreactor for the Investigation of Planar Substrates

Clara Eisebraun<sup>a</sup>, Martin Tschurl<sup>b</sup>, Ueli Heiz<sup>c</sup>

<sup>a</sup>clara.eisebraun@tum.de, <sup>b</sup>tschurl@tum.de, <sup>c</sup>ulrich.heiz@mytum.de



Figure 1: Photocatalytic methanol reforming on a metal decorated single crystal model catalyst.

Harvesting solar energy by converting abundant chemicals photocatalytically into valuable products is still far from being applied on a large scale. Aspirant applications are the production of hydrogen by water splitting, biomass reforming or the fixation and valorization of greenhouse gases such as carbon dioxide and methane.[1,2]

Investigations of model catalysts under ideal conditions, (single crystals in ultra-high vacuum) give essential insights into fundamental photocatalytic processes. Yet, due to a phenomenon known as "pressure gap" conclusions drawn from UHV studies cannot always be readily transferred to environmental conditions.[3] Reactions on a macroscopic scale are usually carried out at ambient conditions and require large amounts of photocatalyst. However, the availability of active material might be limited, either due to intensive synthesis

procedures, or due to a planar catalyst shape, which impedes a simple increase of catalyst amount in the photoreactor. While few existing setups already allow the investigation of low surface area samples, their reactor design impedes the analysis of planar catalysts. [4,5] A further disadvantage of those setups is the single use of the reactor due to irreversible sealing inhibiting post-characterization without applying mechanical stress.

Hence, we design a novel gas phase reactor for photocatalysis, which is compatible for different planar substrates, allows easy sample exchange and handling and enables the highly sensitive detection of small molecules to track even very small changes in catalyst performance.

This is achieved by downscaling the reactant gas flows to the  $\mu$ L/min range to achieve sufficient product to total gas ratio for quantitative mass spectrometry and to decrease reactor size to ensure adequate contact times and fluid dynamics. For this, the reactor chamber as well as inlet and outlet including a capillary will be etched into the UV/VIS-transparent reactor lid. The planar substrate supported by a metal plate will serve as the reactor bottom sealed by a thin O-ring. In contrast to tube reactors commonly used in thermal catalysis, the circular shape ensures maximum and homogeneous light intensity on the photocatalyst surface provided by LEDs or a laser.



Figure 2: µ-Photoreactor for planar substrates

This versatile setup enables the study of photocatalytic processes for highly defined model samples, such as single crystals, which could not be tested under applied conditions to date and thus, has great potential to improve the conceptual understanding of structure-property relations in photocatalysis.

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