# Highlights in Energy Research

7th Colloquium of the Munich School of Engineering
July 13, 2017

On the 26th of June 2017, the state minister Dr. Ludwig Spaenle, MdL, the mayor of Garching, Dr. Dietmar Gruchmann and the president of TUM Professor Wolfgang Herrmann, opened the new Centre for Energy and Information (Zentrum für Energie und Information, ZEI). All three emphasised the importance of energy research for the future development. The new building is the new home for interdisciplinary energy research at the Technical University in Munich and it is also home of the Munich School of Engineering.

Three new laboratories will offer a unique environment for the scientists at TUM to promote new energy technologies. The new microgrid COSES will be a valuable testbed to develop the distribution grid of the future and the organic PV lab and the battery lab will complement these efforts. The Geothermal-Alliance Bavaria is also hosted in the new building.

The energy transformation is on the edge of entering a new phase. The cost of renewable energies is competitive in many parts of the world by now. Questions of integration and optimal market design remain.

The Munich School of Engineering has proven that interdisciplinary energy research is possible and offers unique opportunities for a university. The new building is like a clarion set in stone of the new energy age.

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 *Geothermal-Alliance Bavaria* combines interdisciplinary research strategies in order to strengthen deep geothermal as a sustainable and controllable source of renewable energy.

- In the *Center for Power Generation* the efficiency and the environmental sustainability of existing and future power plants is increased and improved by modern and innovative technologies.

- 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 *Science Center for Electromobility* contains a wide spectrum of topics from fundamental battery research, development and design of electric vehicles as well as future mobility concepts.

- 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 *Combined Smart Energy Systems Center* focuses on modeling the interdependency of electricity distribution, heat and communication networks. The goal of the center is to develop strategies for integrating extensive distributed energy sources in the energy grid of the future, the smart micro grid.

# Programme

**8:30 – 9:00 a.m.**
**Registration**

**9:00 – 9:15 a.m.**
**Opening**
Thomas Hamacher, Director Munich School of Engineering

**9:15 – 9:45 a.m.**
**Keynote: "The Energiewende, a show case for technical and policy innovation and what other countries can learn from Germany"**
Dr. Fabian Joas, Agora Energiewende

**9:45 – 11:00 a.m.**
**Session**
**Session Chair: Dr. Markus Becherer**

**Second Generation $CO_2$ Methanation Catalysts**
Thomas Burger, Chair of Chemical Technology I

**Modeling Occupational Disorder in $Li_4Ti5O12$ Battery Materials: Intrinsic Complexity and its Effect on Ion Mobility**
Hendrik Heenen, Chair of Theoretical Chemistry

**Perovskite: The New Crystalline Sheriff in the Photovoltaic County**
Shambhavi Pratap, Functional Materials

**11:00 – 11:45 a.m.**
**Poster Presentation, Coffee Break**

**11:45 – 1:00 p.m.**
**Session**
**Session Chair: Prof. Hartmut Spliethoff**

**Simulation and Optimization of Open Algae Ponds**
Andreas Rarrek, Chair of Plant and Process Technology

**The Hybrid Transmission Grid Architecture:
A Topology-Preserving Capacity Expansion Strategy**
Matthias Hotz, Associate Professorship of Signal Processing

**High Pressure Evaporation Rig for the Investigation of Stationary and Transient Heat Transfer Phenomena**
Tobias Gschnaidtner, Energy Valley Bavaria

**1:00 – 2:30 p.m.**
**Poster Presentation, Lunch Break**

**2:30 – 4:10 p.m.**
**Session**
**Session Chair: Prof. Gunther Friedl**

**Synergistic Value of Hybrid Energy Systems: Renewable Power and Hydrogen Production**
Gunther Glenk, Chair of Management Accounting

**Mine or Ours? Willingness to Pay for Innovative Battery Storage Concepts**
Bernhard Kalkbrenner,
Chair of Marketing and Consumer Research

**With Innovative Highlights Towards a Sustainable TUM Campus**
Benedikt Schweiger, Chair of Energy Systems

**Nearly Zero Energy Laboratory Buildings?**
Michael Keltsch, Institute of Energy Efficient and Sustainable Design and Building

**4:10 – 4:40 p.m.**
**Poster Presentation, Coffee Break**

**4:40 – 5:10 p.m.**
**MSE-Research**
**Geothermie-Allianz Bayern – Scientists United for Geothermal Energy**
Dr. Katharina Aubele, Munich School of Engineering

**5:10 – 5:40 p.m.**
**Keynote: "TUM Startup Li.plus - Battery diagnostics - fast. precise. simple."**
Christian Huber, Li.plus

**5:40 – 5:55 p.m.**
**Summary, Closing**

**5:55 – 8:00 p.m.**
**Poster and Presentation Award,
Colloquium Dinner**

**Abstracts**

## Posters - Energy Systems and Buildings 54

# 1. Oral Presentations

# Second generation $CO_2$ methanation catalysts

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The power-to-gas concept (Figure 1) is widely believed to be one approach to deal with future challenges arising from increasing energy consumption and depleting fossil energy carriers, at the same time limiting the emissions of $CO_2$. Based on the exothermic Sabatier process [1], $CO_2$ is reacted with $H_2$, which is supplied using electrolysis driven by surplus energy from renewables, to form synthetic natural gas (SNG). The produced SNG can be stored in the existing natural gas distribution grid and used for heat generation on demand. From the exothermal character of the reaction (-165 kJ/mol), two basic catalyst requirements can be deduced: High activity, to gain high purity SNG at low temperatures, and high thermal stability, to increase catalyst lifetime under reaction conditions. This study deals with the improvement of a benchmark $Ni/AlO_x$ catalyst system with respect to activity and thermal stability by metal doping.
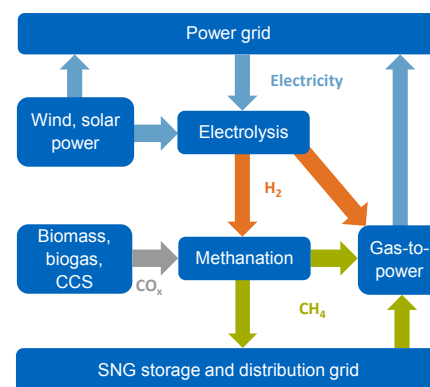


Figure 1: Power-to-gas concept.

The catalysts were prepared by reverse co-precipitation at pH 9 using 1 M metal nitrate solutions and a 0.5 M mixture of NaOH and $Na_2CO_3$ as precipitation agent. After aging for 18 h at 30 °C, washing and drying, the precursors were calcined at 450 °C for 6 h. A kinetic test setup was used to investigate the catalytic activity by determining the $CO_2$ conversion in the temperature range between 175 and 500 °C at 8 bar using stoichiometric feed gas composition. Data on the thermal stability was obtained from a second temperature variation cycle after an aging treatment for 32 h at 500 °C and 7 bar.
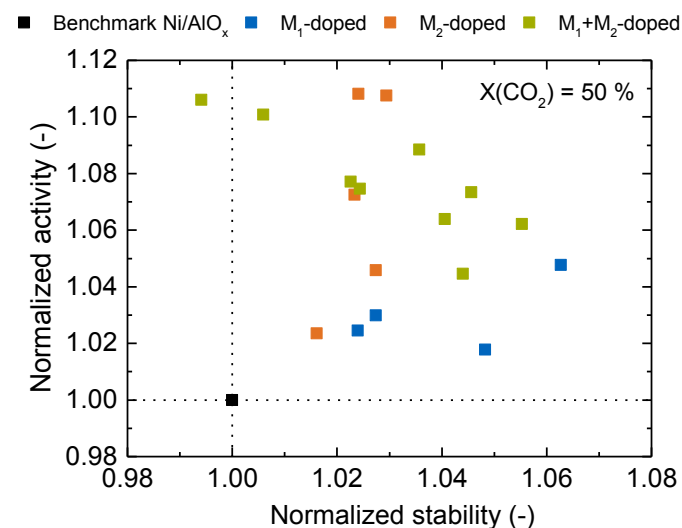


Figure 2: Promoter effects on the activity and thermal stability of NiAlOx in CO2 methanation.

The impact of the dopants on catalyst activity and stability can be resolved by determining the temperature necessary for 50 % $CO_2$ conversion and normalizing them to the benchmark catalyst system (Figure 2). Doping with $M_1$ results in a significant increase of the catalytic activity, while $M_2$ enhances the thermal stability. Most noteworthy, in the temperature range from 175 to 400 °C, methane selectivity was higher than 99 % for all catalysts. By co-doping $M_1$ and $M_2$, catalysts with improved activity and thermal stability can be synthesized, with the catalytic behavior strongly depending on the promoter loadings.

Detailed characterization studies comprising $N_2$ physisorption, $H_2$ and $CO_2$ chemisorption, X-ray photoelectron spectroscopy, X-ray powder diffraction analysis and temperature-programmed reduction contributed to gain insights into the state of the promotors and structure-activity relationships. The main reason for the high activity of the $M_1$-promoted catalysts is supposed to be caused by the formation of a $NiO-M_1O_x-AlO_x$ structure, which leads to an improved $CO_2$ management during the reaction. In contrast, the improved stability under hydrothermal reaction conditions observed when adding $M_2$ is attributed to the formation of a $NiM_2$ alloy phase.

[1]     P. Sabatier, J. B. Senderens, *CR Acad. Sci.* **1902**, *134*, 689–691.

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# Modeling occupational disorder in $Li_4Ti_5O_{12}$ battery materials: Intrinsic complexity and its effect on ion mobility

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Lithium-titanium-oxide ($Li_4Ti_5O_{12}$, LTO) is unique among battery materials due to its exceptional cyclability and high rate capability. This performance is assumed to derive at least partly from the occupational disorder introduced via mixed Li/Ti occupancy in the LTO spinel-like structure. Notwithstanding, the exact atomic-scale influence of this disorder on Li ion mobility remains an open question.

We explore the vast configuration space accessible during high-temperature LTO synthesis by Wang-Landau sampling. Use of a numerically efficient, density-functional theory validated interatomic potential [1] allows for extensive sampling in simulation cells large enough to appropriately capture the long-range disorder. The determined configurational ensemble is indeed characterized by a large degree of microscopic inhomogeneity. Subsequent room-temperature molecular dynamics simulations reveal the dominant fraction of Li ions in this ensemble to be immobile on nanosecond timescales. However, certain disorder motifs give rise to a novel correlated ion diffusion mechanism. We discuss this mechanism in the context of the evolution and morphology of the so-called two-phase reaction appearing during Li intercalation [2].

[1] M. Vijayakumar et al., *J. Power Sources* **2011**, *196(4)*, 2211
[2] M. G. Verde et al., *ACS Nano* **2016**, *10*, 4312

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# Perovskite: The new crystalline sheriff in the photovoltaic county

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Silicon based technologies are a mature field which lead to many exciting applications, especially in the field of electronics. Thus, it is not surprising that the photovoltaic market too is dominated by silicon based modules, which offer good energy conversion efficiencies with long performance lifetimes. However, the growing sophistication of upcoming architectures call for smarter, more versatile technologies which can harness the solar energy not merely in a stand-alone, but rather an integrated fashion. The old reliable silicon solar cell being bulky, rigid, opaque, thus is not the best candidate for such niche, urbane applications.

A novel class of materials, termed organometallic lead halide perovskites have attracted and inspired a whirlwind of research in the photovoltaic community. Discovered only about half a decade ago [1], perovskite based solar cells have established certified record photoconversion efficiencies of over 22%, justifying the title of one of the most promising breakthroughs in the field today. Being solution processed, from earth-abundant raw materials, their production process requires temperatures around 100-200°C, thereby making their manufacturing considerably more facile as compared to silicon based solar cells. Owing to their strong absorption properties, sub-micron thin films of the material are sufficient to capture incoming solar radiation, as against silicon which requires 1000 times more material to absorb the same radiation. Calculations suggest that perovskites photovoltaic technologies would help reduce the cost of generating solar energy, as much as by three-quarters.

The properties of these perovskites are highly tunable by simple compositional engineering giving rise to colorful, semitransparent solar cells. Tandem solar cells maybe designed with such tunable materials harnessing a larger part of the solar spectrum. However, there is a caveat to this promising material, which is responsible for hindering the commercialization of the technology. The perovskites have poor stability due to changes that their structure undergoes.



Figure 1: Semitransparent, colorful perovskite thin films
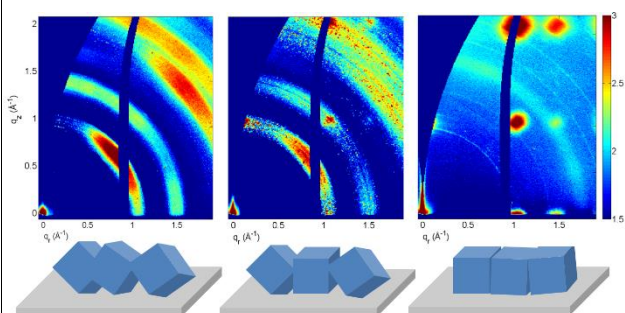


Figure 2: Changing morphology of perovskite crystals probed by grazing incidence wide angle x-ray scattering (GIWAXS

In order to understand and control these changes, the crystal structure and thin film morphology was probed with the aid of advanced x-ray scattering techniques. It was demonstrated that a high degree of control over crystalline structure and morphology can be exercised with rational chemical control [2,3], which give clues towards stabilizing perovskites and help make their commercialization a reality in market today.

References:
[1] A. Kojima, et al., J. Am. Chem. Soc., 2009, 131 (17), 6050–6051
[2] L. Oesinghaus et al., Adv. Mater. Interfaces 2016, 3, 1600403
[3] Giesbrecht et al., ACS Energy Lett. 2016, 1, 150-154

# Simulation and optimization of open algae ponds

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## Motivation

Renewable energies already have a significant share in the world's energy production and it will get even bigger in the future. However, their part in the transport sector is low, because this sector needs energy that is stored with a high density and can easily be handled. Biofuels are a very good option to bring renewable energy into conventional tanks. One option to get biofuels is to grow algae in large open ponds. The algae consume $CO_2$ to increase their biomass and can then be converted to biofuels. Although growing algae in open ponds has been done for decades, there is still a lot of research necessary how to efficiently grow algae in large systems in order to produce biofuels.
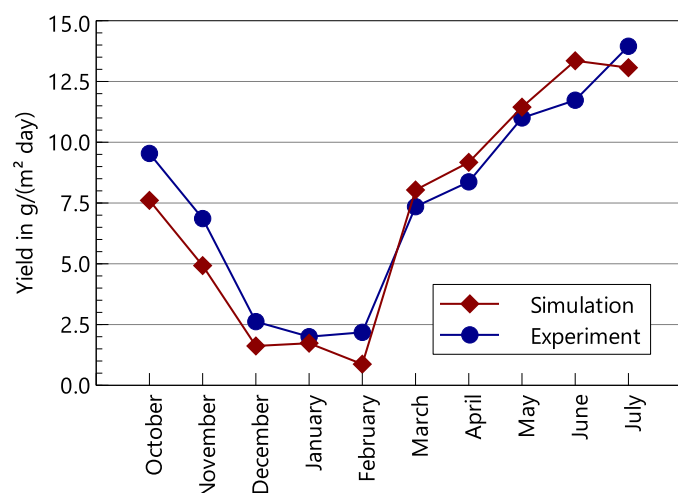


## Simulation model

This work presents a model that simulates the behavior of open algae ponds. The model is written from scratch in MATLAB and can be used to evaluate the performance of raceway-type open algae ponds at different locations and dates. The model is fully dynamic and considers environmental effects like weather as well as the dynamic behavior of the pond.

The model was validated with experimental data from a 450 m²-raceway algae pond, which was located in Malaga (Spain) and operated for 10 month. The simulation covered the real weather effects of the experiment as well as the behavior of the algae Spirulina platensis, which was grown.

## Investigations

The yield of ponds at different locations are evaluated over the year. Multiple operating conditions of the algae ponds are varied and their effect on the yield is evaluated. The ponds are fed with flue gas as $CO_2$ source. The $CO_2$ is the carbon source for the algae and is also used to keep the *pH*-value in a desired range that is optimal for the algae growth.

The harvest rate shows a strong influence on the yield of the ponds. Adjusting the harvest rate to the summer and winter conditions improves the yield at some locations significantly. Operating the algae pond over the whole year is not reasonable at all locations, because at some locations the major contribution to the total yield is obtained in 2/3 of the year.

In general, the yield of an algae pond can be increased significantly by systematic investigations with this simulation model.
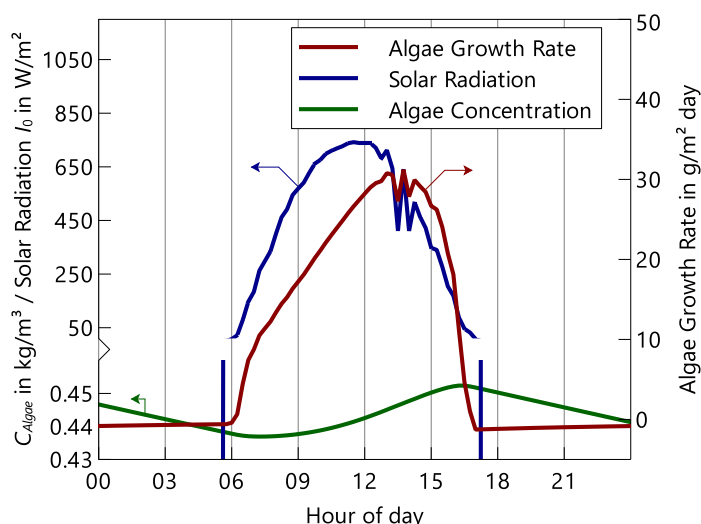
# The Hybrid Transmission Grid Architecture:
# A Topology-Preserving Capacity Expansion Strategy

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The energy transition in Germany entails a shift towards an increasingly distributed and fluctuating energy production due to the growing use of wind, sun, and biomass as energy sources. These changes in the energy mix further lead to a geographic shift of power generation, inducing a growing energy surplus in the north and an energy demand in the south of the country. This transformation of generation structure renders capacity expansion of the German transmission grid a key issue of the energy transition. Adequate expansion measures are determined jointly by the German transmission system operators and the Federal Network Agency via a multi-stage process. Throughout, the proposed measures are repeatedly subject to consultation and public debate to ensure validity and acceptance. The current expansion plan identifies four new high-voltage direct current (HVDC) transmission lines as a necessary countermeasure for the north-south generation imbalance. While these HVDC lines are virtually the transmission backbone of the energy transition, they also constitute the primary subject of objection during consultation and public debate.

In our work, we explored alternative approaches to capacity expansion that rely on *existing* transmission corridors to foster public acceptance, which resulted in the concept of the *hybrid architecture*. The hybrid architecture also takes advantage of HVDC technology, but adopts a different perspective in its utilization. While the current expansion strategy uses *additional* HVDC lines as a *focused* measure against the north-south imbalance, the hybrid architecture comprises a systematic and *system-wide* conversion of certain *existing* AC lines to HVDC, i.e., it is environmentally minimally invasive. The conversion to (VSC) HVDC enables a line capacity increase by a factor of two or more and, additionally, introduces controllability to the line power flow as well as reactive power support at the terminals. Therewith, the system-wide conversion of certain lines does not only selectively increase line capacity, but also introduce substantial *flexibility* to the grid, which can be vital to handle, balance, and distribute the fluctuating power injections of RES.



Selective conversion: HVAC → HVDC
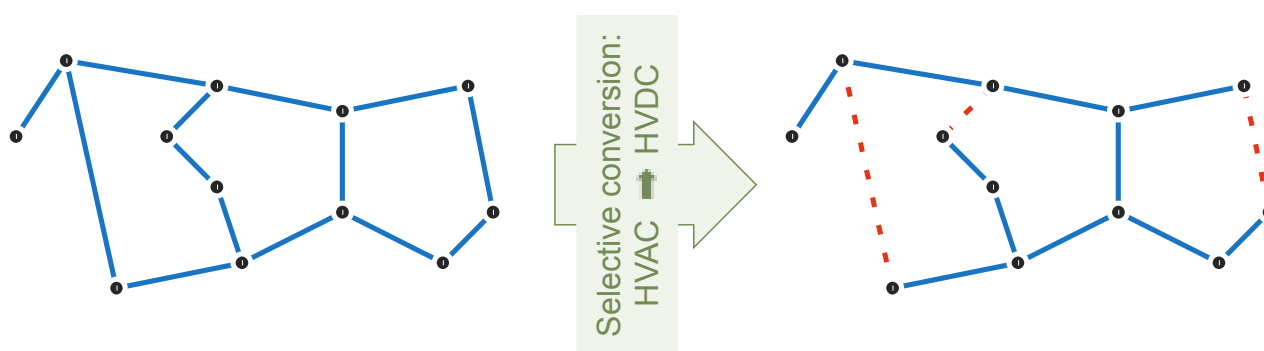
We have shown that the hybrid architecture can not only increase the effective transmission capacity, but also induce a transition in *system structure* that supports an efficient operation. For example, the hybrid architecture gives rise to an efficient optimal power flow (OPF) method. Its structural properties enable a shift of the nonconvex OPF problem into the *convex* domain, which renders it amenable to efficient solution algorithms as well as a powerful framework of mathematical theory. Due to this, resorting to simplified system models like the "DC power flow" becomes largely unnecessary, enabling more accurate decision making. Furthermore, the flexibility in power flow induced by the hybrid architecture facilitates a more effici-ent utilization of generation facilities that can reduce total generation costs and mitigate trading restrictions. In our current research, we investigate the potential of this hybrid architecture as an alternative capacity expansion strategy for the German transmission grid. By preserving the existing grid topology, this approach fosters public acceptance of capacity expansion measures and, therewith, the energy transition as a whole.

# High Pressure Evaporation Rig for the Investigation of Stationary and Transient Heat Transfer Phenomena

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Heat transfer to supercritical water in heated tubes and channels is of particular importance for steam generators in future concepts of nuclear and solar-thermal power plants. The main objective of these future nuclear and solar-thermal power plants is to achieve an increased thermal-efficiency. Moreover, as more and more electricity generated by renewable, volatile energy sources is fed into the public grid, existing as well as new supercritical power plants are facing the problem of a more flexible operation mode in order to sustain the security of supply. To tackle this issue it is necessary to expand their range of operation parameters, leading to off-design conditions in their steam generators. Although investigations on supercritical heat transfer in tubes have been conducted by numerous researchers, the corresponding heat transfer mechanisms are still indistinct.

Hence, a new experimental facility, the High Pressure Evaporation Rig HIPER, engineered, constructed and commissioned at the Institute for Energy Systems aims to provide heat transfer data to fill the existing knowledge gaps at these conditions. The test rig is schematically shown in Figure 1. It consists of a closed loop high pressure cycle, in which de-ionized water is fed to a vertical test section. The test section is a 15.7 mm x 5.6 mm smooth tube, which is heated over a length of 7000 mm by means of direct current (1 $MW_{el}$). It is designed to withstand a maximum pressure of 380 bar at 580 °C. 70 thermocouples distributed evenly along the heated length of the test section enable the investigation of heat transfer phenomena at stationary and transient conditions.

In a first series of tests, experiments are conducted to provide data on heat transfer under vertical upward flow conditions (see Figure 2). Selected stationary as well as transient results on the heat transfer to supercritical water are presented. In addition, the obtained data are compared to existing models from the literature.
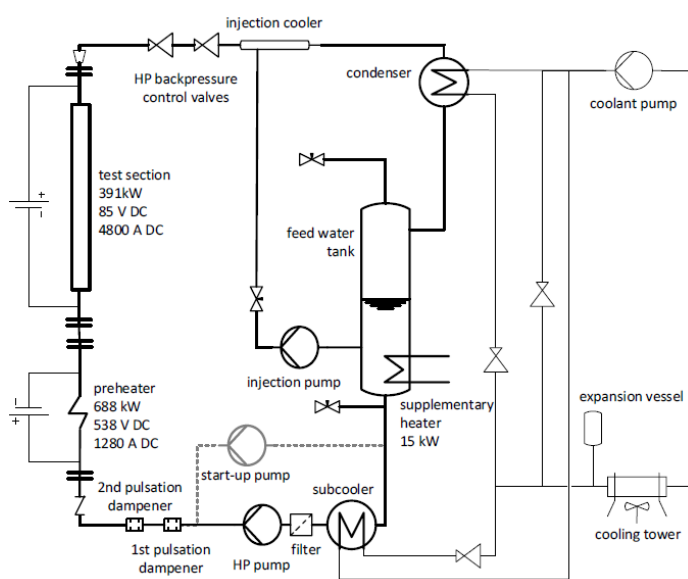


**Figure 1: Process flow diagram of the High Pressure Evaporator Rig (HIPER) at the Institute for Energy Systems.**
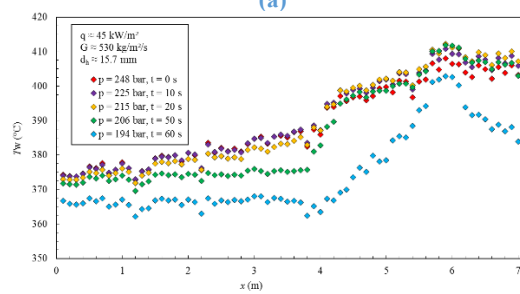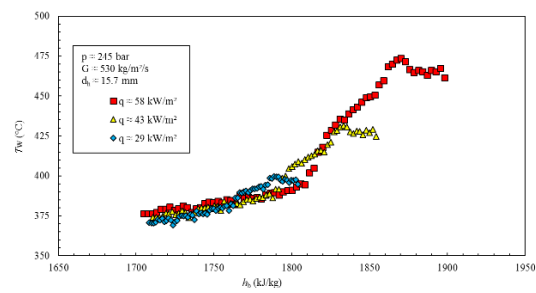


**Figure 2: First series of experiments for stationary (a) and transient data (b).**

# Synergistic Value of Hybrid Energy Systems: Renewable Power and Hydrogen Storage

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Reaching climate goals requires companies to switch from fossil fuels to renewable energy. While this switch is regularly considered a financial burden, combining the business operation with a renewable energy source in a hybrid energy system may entail valuable synergies from reduced energy cost. At the same time, operators of renewable energy sources, such as wind and solar, find their market value decrease with their increasing share of power generation. The effect is due to similar weather in an area causing concurrent power generation, suppressing market prices at a given demand. Combining a renewable energy source with a business operation in a hybrid energy system may entail valuable synergies from price arbitrage.

We call the combination of a renewable energy source with an energy consuming operation (a production or service) a *hybrid energy system*. Both energy systems require upfront capacity investments to deliver the product or service. They can be installed stand-alone and may succeed or fail to be cost competitive. For an investor, the fundamental question then is when a hybrid energy system is valuable over and above two stand-alone energy systems.

We show analytically that a company should invest in both systems if the combination yields synergistic value. In case of a stand-alone negative net present value of either or both energy systems, the hybrid energy system has synergistic value if the synergies overcompensate stand-alone loss(es). Our results seem trivial if synergies are constant, but here the synergies are limited and vary over time because of intermittent renewable energy and fluctuating energy prices. These variations are typical for a particular technology in a particular market and determine an optimal ratio of the energy producing and consuming capacity sizes. Our model can thus pin down a rule-of-thumb for the optimal ratio of capacity sizes for each technology-market setting.

We apply the model to wind energy and Power-to-Gas (PtG) in Germany and Texas, two jurisdictions with rapid wind growth and different market structure. PtG is the conversion of electricity to hydrogen through water electrolysis and considered a suitable complement for intermittent renewable energy sources because of its dynamic operation and the renewably produced hydrogen for energy storage (Sterner and Stadler, 2014). We find that a wind-PtG hybrid energy system fails to have synergistic value today, in a sense that hydrogen production from renewable energy is not cost competitive with hydrogen production from fossil fuels. However, estimating learning curves and market development, we find that PtG may become cost competitive in combination with wind within the next decade. We also find that a feed-in premium for renewable energy, like in Germany, reflects a high opportunity cost for renewable energy conversion and thus prevents hybrid energy systems. We suggest reconsidering the feed-in requirement to enable the industrial decarbonization and reach climate goals.

**Keywords**: renewable energy, hybrid energy systems, decarbonization, power-to-gas

# Mine or ours? Willingness to pay for innovative battery storage concepts

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A decarbonized energy system is a key challenge on the path towards sustainability. Sustainable energy systems involve renewable energy sources that are characterized by a lack of temporal and spatial consistency. Battery storage systems can offset this intermittency, facilitate the integration of electricity from renewable sources, and enhance decarbonization – but they are still expensive technologies. Innovative business models can improve customer value and foster the diffusion of such systems. However, there is a lack of understanding on how to design appropriate business models for storage systems.

This study aims at analyzing relevant business model components for battery storage systems. We implement a choice experiment building on a model by Walker and Cass (2007). As Figure 1 shows, our framework consists of technology, economic factors, an implementation concept (i.e., residential vs. joint community systems), ownership mode, autarky levels, control and provision of grid services, and the partner company. Technology is defined as storage systems based on lithium-ion batteries.

| Technology | Economic factors | Implementation concept | Owner-ship mode | Autarky | Control and grid services | Partner company |
|---|---|---|---|---|---|---|

Figure 1: Framework for analyzing energy storage systems

We conducted an online survey in Germany during March and April 2016. Our analysis samples German adopters of a photovoltaic system (n=752) and interested non-adopters (n=84). In the choice experiment respondents had to choose among different battery storage systems (see Figure 2). We estimate a mixed logit model and present willingness to pay estimates for the business model components.

Almost 70 percent of the sample indicated willingness to purchase a system. Consumers prioritize cheaper systems and short payback periods. We find differing preferences as regards the concepts. Some end-users value residential and some joint community battery systems. Consumers prefer ownership over use rights. End-users desire autarky of 75% and higher. These findings extend recent research into autarky and confirm its importance. Consumers want assured control, but prefer full automation over low levels of control. We find support for business models that use storage systems as a means to contribute to grid operation. As regards operators, we find market opportunities for regional providers and cooperatives to control and maintain systems, but also for third-party operators, automotive or battery manufacturers.

|  | Option A | Option C | Option D |
|---|---|---|---|
| Location of the storage system | In your house | In your neighborhood | I don't choose any of the displayed options. |
| Costs and ownership mode | 12.000 € one-time payment | 85€ per month for 10 years | |
| | Ownership | Use rights | |
| Payback period | 18 Years | - | |
| Average level of autarky regarding electricity | 100% | 75% | |
| Control & provision of services for grid | Own control by default | External control by default | |
| Partner companies (e.g. maintenance and control) | Nationwide electricity supplier | Regional electricity supplier | |
| I choose: | ☐ A | ☐ C | ☐ D |

Figure 2: Exemplary choice set

Our study offers an informative foundation for policy makers and businesses to drive innovation in the field of energy storage. Potential for the residential and community storage concept with joint usage is found. Hence, possibilities for collaborative business models and resource sharing in the energy sector exist. The study's results can assist in creating customer-focused business models and diffusing storage systems. Collaborative business models could foster joint community systems and an orientation away from household-scale solutions to resource-sharing – indicating a step towards sustainability. Furthermore, simultaneous use of end-user and grid applications can provide financial benefits for parties involved.

# With innovative highlights towards a sustainable TUM Campus

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Sustainability is currently not only an extremely fashionable term, but also politically of great interest. To achieve sustainable development, the three pillars ecology, economy and society must be equally balanced. At present, economy runs mainly on burning fossil fuels. Therefore, the reconstruction of the energy sector has a key role in transforming society into a $CO_2$-neutral resp. sustainable one. The TUM Campus Garching has a high energy demand with time sequences typical for commerce, trade and service sites. Combined with its own energy supply system of fossil fuel power plants and grids, the campus represents an ideal test field for the transformation of a complex energy system. Based on various energy demand and $CO_2$ emission reduction scenarios this talk aims to encourage an interdisciplinary discussion on achieving a good trade-off between ecology and economics by demonstrating different future energy supply scenarios.

With more than 15,000 students and 3,500 employees the TUM Campus Garching is already ranked among the biggest university sites in Germany. If the rapid growth of previous years pertains, regardless of $CO_2$ emissions a realignment of the outdated energy supply is indispensable. Currently, the Campus Garching has an annual electricity and heat demand of 73 $GWh_{el}$ resp. 68 $GWh_{th}$. A flexible gas turbine cogeneration plant, a 3.9 $MW_{el}$ and 7.2 $MW_{th}$ Cheng Cycle, covers about half of the electricity demand and together with two 18.5 $MW_{th}$ gas boilers the complete heating demand on-site. The remaining amount of electrical energy is delivered by an external energy supply company. The cooling demand must be calculated due to the lack of measured data. The estimated 14 GWh of final cooling energy are provided by a combination of absorption chillers, electrical driven compression chillers and numerous split-system air-conditioning units.

To supply the future energy demand entirely on-site while simultaneously decreasing the specific primary energy requirement and emissions, the share of renewable energies and highly efficient cogeneration must increase. Therefore, especially low carbon state-of-the-art technologies, e.g. photovoltaics, gas engine cogeneration plants and geothermal heat, are considered as well as promising innovative technologies like fuel cell cogeneration plants such as solid oxide and molten carbonate fuel cells, "Naturwärmespeicher", etc.

The deployment of the considered technologies for a given energy demand is assessed by the optimisation tool URBS. This integer linear programming model calculates the most economic power system, that covers the electricity, heating and cooling demand as well as fulfils prescribed boundary conditions such as $CO_2$ emission limits at any point in time.

First results indicate that $CO_2$ reduction does not necessarily contradict with profitability. Except for very strict $CO_2$ limit values the annual total costs of the computed power systems are lower than the costs for the existing energy system. At current prices for $CO_2$ emissions, that are presently at the lower end of the range (with ca. 5 €/t), no direct incentive for $CO_2$ reduction is present and a trade-off between economic and ecological aspects must be made for the selection of the most sustainable energy systems. The goal is to set out different low carbon energy supply systems, that are resilient to changes in fuel costs, energy demands, $CO_2$ costs, etc. In view of the research mission of the university particular attention is payed to innovative technologies. By implementing these technologies, the TUM Campus Garching could contribute not only to the reduction of $CO_2$ emissions, but also to the possible breakthrough of an innovative supply technology.

# Nearly Zero Energy Laboratory Buildings?

Michael J. Keltsch

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The Energy Performance of Buildings Directive 2010 calls for the Nearly Zero Energy Standard for new buildings from 2021 onwards: Buildings using "almost no energy" are powered by renewable sources or energy produced by the building itself. For residential buildings, such an ambitious new standard has already been reached, but for other building types this goal is still far away. These building types make up only a small part of the annual volume of new construction but consume a relatively large amount of energy which cannot be covered by building and property-related energy generation. One of the most critical building types is the laboratory. Due to strict safety regulations, efficiency increases are difficult to implement. Nevertheless, laboratory buildings have great potential for reductions in energy consumption.
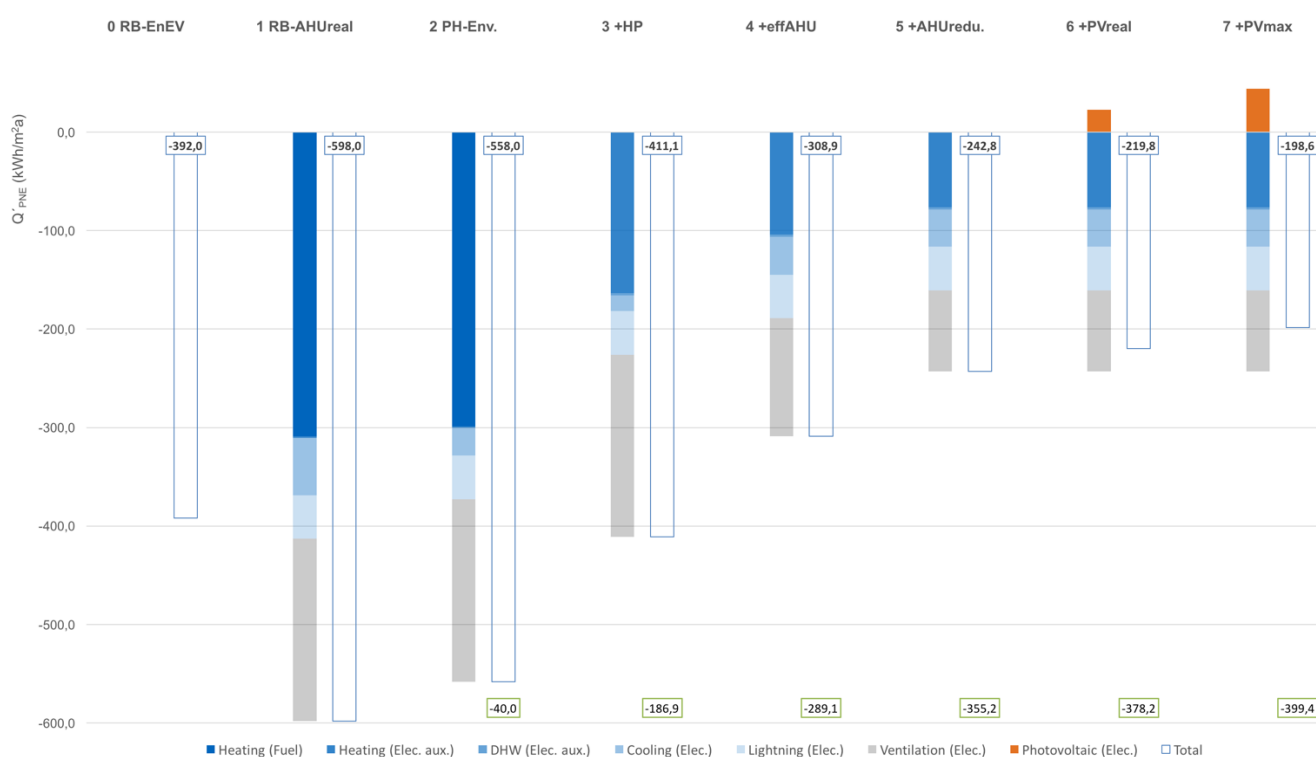


**Figure 1: Primary energy balance (Q'$_{PNE}$ (kWh/m$^2$a)) of the case study laboratory building balanced with stepwise measures of efficiency, consistency and sufficiency (own representation).**

This presentation shows the results of a study, which investigated a combination of measures from the areas of efficiency, consistency (renewable energy sources), sufficiency (user requirements) and coexistence (neighbourhoods). The main aim was to analyze the potential of these measures to support the realization of Nearly Zero Energy laboratory buildings. In terms of non-renewable primary energy demand laboratories can be improved by considerable 55% compared to a reference building according to DIN V 18599. For the Nearly Zero Energy Standard, as it is defined in this research on the basis of a data analysis of non-residential buildings, this is not sufficient. A case study will be presented that shows, that a Nearly Zero Energy Laboratory can be achieved virtually by including sufficiency and coexistence in an optimized way. However, these measures must be individually investigated and applied for each project and need the agreement and support of all involved parties.

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16

# 2. Poster Presentations

## Materials

# Controlling the nano-morphology of inorganic thin films for efficient solar energy conversion

Nuri Hohn[a], Michael Giebel, Wiebke Ohm, Stephan V. Roth, Thomas F. Fässler and Peter Müller-Buschbaum[b]

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The conversion of light into electricity is an indisputable promising option to tackle future energy supply shortages. Nowadays, standard devices to harvest this clean and abundant energy are commonly based on silicon (Si). With efficiencies exceeding 26% the market share to electricity generation is continuously increasing. Within this frame, the so-called energy payback time is of major importance when it comes to domestic and industrial applications. Since the fabrication of Si solar cells is a rather energy consuming process and the efficiency is very much dependent on the specific geographic circumstances, the energy payback time of such devices is still improvable. Furthermore, the rigid and heavy character of this type of devices complicates the integration into buildings. Current research aims to overcome the above mentioned first-generation challenges via the research of so-called third generation solar cells.
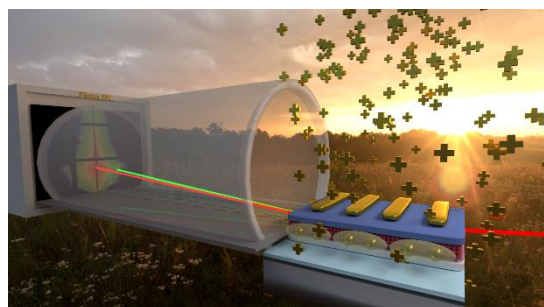


Figure 1: Morphology of a hybrid solar cell characterized via grazing incidence small angle X-ray scattering

Among those third generation solar cells inorganic-organic hybrid photovoltaics (HPV) face these challenges through combination of the advantages of both organic and inorganic materials. The inorganic material acts as a framework, which inhibits morphological degradation and contributes high charge carries mobility. In addition, the organic counterpart offers the possibility for large scale/low cost processability and flexibility. Thereby, the overall energy consumption during the fabrication can be reduced, which then leads to a reduced energy payback time [1]. Likewise, the integration into buildings is facilitated through the possibility of thin film printing or spray-coating of such devices.

Nevertheless, there is a vast range of possible candidates for inorganic components, which must fulfill several conditions to be suitable for a HPV device. Primarily, the possibility of infiltrating the layer with an organic hole-conducting material must be assured. Therefore, precise control over the degree of porosity and pore sizes on the nano-scale is of major importance. One promising pathway to build up such an inorganic framework consists of a polymer-templated sol-gel chemistry, which allows for the synthesis of high surface-to-volume ratio thin films.
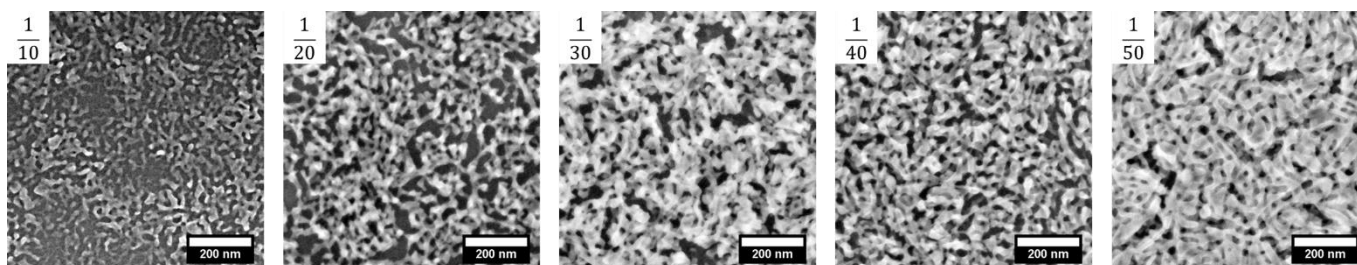


Figure 2: Nano-structured germanium thin films for hybrid photovoltaic applications with varying ratio of template to precursor

On this basis, a novel technique was established to control the nano-morphology of inorganic germanium thin films and, thereby, introducing a broad range of new possible material systems for HPV applications.

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# Hybrid thermoelectrics based on a polymer/nanoparticle composite

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The usage of fossil fuels has led to increased levels of greenhouse gases, which in turn result in devastating meteorological phenomena. Indications of this imminent change in global climate have, over the past years, been responsible for an increased interest in techniques for power generation based on renewable energies. Solar cells possess the ability to convert visible solar radiation into electrical power. While they are already highly efficient and have been implemented in daily life, it is also feasible to think of alternative ways of harvesting energy. Heat is lost in almost all processes which occur in daily life, which is evident looking at the heat production in the human body or in combustion engines in cars. It is desirable to transform this low-quality form of energy into high-quality energy in the form of electrical power.

Thermoelectric materials are able to generate an electrical voltage upon application of a temperature gradient along the material. The gradient leads to a flow of charge carriers from the hot to the cold side and therefore to an imbalance in the charge distribution. The occurring thermovoltage or Seebeck coefficient (S), along with electrical ($\sigma$) and thermal conductivity ($\kappa$) can be put into the following equation for the temperature-dependent figure of merit ZT, which directly correlates to the energy conversion efficiency at a given average temperature: $ZT = (\sigma S2/\kappa)T$.

Although inorganic thermoelectrics based on elements such as Te, Se, Pb, Bi, As, etc., exhibit high values for ZT, the price, low abundance, potential toxicity and environmental concerns regarding the raw materials have impeded the large-scale application for heat conversion.

Using the electrically conducting polymer blend PEDOT:PSS, we want to overcome the limitations of inorganic thermoelectrics, by making use of the high abundance of raw materials, facile solution-based processing and lowered toxicity. In literature, many different procedures for improving the electrical conductivity, usually by treating thin films with high-boiling solvents or other chemical agents, have been shown [1].

In our approach, we wish to tune the thermoelectric parameters, especially the thermal conductivity, by means of nanostructuring using inorganic nanoparticles. While maintaining a high electrical conductivity it should reduce the thermal conductivity through phonon scattering. We are able to fully characterize the polymer films regarding their thermoelectric properties, by using standard techniques for determination of S and $\sigma$ and IR thermography for determination of $\kappa$. This enables the calculation of ZT values for PEDOT:PSS thin films. In addition, we performed resonant tender x-ray scattering (R-TeXS) experiments on the PEDOT:PSS/Si-NP composite films using synchrotron radiation energies close to the sulfur K-edge. Using the contrast variation capabilities of this technique, we are able to devise a structural model and attempt to correlate this with the thermoelectric properties of the composite films [2].

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[2] N. Saxena, A. Greppmair, M. Coric, J. Wernecke, M. Pflüger, M. Krumrey, E. M. Herzig, M. S. Brandt, P. Müller-Buschbaum, submitted

# What do Laser Induced Transient Techniques reveal for the Electrochemical Systems?

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The great urgency of finding new energy sources resulted in an upsurge in the electrocatalysis and battery research. However, optimization and improvement of various energy conversion and storage systems require a better understanding of the electrochemical processes limiting their performance. Thus, further development of new in-situ characterization methodologies is of great importance. One of the methods providing a deeper insight into the electrode/electrolyte interface processes is the laser induced current transient (LICT) technique. This technique can be easily combined with other commonly used methods (i.e. cyclic voltammetry, electrochemical impedance spectroscopy and electrochemical nanogravimetry), providing a powerful tool for detailed characterization of various systems.

The LICT method utilizes the so-called temperature jump effect.[1] The rapid illumination of the electrode surface results in an increase in its temperature directly influencing the inner Helmholtz plane of the electric double layer.[2] As a consequence, one observes current transients whose sign, in the simplest case, corresponds to the sign of the excess electrode surface charge. The LICT is also a relatively simple technique of evaluating the potential of maximum entropy (PME) and, closely related to it, the potential of zero charge (PZC)- the fundamental properties of the electric double layer.

We present for the first time the results of the in-situ LICT technique implementation for battery systems investigating $Na_2Ni[Fe(CN)_6]$ thin films as model electrodes. Surprisingly, the electrode surface charge stays positive within the whole potential range of intercalation/de-intercalation of sodium (Figure 1) and potassium cations from aqueous media. This indicates that the complexity of intercalation mechanisms of alkali metal cations into the films might be over-simplified. Further, we demonstrate the influence of the electrolyte pH on the net charge of the Pt(poly) electrode surface. Apparently, the behavior of the system is not only governed by the concentration of $H^+$ cations but also by the metal cations present in the electrolyte.
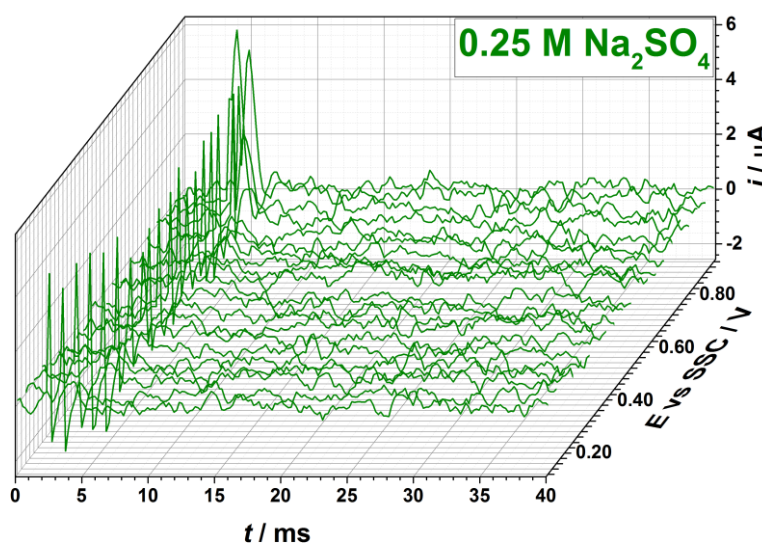


**Figure 1. LICT characterization of the $Na_2Ni[Fe(CN)_6]$ film in aqueous 0.25 M $Na_2SO_4$.**

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# Investigation of an n-type conducting polymer for potential use in all-polymer thermoelectric generators

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Thermoelectric generators are a promising approach in renewable energies, as they are able to convert waste heat into electricity. Possible applications are large scale applications like recovering the waste heat of a car engine as electricity as well as niche applications like using the heat emitted by human skin to drive a watch.[1]
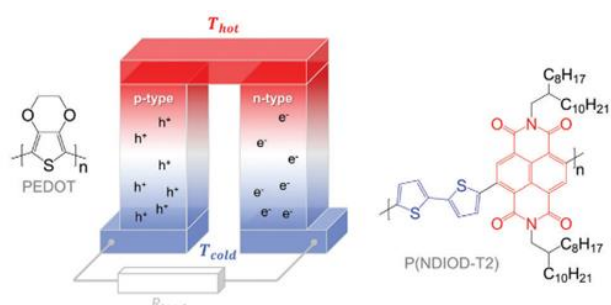


**Figure 1: Sketch of a thermoelectric generator and the chemical structure of the investigated n- and p-type polymers next to the respective leg (modified from [2]).**

In practice, a thermoelectric generator traditionally consists of a p- and an n-type semiconductor electrically connected as shown in Fig. 1.

In order to put the device into operation, a temperature gradient is applied along the legs. As a consequence, charge carriers, i.e., holes in the p-type and electrons in the n-type leg, respectively, diffuse from the hot to the cold side. This diffusion current causes a build-up of charge at the cold end that can be extracted by connecting a load. All in all, a thermoelectric generator is able to convert a temperature gradient into electric energy.

To build high efficiency thermoelectric devices, suitable thermoelectric materials are needed. Unfortunately, state-of-the-art thermoelectric materials have the drawback of using toxic or less abundant constituents, making it necessary to look for alternatives. One promising approach to overcome such challenges is to use conjugated polymers. They have the encouraging ability of easy and various types of scalable solvent processes like roll-to-roll printing. Although they are still less efficient than their inorganic counterparts, their potential flexibility and eco-friendliness make them a valuable alternative.

Various, especially p-type, conducting polymers have been investigated as thermoelectric materials. A very promising candidate among them is the hole-conducting PEDOT. Unfortunately, n-type polymers have rather been neglected which might stem from their low stability towards oxygen and moisture. Nonetheless, both types are needed for a thermoelectric device as explained before. Therefore, we also focus on the thermoelectric properties of the n-type polymer P(NDI2OD-T2). Its successful application to transistors [3] and solar cells [4] encourages an auspicious attempt in building an all-polymer thermoelectric generator. Both polymers which are investigated in our group are shown in Fig. 1 next to the leg where they are of potential use.

The main focus of this work is to enhance the so-called power factor $pF = \sigma \cdot S^2$ where $\sigma$ is the electrical conductivity and $S$ is the Seebeck coefficient. As already indicated by its name, the larger the power factor the larger the power output and subsequently the efficiency of the device.

Therefore, we successfully doped P(NDI2OD-T2) with an organic small molecule which can even be seen in a color change depicted in Fig. 2. The experiment resulted in a maximum power factor of $(1.2 \pm 0.08)\ \mu W\ K^{-2} m^{-1}$.



**Figure 2: Color change of polymer upon doping**

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[1] G. J. Snyder, The Electrochemical Society Interface (2008)
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# Investigation of ZnO scattering layers for OLED applications

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Organic light emitting diodes (OLED) are an interesting alternative to conventional lighting techniques as the significantly reduced operation power enables large energy savings. Given the amount of energy spent in lighting such type of new technology would significantly contribute to a reduction in energy consumption. OLEDs are based on thin film technology and enable transparent and flexible devices. During the last years their initial main problem, a limited lifetime, was overcome which allows commercial use. However, still some improvements are necessary. OLEDs are reaching inner quantum efficiencies close to 100%, but the overall efficiency of conventional devices is limited to about 20% mainly by the photon extraction. The other photons are either trapped in substrate and organic modes or are subjected to internal total reflection and finally get absorbed.
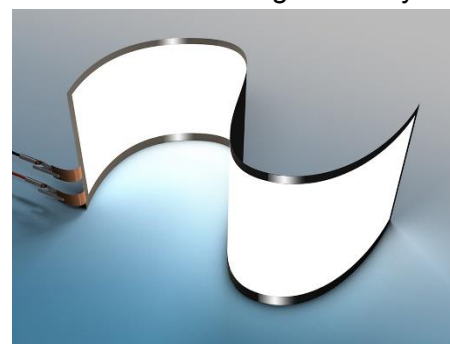


**Figure 1: Sample flexible OLED by Schott [1]**

One approach to overcome this issue is the implementation of an additional scattering layer into the device. This layer can either be created by a direct surface structuring or the introduction of an additional transparent layer. ZnO is a suitable choice for the latter due to its transmittance in the entire visible spectrum, caused by its direct optical band gap of 3.3eV. This scattering layer is inserted between the transparent substrate and the devices bottom electrode. This architecture means either using the ZnO layer as an electrode itself by building an inverted OLED or using an ITO-free device on top. The scattering layer is deposited via spray coating directly on a glass substrate. The micro- and nanostructure of ZnO can be adjusted by combining a structure-giving diblock copolymer with sol-gel chemistry, the insertion of polymer nano spheres as well as variations during the calcination step.
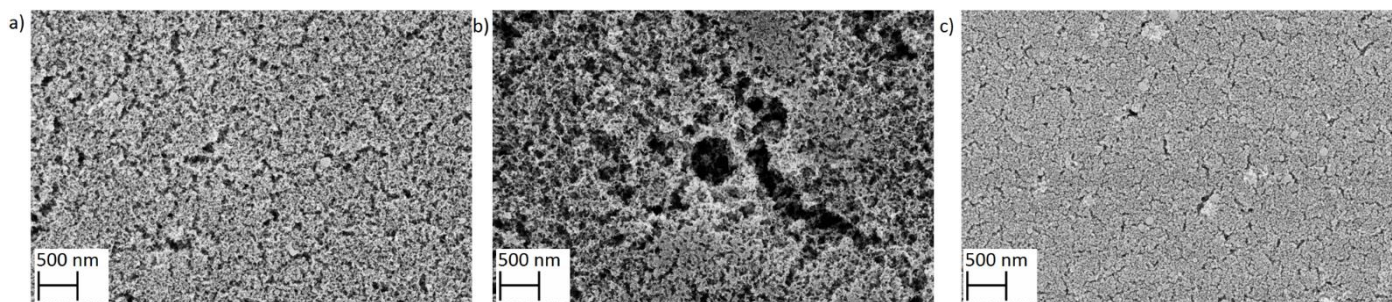


**Figure 2: SEM images of three differently prepared ZnO layers**

The OLED itself is based on the simple standard architecture using the commercially available emitter Super Yellow, featuring the addition of additional transporting layers to improve the efficiency as well as being ITO-free. It is investigated how different structuring and thicknesses of the scattering layer influence the angular resolved transmission of light. Furthermore, it is researched if the addition of a scattering layer into an OLED leads to changes regarding the I-V curve as well as the external quantum efficiency.

[1] http://www.schott.com/newsfiles/com/foto_tesa_oleds_bildschirm.jpg

# Facile Wet-Chemical Synthesis of Microporous Ge Thin Film with Inverse Opal Structure as Anodes for Lithium Ion Batteries

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Silicon and germanium are of great interest as anode materials for lithium ion batteries due to their large theoretical energy densities. Germanium is less abundant but stands out due to its two orders of magnitude higher lithium ion diffusivity and four orders of magnitude higher electronic conductivity than silicon. [1]

Herein we report a straightforward synthetic route to inverse opal structured Ge anodes for lithium ion batteries starting from the soluble binary alloy $K_4Ge_9$. The presented method involves controlled coupling of $[Ge_9]^{4-}$ clusters in a poly(methyl methacrylate) (PMMA) scaffold. Based on a synthetic protocol developed before for thin film solar cells on a wide variety of substrates (silicon, silica, sapphire, FTO, ITO)[2] we now designed Ge films on copper substrates to be used as electrodes and performed electrochemical measurements to investigate their cycling performance and rate capability.



Figure 1: SEM micrograph of a Ge film on a copper substrate.

Morphological analysis of the obtained films by scanning electron microscopy (SEM) displays the formation of ordered mesoporous networks. The prepared electrodes show high capacities and capacity retentions and outstanding rate capabilities. The very high capacity retention after a small initial capacity fading makes them promising candidates for long life applications. The very simple preparation method theoretically allows for easy up-scaling and industrial-scale application.[3]

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[3] S. Geier, R. Jung, K. Peters, H. A. Gasteiger, D. Fattakhova-Rohlfing, T. F. Fässler, *manuscript in preparation* **2017**.

# Morphology improvement of ZnO/P3HT-b-PEO bulk heterojunction films by using a low temperature route

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Hybrid solar cells, a combination of conventional inorganic and organic photovoltaic systems, offer outstanding potential due to their minor investment compared to inorganic solar cells and higher stability compared to organic solar cells. In this kind of cells, nanostructured inorganic metal oxides with tunable morphologies are of great importance. Among the inorganic metal oxides, ZnO has been widely explored due to its outstanding electrical and optical properties and rich variety of morphologies. To date, many different routes towards ZnO nanostructures have been reported, such as hydrothermal synthesis, metal–organic chemical vapor deposition and so on, of which sol-gel process is one of the most widely used methods in solar cells due to the production of a homogeneous material and fabrication of ceramic coatings from solutions by chemical means. However, the structures obtained by the sol-gel process are limited, regarding both morphologies and structure sizes. A possible way to improve the film structure is to introduce amphiphilic block copolymers into sol-gel process. The hydrophilic and hydrophobic polymer blocks of amphiphilic block copolymers are covalently bound, which could modify the interface of ZnO. Unlike the traditional diblock copolymer, in the present approach we make use of a new functional block copolymer PEO-b-P3HT. In the PEO block the ZnO phase is synthesized and the P3HT block can be used directly as the hole transporting layer.

GISAXS is a powerful analysis tool, which could detect the nanostructure inside thin films. Moreover, SEM and AFM detect the surface morphology of the composite films. The optical properties are examined with UV/Vis spectroscopy and the thickness is investigated by profilometry measurements.
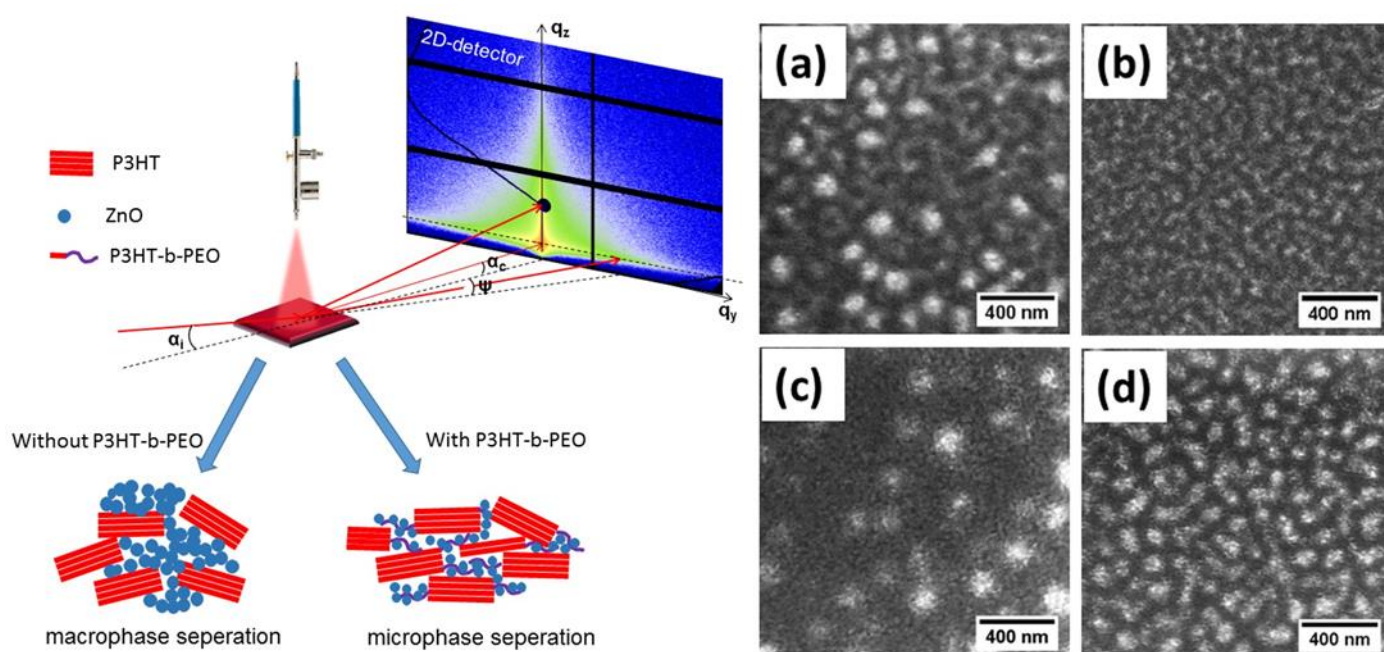


Figure 1: Scheme of the sprayed samples and the SEM images of the prepared composites.

# Morphology of perovskite-based hybrid solar cells

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Hybrid organometal perovskites, which are of the form $ABX_3$, where A is an organic cation (most commonly $CH_3NH_3$), B is a divalent metal ion (like Pb or Sn) and X is a halide (or a mixture of halides), have been shown to be great candidates for photovoltaics, owing to the strong absorption, and high mobility and diffusion length of photo-generated charge carriers. Subsequently, solar cells employing perovskite thin films have reached efficiencies of more than 20% [1], making them comparable with commercially available silicon solar cells. Perovskites offer huge versatility and tunable properties by modifying the cation, metal, and halide components. Solution processing can be used to achieve low-cost manufacturing of these solar cells. Despite all this, such cells have stability issues against humidity and UV light, are not reproducible, and contain toxic materials.
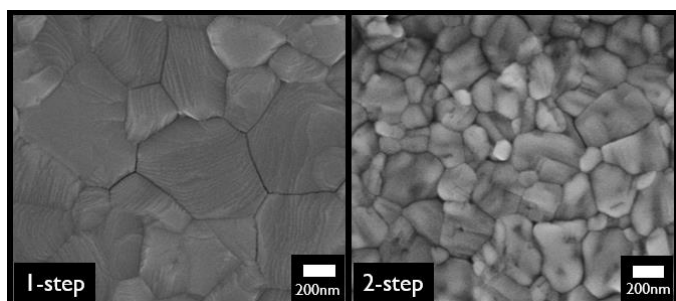


**Figure 1: Scanning electron microscopy images showing differences in the 1-step vs 2-step preparation methods**

The performance of perovskite solar cells greatly depends on their crystal morphology, which in turn seems to be affected by the preparation route adapted. We focus here on the composition methylammonium lead iodide ($CH_3NH_3PbI_3$). We follow the commonly advocated one-step and the two-step method approaches for perovskite synthesis. The one-step method used involves mixing lead iodide and methylammonium iodide (MAI) in a mixed 4:1 DMF:DMSO solvent [2], and adding chlorobenzene as an anti-solvent during spin-coating of the perovskite layer. The two-step method has lead iodide and MAI spin-coated on the sample, one after the other, wherein some delay is introduced in the second step between adding the MAI and starting the spin-coating process (usually referred to as "loading time") [3]. All samples are annealed after spin-coating.

We vary the annealing time, annealing temperature and the loading time of these methods and study the differences in the resulting perovskite by means of UV-Vis spectroscopy, photoluminescence measurements, scanning electron microscopy (SEM), X-ray diffraction (XRD) and grazing incidence wide angle X-ray scattering (GIWAXS). After optimizing these parameters based on the results from our measurements, we focus on building solar cells of the architecture FTO/planar titania/perovskite/spiro-OMeTAD/gold. The best performing solar cell achieved an efficiency of 13.2%. It is seen that our cells exhibit considerable hysteresis, where in the current-voltage curves depend on the direction and speed of the voltage scan.

In addition to this, we perform in-operando X-ray scattering measurements on our solar cells at room temperature and elevated temperatures to better understand the morphological changes under operating conditions, including the changes associated with hysteresis.



$J_{sc}$= 18.293 mA/cm$^2$
$V_{oc}$ = 1.106 V
$J_{MPP}$ = 18.316 mA/cm$^2$
$V_{MPP}$ = 0.722 V
FF = 65.354%
PCE = 13.217%
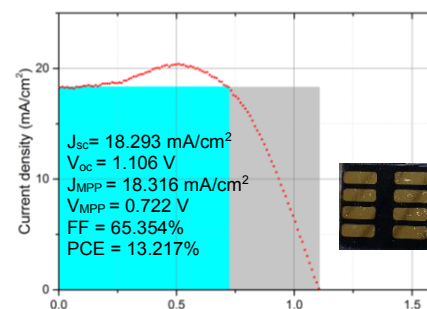
**Figure 2: Current-voltage curve of the best cell**

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# Lithium ion mobility in lithium rich phosphidotetrelates

Henrik Eickhoff, Stefan Strangmüller, Lorenzo Toffoletti, Holger Kirchhain, Johannes Landesfeind, Christian Dietrich, Wilhelm Klein, Wolfgang Zeier, Leo van Wüllen[a], Hubert A. Gasteiger[b], Jürgen Janek[c], and Thomas F. Fässler[d]

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Recently lithium phosphidosilicates have been reported to exhibit ionic conductivities higher than $10^{-5}$ S/cm making this material class a possible solid electrolyte for rechargeable all-solid state batteries. Of this diverse group of compounds the most promising properties are found in the compound $Li_8SiP_4$.[1] Herein we report revised ionic conductivities of $Li_8SiP_4$ for highly densified samples and present the two isomeric lithium phosphidogermanates $\alpha$-$Li_8GeP_4$ and $\beta$-$Li_8GeP_4$ and the lithium rich isotypic phosphidotetrelates $Li_{14}SiP_6$ and $Li_{14}GeP_6$.

The ionic conductivity determined with impedance spectroscopy of $\alpha$-$Li_8GeP_4$ and $\beta$-$Li_8GeP_4$ ranges from $1.81 \cdot 10^{-5}$ S/cm and $8.12 \cdot 10^{-5}$ S/cm, respectively, at room temperature to $1.69 \cdot 10^{-4}$ S/cm and $6.56 \cdot 10^{-4}$ S/cm at 75 °C. Resulting Li-ion hopping energies of 42.2 kJ/mol and 38.8 kJ/mol are slightly higher than values of 35 kJ/mol and 34 kJ/mol obtained from temperature dependent $^7$Li-NMR spectroscopy. NMR measurements of $Li_{14}SiP_6$ and $Li_{14}GeP_6$ revealed even lower hopping energies of 30 kJ/mol for both compounds, suggesting higher ion mobilities.



All compounds were synthesized from elements via ball milling and subsequent heating in resistance furnaces or, for highly densified samples, in spark plasma sintering systems. The compounds were structurally characterized by X-ray diffraction methods. While $\alpha$-$Li_8GeP_4$ and $\beta$-$Li_8GeP_4$ are solely composed of ordered $[GeP_4]^{8-}$ tetrahedra in a lithium matrix, in $Li_{14}SiP_6$ and $Li_{14}GeP_6$ occur $P^{3-}$ ions next to $[SiP_4]^{8-}$ or $[GeP_4]^{8-}$ tetrahedra. Silicon or germanium atoms fill with lithium a statistically occupied sublattice in a cubic closed pack of phosphorous atoms.
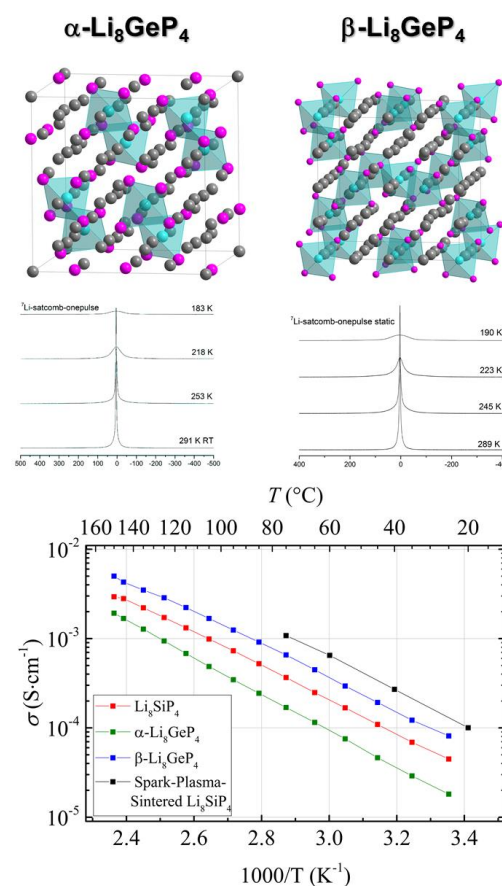
[1] Lorenzo Toffoletti, Holger Kirchhain, Johannes Landesfeind, Wilhelm Klein, Leo van Wüllen, Hubert A. Gasteiger, and Thomas F. Fässler, Chem. Eur. J. 2016, 49, 17635-17645

# Introducing small band-edge semiconductor nanocrystals in organic solar cells

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Semiconductor nanocrystals (NCs) have been widely used in light emitting diodes (LEDs), photodetectors as well as photovoltaic devices due to the attractive characteristics like tunable energy levels, low cost of fabrications, low materials utilization and etc [1-3]. Comparing with current organic photovoltaics (OPV) or perovskites photovoltaics, NCs based photovoltaic devices still present attractive advantages on the stability about not only the final device operation but also the fabrication process [2,3]. For example, NCs based solar cells could be fabricated in air ambient conditions without any specified facilities like glove box, which make it more suitable for low-cost mass production. Moreover, the performance of NCs based photovoltaics device has reached a certified power conversion efficiency (PCE) of 10.6% by employing surface optimized lead chalcogenide NCs (PbX) [3].
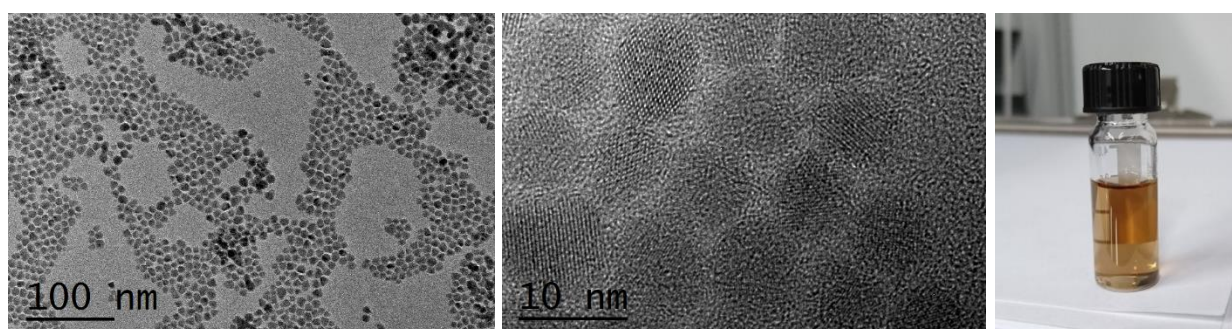


Figure 1: TEM (left), HRTEM (middle) and photograph of as prepared NCs

Although great progress has been made by the surface chemistry engineering on mentioned lead chalcogenide NCs and therefore improved the device performance, the toxicity of lead remains an issue which is also cannot be ignored [4]. Moreover, the NCs were supposed to absorb large area from the spectrum, so the band gap of NCs was required to be designed as small as possible.

In this work, we have fabricated NCs without toxic metal elements. The band gap of the NCs was designed around 1.5 eV determined from the photoluminescence spectrum, as seen in Figure 2. Moreover, we have also introduced the NCs into our organic solar cells as additional acceptor components by optimizing of absorption behavior of active layer. Additionally, we have fabricated pure NCs active layer solar cells. The surface engineering by specified organic regents or inorganic regents on the NCs was supposed to improve the charge transportation in our solar cells and therefore improve the device performances.
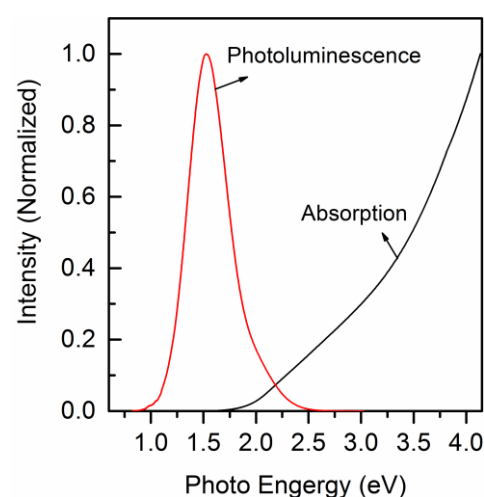


Figure 2: Photoluminescence and absorption spectrum of as prepared NCs in photovoltaics

References:

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[3] Lan, X. *et al Nano Lett.* **2016**, 16, 4630.
[4] Bernechea, M. *et al Nat. Photonics* **2016**, 10, 521-525.

# Investigation of titania thin film morphologies via GISAXS and SEM for hybrid solar cells

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As the need for sustainable energy sources is steadily increasing, the concept of photovoltaics has attracted both scientific and economic interest. Whereas conventional semiconductor-based solar cells are already well researched and their efficiencies are promising, their energy need for the mere production and their lack of versatility remain a major drawback. Therefore, concepts are needed, which combine competitive efficiencies with the possibility for energy-inexpensive large-scale production. Hybrid solar cells, which combine the mechanical stability of inorganic semiconductors and the versatility of organic semiconductors, meet these criteria. Titania thin films as an inorganic material in combination with a conjugated polymer as an organic semiconductor are common for application in hybrid photovoltaics. Excitons are generated via light absorption in the p-type conducting polymer and split at the interface of the two compounds due to the band offset. Afterwards, the electrons are transported in the titania and the holes in the p-type polymer respectively.

Due to the restriction of the charge separation to the interfacial area, a nanoscale structure of the active layer is necessary in order to enhance the charge separation. Therefore, mesoporous titania structures, which serve as a matrix for infiltration with the polymer are a promising concept for high-efficiency active layers. Challenges concerning this concept arise due to the difficulty of the infiltration with the polymer, since occlusion of the pores in the upper part of the layer can occur and prevent backfilling of pores in lower parts of the layers. Accordingly, ways to control the structure of mesoporous titania films are of major importance.

We focus on the tuning of the pore size of mesoporous. In our experiments, a solution composed of an amphiphilic block copolymer as a structure-directing agent and a precursor dissolved in an organic solvent is applied as a wet film. Immersion in an antisolvent after an evaporation step leads to a structure formation process in the composite film, so that the morphology depends both on the evaporation time and the immersion bath. By controlling the evaporation step, the porosity of the film can be tuned. After calcination, mesoporous titania films are obtained. The films are characterized concerning their suitability for photovoltaic application, which regards their morphology, crystallinity and thickness. Surface morphologies are experimentally investigated by scanning electron microscopy as well as atomic force microscopy. These methods are suited for the estimation of the porosities of the film and for showing the dependence of the morphology on the processing parameters. In addition to the surface morphology, also the inner morphology is investigated. Therefore, grazing incidence small angle X-ray scattering is applied as a non-destructive method to probe the deeper layers.
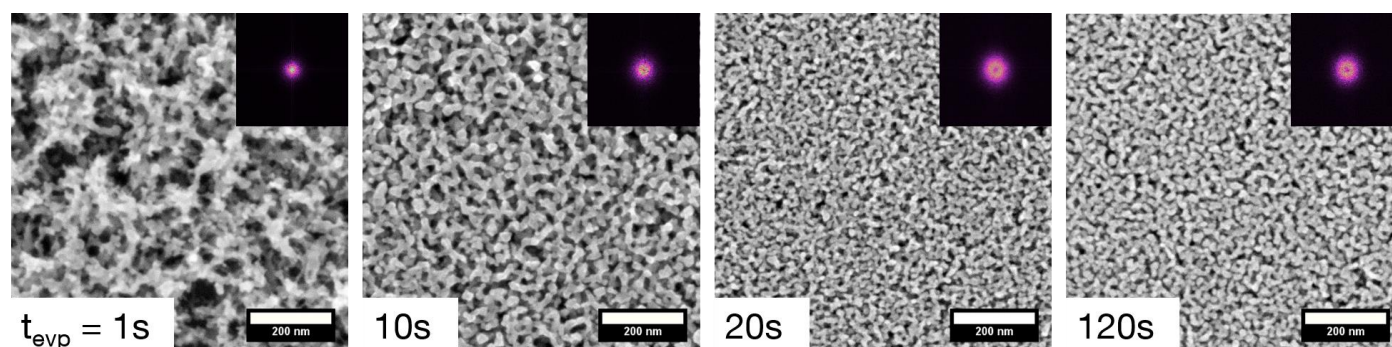


**Figure 1: surface morphology of titania thin films with dependence of evaporation time before immersion**

# Germanium-based hybrid photovoltaics

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Electricity is needed in many situations of our daily life at many different locations around the globe. Solar energy has the major advantage that the conversion process light/energy is simply available during daylight. It does not have to be actively transported or stored and is free of political control. Therefore, a strong interest in solar energy conversion has manifested over the last decades with solar cells taking the role of converting solar energy to electricity.

Hybrid solar cells are a promising technique for future energy generation as they combine the advantages of organic and inorganic solar cells. Organic materials are solution processable. Thus, they enable large scale and cheap production with little energy demand. They also allow for thin film devices sparing scarce resources. Furthermore lightweight and flexible cells are suitable for new applications. On the other hand the usage of inorganic material provides high charge carrier mobility and avoids degradation, which enhances HPV lifetime stability.

Starting from an organic solar cell, the main objective is to incorporate an inorganic component into this structure in order to make a hybrid photovoltaic device. In this case, we use a wet chemical precursor for the germanium layer. First for this work, we focus on an inverted geometry system, which includes an additional compact titania blocking layer (figure 1). Therefore, the approach is to characterize and optimize every step of this organic system, especially the active layer which strongly influences the efficiency of the solar cell. Thus, its morphology needs to be optimized and a homogenous film is desirable. In order to achieve this, we investigate the different layers using several techniques such as an optical microscope (figure 2), UV-Vis (figure 3), Dektak, and a solar simulator. With these facilities, we are able to enhance our way of working, and thus in short term to integrate the germanium layer into it as the electron conductive film.
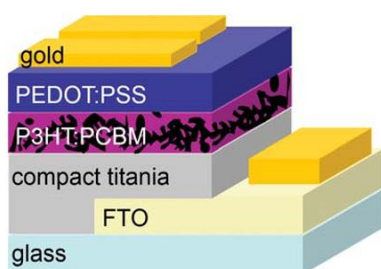


**Figure 1: Inverted organic solar cell [1]**



**Figure 2: P3HT layer in optical microscope**
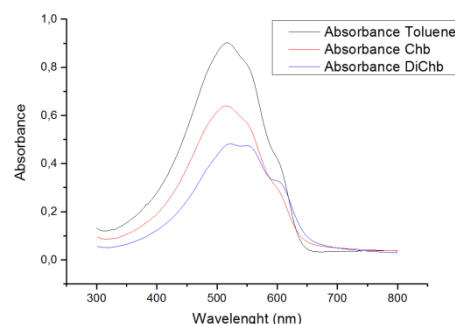


**Figure 3: Spectrum of the P3HT layer absorbance made with different solvents**

Reference:

[1] Weijia Wang, Christoph J. Schaffer, Lin Song, Volker Körstgens, Stephan Pröller, Efi Dwi Indari, Tianyi Wang, Amr Abdelsamie, Sigrid Bernstorff and Peter Müller-Buschbaum, J. Mater. Chem. A, 2015, 3, 8324

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29

# Computational hydrogen electrode modelling of water electrolysis at iridium oxide nanoparticles

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IrO$_2$ is the primary active anode component of proton-exchange membrane cells for water electrolysis in acidic operating conditions. Its superior performance has generally been rationalized through the optimized binding of relevant reaction intermediates at IrO$_2$ (110) as assessed within the computational hydrogen electrode (CHE) approach based on density-functional theory (DFT) calculations. At present, it is unclear though whether this level of theory is sufficient to guide ongoing activities that aim at improving the anode activity and stability through nanostructuring and doping. To this end we revisit critical practical components of the CHE approach, such as the employed DFT functional or the degree of hydroxylation under operating conditions. Extending the calculations to other low-index facets allows to attempt a first description of IrO$_2$ nanoparticles through an ab initio thermodynamics based Wulff-construction.

# *In situ* small angle X-ray scattering investigation of solid-state polymer electrolyte for lithium-ion batteries

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Many present problems regarding the safety of liquid electrolytes in lithium-ion batteries may potentially be overcome by the use of solid-state polymer electrolytes. Polystyrene-block-polyethylene oxide PS-b-PEO diblock copolymer (DBC) electrolyte have been recently investigated as a membrane for Li-ion battery. The performance of these DBC electrolytes strongly depends on its morphology, serving highly oriented PEO domains as pathways for lithium ions migration. Thus, in situ structural investigation of these Li-ion doped DBCs systems during cycling in an operating battery is essential, which can be done by neutron or X-ray small angle scattering. In situ small angle neutron scattering on a working pouch cell has been performed, which proved the structural stability of the polymer electrolyte. Also, capillary-based micro-battery cell allowing simultaneous electro-chemical and structural evaluation by X-ray scattering has previously been reported [1].
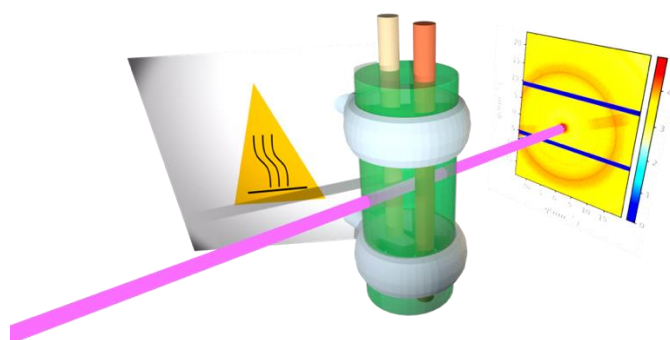


**Figure 1: Schematic of the in situ SAXS setup.**

The current in situ small-angle X-ray scattering (SAXS) study of the solid-state polymer electrolytes using a modified version of the micro-battery cell provides a deeper insight into the structural modification. Figure 1 shows the currently used setup used for the X-ray experiments. A battery cell is assembled inside a glass housing, consisting of a flat capillary tube. Lithium iron phosphate (LFP) and lithium/graphite (Li/C) are used as cathode and anode active materials for this system. Composite electrodes as well as the polymer electrolytes are prepared by solution casting onto copper current collectors [2].

Figures 2 and 3 show 1d radial averages of the SAXS data acquired while cycling the battery for LFP/C (2) and LFP/Li (3) cells. While the system with the graphite anode shows a stable structure over big number of cycles, the LFP/Li system is less structured from the beginning of the measurements and loses the remaining ordering over cycling. The influence of the lithium metal on the polymer electrolyte and the interface between the two layers will be further investigated in this work in order two determine the applicability of lithium metal anodes.

[1] R.E. Johnsen, P. Norby, J. Appl. Cryst. (2013), 46, 1537.
[2] R. Bouchet, S. Maria, R. Meziane et al., *Nature materials* (2013), 12, 452-7
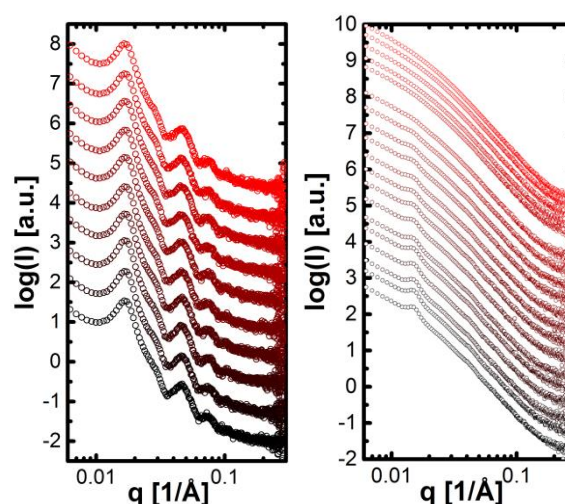
**Figures 2 and 3: 1d radial averages of the SAXS data acquired during the cycling of a LPF/C (left) LFP/Li cell (right).**

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31

# Selective ex-situ sulfur poisoning of co-precipitated NiAlOx catalysts

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Catalyst deactivation due to sulfur poisoning is a common problem for a wide range of catalytic processes. Examples include petrochemical processes, methanol synthesis and methanation reactions. Only trace amounts of gaseous sulfur ($H_2S$, thiophenes, thioles, etc.) bind irreversibly to the active sites, leading to a rapid and hard-to-regenerate loss in activity and/or selectivity. As a result of poisoning, catalyst beds suffer from a reduced lifetime and need to be exchanged more frequently, leading to an increase in production costs. In the future the impact of sulfur poisoning might even become more significant, since the chemical industry has begun to move from comparable clean feedstocks, such as natural gas and crude oil, to alternative feedstocks, such as bitumen tars and some forms of biomass. Therefore, the demand for catalysts with the ability to operate in the presence of higher levels of poison is possibly increased.
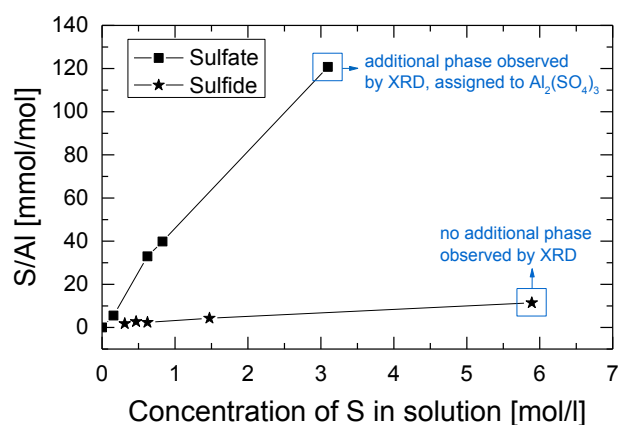


**Figure 1: γ-Al2O3 impregnated with different amounts of sulfate or sulfide in solution, dried and calcined.**
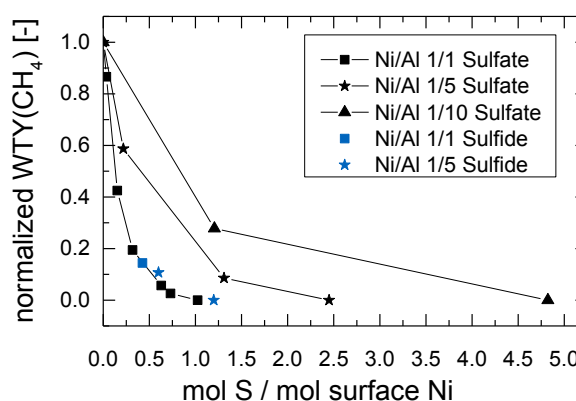


**Figure 2: Normalized weight time yield of CH$_4$ at 300 °C over moles of sulfur per moles of surface nickel (H$_2$ chemisorption).**

The current study aims at understanding the poisoning effect of sulfur on the methanation reaction of $CO_2$ over NiAlO$_x$ systems, using an *ex-situ* impregnation method. Therefore, catalysts with different Ni/Al ratios have been prepared by a co-precipitation recipe described elsewhere and poisoned in a subsequent step, using an aqueous solution with varying concentrations of either $(NH_4)_2SO_4$ or $(NH_4)_2S$. In order to study the role of the supporting Al-species, the poisoning step was also carried out for pure γ-Al$_2$O$_3$. The actual S-loading was determined by CHNS and the Ni/Al ratio by ICP-OES analysis of the calcined catalyst. The active metal surface area of the activated, non-poisoned samples was determined by H$_2$ chemisorption. XRD was applied to monitor possible phase changes in the poisoned samples. The performance of the activated catalysts was analyzed in a plug flow reactor apparatus.

Elemental analysis of pure γ-Al$_2$O$_3$ treated with sulfate and sulfide lead to the conclusion, that there is a stronger interaction between sulfate and the support than with sulfide. This was confirmed by XRD analysis of γ-Al$_2$O$_3$ treated with saturated solutions of $(NH_4)_2S$ and $(NH_4)_2SO_4$ (Figure 1). After calcination, an additional phase was detected in the latter case, which was assigned to aluminum sulfate. Contrarily, no additional phase was observed in the case of $(NH_4)_2S$. Catalytic tests also gave different results depending on the type of the used precursor (Figure 2). Catalysts treated in $(NH_4)_2SO_4$ were observed to anneal more moles of sulfur per mole surface nickel at low nickel loadings and vice versa. Catalysts treated in $(NH_4)_2S$ did not show a dependency on nickel loading. Therefore, we assume that selective poisoning of low loaded Ni/Al(O)$_x$ catalysts is only achieved in sulfide solutions, whereas impregnation with sulfate might lead to an overestimation of the sulfur tolerance.

# Deactivation of Ni catalysts for CO$_2$ methanation

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Although it was first described in 1902, the hydrogenation of CO$_2$ has only recently come back into the focus of research as an efficient method to store renewable energy [1]. Since the rediscovery of CO$_2$ methanation, a broad range of active metals, promotors and support materials have been investigated. However, detailed deactivation studies and information about deactivation kinetics remain scarce. In this contribution a systematic deactivation study of precipitated Ni catalysts is presented comprising both standard and transient characterization techniques. A kinetic description of the deactivation behavior is derived.

Catalysts with varying Ni loadings were synthesized via co-precipitation of the corresponding metal nitrate solutions [2-3]. Deactivation studies were conducted at 623 K in a setup equipped with four simultaneously operated fixed bed reactors. The feed gas composition during deactivation was H$_2$/CO$_2$/Ar/N$_2$ = 8/2/5/1 with a flow rate of 15 sccm. Periodic activity measurements were performed at 523 K under differential conditions. Results indicate that catalyst stability is improved with decreasing Ni/Al ratio (not shown here).

For a more detailed deactivation study a catalyst with Ni/Al = 3 was chosen. After 0 h, 25 h, 95 h and 165 h of reaction a catalyst sample was removed from the aging setup under inert gas atmosphere for characterization. Transient characterization methods, such as temperature-programmed desorption of hydrogen (H$_2$-TPD) and pulsed hydrogen adsorption, were conducted in a single-pass setup. For the kinetic description of the deactivation the power law model (PLM) in equation 1 was applied.

$$\frac{da_{rel}}{dt} = -k_d \cdot a_{rel}(t)^m \qquad \text{with} \qquad a_{rel}(t) = \frac{WTY\,(t)}{WTY\,(t=0)} \qquad (1)$$

The results of the PLM fit depicted in Figure 1 match the experimental data. The rate constant can be calculated to $k_d$ = 2.1 h$^{-1}$ and the reaction order is m = 8.4. The trend in specific Ni surface area is very similar to the development of the catalyst activity suggesting that the loss of Ni surface area is a predominant deactivation mechanism. The results form H$_2$-TPD (Figure 2) support this assumption. A signal shift can only be seen in the temperature range from 500 K to 600 K most likely caused by the reduction of defects [4].

The effect of aging temperature on catalyst deactivation is being investigated in an ongoing study. Complementary studies of changes in CO$_2$ adsorption with time on stream will be conducted to elucidate additional deactivation mechanisms.
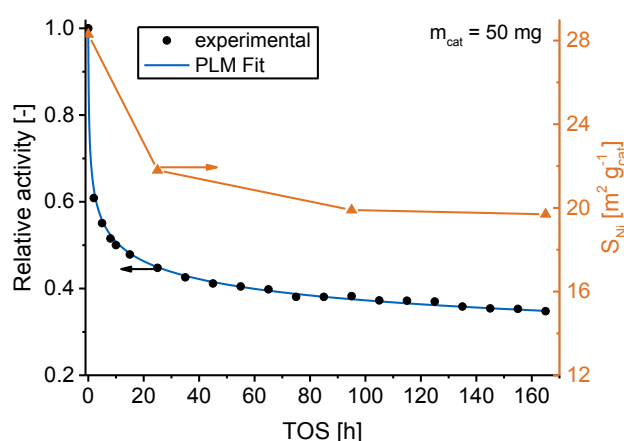


**Figure 1: Correlation between catalyst deactivation and specific Ni surface area.**
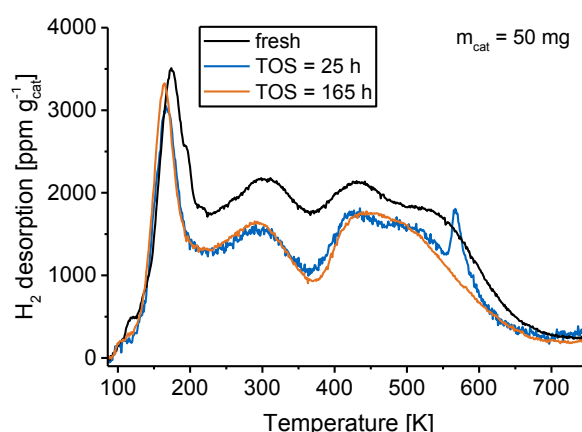


**Figure 2: Results from H$_2$-TPD of fresh and aged catalysts samples.**

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[6] L. Znak, J. Zieliński, *Appl. Catal., A* **2008**, *334*, 268-276.

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# Tuning the morphology of insoluble semiconducting polymer films for organic solar cells

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Organic photovoltaics (OPV), mostly polymer solar cells, have shown a lot of promise as an emerging technology with their potential as a low cost, easily produced alternative to conventional photovoltaics. Additional qualities such as their light weight and flexible properties could further expand their areas of application; however, low efficiencies and short lifetimes of OPVs have been a hurdle to their commercial acceptance. Research behind morphology of polymers serves to tackle these issues, aiming to strengthen OPV technology as a worthy contender in global energy production.

Polymer solar cells come in several junction types. For a bilayer solar cell (fig. 1a), two layers – a donor material and an acceptor material – with different electron affinities are applied in between two conductive electrodes. Although simple to fabricate, there is only one interface where charge separation can occur. This means that there are less excitons dissociated due to less surface area, and high losses of charge carriers due to the long distances they must travel to the next active interface. Both of which negatively affect the power conversion efficiency of the solar cell.
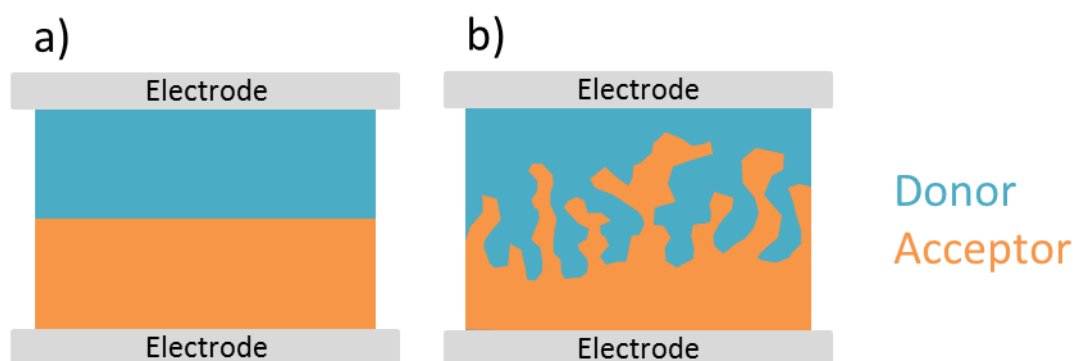


**Figure 1 a) Schematic drawing of a bilayer solar cell, and b) a bulk heterojunction solar cell**

Instead of two layers, bulk heterojunction solar cells (fig. 1b) have one active layer which is a mix of some conjugated molecule based donor and fullerene based acceptor. The mixed donor and acceptor self-assemble in-to a disordered structure which increases the surface area for higher exciton dissociation, but also increases the chance that charge carriers recombine. Bulk heterojunction solar cells generally have higher efficiencies than bilayer solar cells, but film morphology is difficult to control and has been shown to be a factor which shortens the lifetime of the solar cell [1].

By utilizing an in-situ polymerization technique and varying the water content within our precursor solution, we attempt to bypass the insolubility of Polythiophene to take advantage of its stable qualities, while influencing the crystallization and film morphology to achieve a complex interface between donor and acceptor [2]. The resulting characteristics are analyzed using the Grazing-Incidence Wide-angle X-ray Scattering technique.

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# Controlling the aggregation of native polythiophene during *in situ* polymerization

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Since the discovery of conjugating polymers in the 1970s their synthesis and the development and optimization of applications has been in the focus of research. Since their conductivity and optoelectronic properties strongly depend on the molecular morphology and crystallinity, controlling the thin film morphology is one of the main challenges when it comes to developing fabrication processes that work on small labs as well as in large industrial scales. As many conjugated polymers are insoluble in most common solvents and do not allow processing directly from solution, they are often equipped with solubilizing side chains. *In situ* polymerization offers the possibility to process polymers from solution without the need for solubilizing side chains. For this purpose, the corresponding monomers are deposited onto the substrate and chemically linked afterwards.

Since it is well known, that the performance of polymeric electronic devices depends strongly on the molecular interactions within the thin films, understanding and controlling the crystallization and film morphology are of crucial importance. Here, we would like to present a solution-based *in situ* polymerization technique for fabrication of thin films of native polythiophene and how we can influence the polymer aggregation by varying easily changeable synthetic parameters.



**Figure 1: In situ polymerized polythiophene films with tuned intermolecular interaction.**

The film morphology and resulting polymer interaction is analyzed combining grazing incidence wide-angle x-ray scattering (GIWAXS) and spectroscopic methods. Moreover, the electronic properties and performance in organic solar cells are correlated to the film morphology to show a clear dependence of the chosen synthetic path on the final film characteristics.
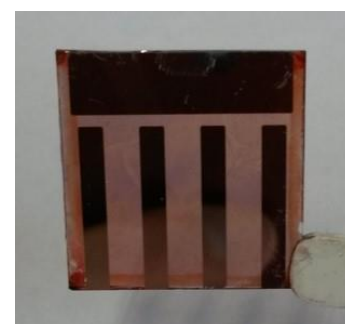


**Figure 2: Lab scale PT/PCBM organic solar cell**

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# Investigating the perovskite crystallization in mesoscopic hole-conductor-free solar cells

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The desire to efficiently convert solar into electric energy has led to increasing activity in the associated field of scientific research in the last decades. Due to major advantages, as low material costs and the applicability of mass production techniques, solution processed solar cells have long been of interest.



**Figure 1: Diagram of recent progress in power conversion efficiencies of perovskite solar cells.**

In particular, organometal halide perovskite based solar cells have emerged as the fastest-advancing photovoltaic technology to date, reaching certified solar cell efficiencies of up to 22.1%, already surpassing silicon based technologies. [1]

Moreover, the focus of research recently broadened beyond high efficiencies to key values like prolonged device lifetime and stability that are required for industrial implementation. A novel perovskite cell architecture utilizing a mesoporous scaffold with embedded perovskite addresses these challenges and is furthermore adaptable for industrial scale production by established printing technologies like screen printing.

Our project partners at NTU Singapore have already succeeded in the production of large scale perovskite solar cells, achieving 10.74% efficiency for a 70cm² perovskite solar cell module. [2] However, little is known about the perovskite crystal formation processes in the utilized mesoscopic device structures, which are of prime importance for further device performance optimization. Our research group at TUM focuses on identifying the crucial processing parameters to gain deeper understanding on the crystallization processes.

In this project, we fabricate a mesoscopic scaffold comprised of a mesoporous triple-layer of titania, zirconia and carbon by screen printing. We further investigate the influence of the processing additive 5- ammonium valeric acid iodide (5-AVAI) on the perovskite solution infiltration and perovskite crystallization in the employed mesoscopic scaffolds. Hereby, our results grant us a better understanding of the perovskite crystallization processes in a mesoscopic scaffold and are of key importance for further device developments.
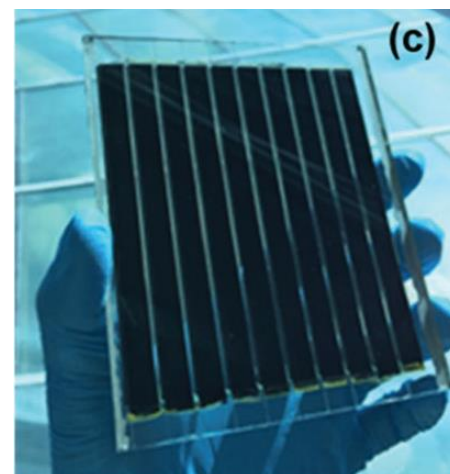


**Figure 2: Photograph showing a 70cm² perovskite solar cell module, reaching 10.74% efficiency by ERIAN, NTU [2].**

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36

# Structure-property relationships of insoluble polythiophene thin films for the application in organic solar cells

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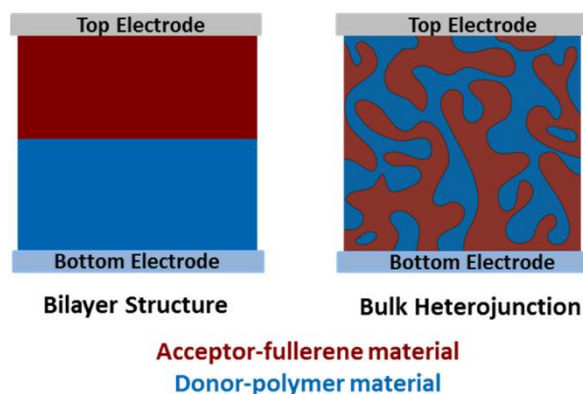
**Fig. 1: schematic drawing of bilayer structure vs. bulk heterojunction [1].**

The increasing demand for energy in the world of a growing population as well the desire to get independent of conventional fossil energy resources have been the driving force behind the extensive research on alternative, sustainable energy sources. As most of the energy today available on the planet origins from the energy of the sun, the most promising approach to meet future energy demands is to convert sunlight into electric energy. Inorganic solar cells with high efficiencies and long lifetimes have been developed and are used commercially today.

However, these devices have certain drawbacks like the energy intensive and expensive manufacturing process as well as the inflexibility of the materials. These factors decelerate the growth in this sector, which is currently tackled with the development of new devices based on organic materials. These devices do not potentially outperform inorganic devices by efficiency and lifetime, however they do seem promising, as very economical manufacturing techniques that can be employed to produce the cells with a high flexibility for diverse applications.

Organic solar cells are based on molecules with delocalized electrons. These materials are either polymers or so-called small molecules. A general problem of the organic materials is the short diffusion length for excitons, which lie in the range of 10 nanometers. However, to yield maximum absorption, a thicker layer of at least several tens of nanometers is necessary. Optimized device structures with two different organic materials, a donor and an acceptor, were developed. The resulting energy differences of the materials at the interfaces allow an efficient exciton splitting, which yield in free charge carriers which can be extracted more efficiently. Therefore, the structure of the interface is of utmost importance for the device performance. The current state-of-the-art is the bulk-heterojunction (BHJ) principle (see Fig. 1), where the two materials are mixed and form regions in the range of the exciton diffusion length.

The basis of the research presented here is a new technique where the active organic layer is polymerized in situ. Hereby, an insoluble thin-film is produced. The insolubility can now be exploited to gain more insight into structure-property relationships of organic solar cells. The advantage is the inertness of the structure for further processing steps, and therefore simple bilayer structures, as well as more complex ones in the direction of bulk-heterojunction can be produced.

Different approaches can be used like hard or soft templates, lithographic methods as well as imprinting techniques. The importance is to get defined structures which can be systematically varied. Data from these experiments like I-V characteristics and mobility can then be used to derive a more general understanding of the processes involved in organic solar cells.

Furthermore the data obtained will be used in an interdisciplinary cooperation with the group of Prof. Alessio Gagliardi to improve the simulation of organic solar cells.

# Investigating the humidity impact on mesoscopic perovskite morphology

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Photovoltaic solar cells have been regarded as a promising energy conversion method to keep up with the world's increasing energy consumption. Organic solar cells yield promising prospects due to their low cost fabrication, light weight and mechanical flexibility. However, the efficiency of organic solar cells are inferior to commercial silicon solar cells. Organometal halide perovskite solar cells are a product of combining the advantages of organic and inorganic systems.
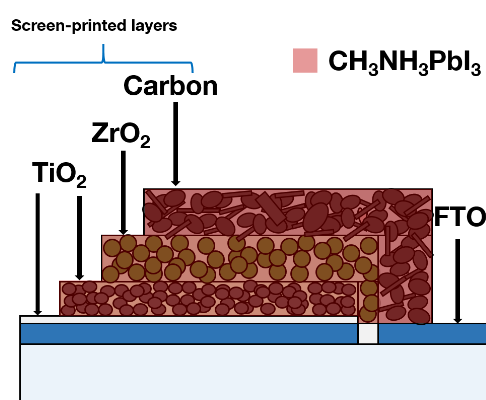


Figure 1: A schematic structure of perovskite solar cell.

The steep rise of the efficiency in the past decade makes them the fastest-advancing solar cell technology to date [1], due to properties like large carrier diffusion lengths, high charge-carrier mobilities and a low exciton binding energy [2]. However, perovskite is sensitive to humidity, which may have detrimental as well as beneficial effects [3].

In this work, we fabricated mesoscopic perovskite solar cells by using a screen printer. Screen printing is an established printing technique where a mesh is used to transfer a paste onto a substrate. The method is easily scalable which is ideal for commercializing solar cells. By adjusting the processing parameters the thickness of each layer can be optimized. Our mesoscopic perovskite architecture is based on a triple-layer scaffold of m-TiO2, m-ZrO2, and m-Carbon. The structure can be seen in figure 1. In this work, methylammonium lead triiodide (MAPI) is drop-casted on top of the scaffold where ideally perovskite crystals form in the scaffold during heating. Perovskite works as an active material and a hole conductor in this architecture.

A humidity atmosphere setup is applied during the perovskite solution deposition and perovskite formation process. When MAPI is exposed to water vapor at room temperature hydrated crystal phases are formed. The impact of humidity on the morphology and device performance will be investigated.

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# Preparation of Carbon-enhanced Nickel Catalyst for the CO2 Methanation Reaction in a Fluidized Bed

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## Introduction

As part of the energy transition, the expansion of renewable energy is focused on reducing $CO_2$ emissions. Here, however, it is challenging to store excess energy effectively. A promising approach to solve this problem is the power-to-gas (PtG) concept [1]. In this case, carbon dioxide with hydrogen obtained by electrolysis of water is converted into methane by means of the Sabatier process. From literature, it is known that Rh-, Ru- or Ni-based catalysts show promising results [2-4]. In this study, the impact of surface-bound carbon species on the performance of CVD-prepared $Ni/SiO_2$ catalysts for $CO_2$ methanation reaction is investigated.

## Catalyst Preparation

The $Ni/SiO_2$ catalysts were prepared by applying of the chemical vapor deposition (CVD) technique. For this purpose, a fluidized bed reactor consisting of a quartz reactor, a saturator and an oven is used. The $SiO_2$ particles are positioned inside the quartz glass reactor, where the fixed bed is transferred into a homogeneous fluid bed. The saturator is loaded with the volatile nickel precursor. Subsequently, the deposition of nickel is started by dosing the volatile nickel precursor into the gas stream. The deposition is run by lowered pressures and elevated temperatures. The calcination process was conducted under different atmospheres to obtain different carbon contents on the surface of the catalyst: catalysts without carbon were calcined under flowing air, while, in contrast, catalysts containing carbon were calcined under static air

## Results

The carbon content of the catalysts can be modified by different calcination parameters. The remaining carbon is stable under methanation conditions. In Figure 1, the conversion of $CO_2$ in the methanation reaction over temperature of two different catalysts is presented.

Cat 2 shows a higher activity compared to Cat 1, although Cat 2 has a smaller active metal surface. This increase in the activity is caused by the additional carbon on the surface of the catalyst. This observation can also be made in Figure 2, where the formation rate of methane at 300 °C is presented (in terms of weight time yield). It is a linear function of the active metal surface. Nevertheless, the catalysts with carbon on the surface show an enhanced formation rate compared to the catalysts without carbon. Moreover, the formation rate increases with rising amount of carbon at unchanged active metal surface.

## Outlook

The next step of this study is to reveal the nature of the carbon on the surface of the catalyst. If the nature is known, the process parameters can be adapted to increase the stable amount of carbon during the reaction to enhance the activity of the catalyst.



Figure 1: CO2 conversion as a function of temperature for two catalysts with different carbon loadings.
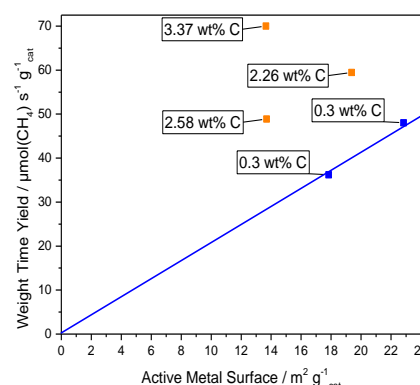


Figure 2: Weight time yield of different carbon containing catalysts

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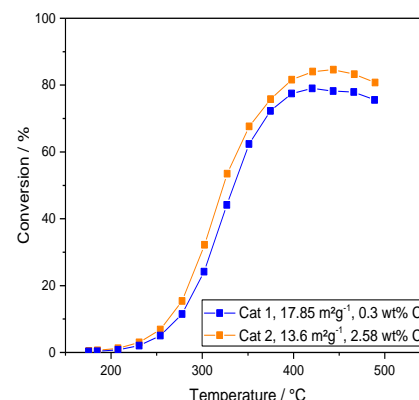[4] G.M. Shashidhara, M. Ravindram, React. Kinet. & Catal. Lett. 37 (1988) 451–456.

# Effect of inorganic nanocrystals on the performance of organic solar cells

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Over the last decades, the negative impact of fossil fuel combustion on the environment got increasingly visible. Furthermore, limitation of oil, gas and coal resources has led to an increasing interest in renewable energies to serve the continuously growing energy demand. A promising candidate for the future energy provision is photovoltaics, as the conversion of solar energy reaching earth to electricity could cover the world energy consumption.

In this context, organic photovoltaic (OPV) devices are a promising technology, offering many advantages over the conventional semiconductor-based solar cells, like light weight, flexibility and semi-transparency. Moreover, organic photovoltaic offer the possibility for large-scale and low-cost processability. Due to these advantages, devices could be implemented in a wide range of applications.



**Fgure 1: Photograph of an organic solar cell.**

Recent research efforts target the photovoltaic performance to make solar cells attractive for industrial purposes. As a consequence new compounds for the synthesis of organic photovoltaics with reported power conversion efficiencies surpassing 11% have been developed. [1] However, organic photovoltaics still exhibit efficiency losses and decreased lifetimes compared to common inorganic photovoltaic devices. Several issues have to be investigated to make organic photovoltaics competitive for industrial applications.

Thus, the inner morphology of the organic thin films used in organic solar cells is one of the key aspects concerning charge carrier separation, diffusion pathways and extraction of the free charge carriers. Thereby, the power conversion efficiency. Furthermore, a promising way to increase the efficiency of organic photovoltaic devices consists in the doping of the active bulk heterojunction with inorganic nanoparticles. Recently the most widely investigated bulk heterojunction donor-acceptor system of P3HT:PCBM was doped with iron oxide nanoparticles, resulting in an increase of the device performance. [2]

Based on this approach, our work takes a deeper look at the effect of inorganic nanoparticles on the electrical characteristics of organic solar cells. Depending on the concentration of nanoparticles doping, current-voltage measurements are performed. Furthermore, we study the influence of the incorporated inorganic nanoparticles on the crystallinity and the inner morphology of the active polymer layer with X-ray diffraction methods, like grazing incidence small angle X-ray scattering (GISAXS). [3] As a result, we want to gain further insight in the correlation of inner morphology and photoelectric characteristics of organic solar cells. Complementary UV-Vis spectroscopy and photoluminescence measurements are carried out in these studies.

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# In situ GISAXS on sputter deposited metal nanolayers on functional polymer thin films

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The increasing demand of electronic devices nowadays still mainly built up from inorganic materials in often dangerous, toxic, expensive and energy-intensive processes drives the necessity to develop alternatives from organic materials. Versatile organic materials like polymers offer the ability to develop, design and fabricate eco-friendly, flexible, and low-cost electronic devices using also self-assembly processes on nanoscale.

Understanding the interface between metals, commonly used as contacts and current collectors, and (conducting) polymers used in organic electronics and organic photovoltaics 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[1]. In situ grazing incidence small angle X-ray scattering (GISAXS) allows investigating the formation, growth and, if desired, self-assembled structuring on appropriate polymer thin films. The sputter deposition process well understood and controlled offers advantages over chemical methods to tailor the nanoparticle size in the sub-monolayer regime and offers a superior adhesion of the deposited material[1] needed for applications like organic sensors[2], field effect transistors[3], light-emitting diodes[4] and organic photovoltaics[5].

Also in polymer electrolyte lithium ion batteries (LIB) the polymer-metal interface between electrode and electrolyte but also between current collector and electrolyte is of great interest especially along with developing thin film LIB. The understanding of deposition and infiltration of sputtered metals and alloys onto the polymer thin film is crucial to understand the limits of the LIBs unexploited development.

In the presented work, the first steps investigating the metal-polymer electrolyte interface with in situ GISAXS during metal sputter deposition is shown to provide a new and efficient way to thin film Li-ion batteries.

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# Hybrid solar cells based on laser-ablated titania

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In the development of non-conventional solar cells not only the achievements of highest power conversion efficiencies and maximum lifetime of devices is of interest. Also the sustainability of the production process of the devices comes into focus. In order to achieve an all-embracing green technology, the materials applied and the required energy for device fabrication are of importance. Materials in terms of functional components or as additives in the processing should be non-toxic and environmentally friendly. In an optimum approach no organic solvents should be used for the coating of any of the layers of the device. High temperature processing steps should be reduced or avoided to increase the energy payback times of the solar cells. Following this idea, we developed hybrid solar cells with an active layer based on low temperature processed titania and a water-soluble polymer [1].

In our approach titania nanoparticles are produced with laser ablation in liquid in order to initiate a functionalization of titania with the polymer for the active layer. Combining these titania nanoparticles and water-soluble poly[3-(potassium-6-hexanoate)thiophene-2,5-diyl] (P3P6T) hybrid solar cells are realized.
For the fabrication of hybrid photovoltaic devices we applied different deposition techniques for the active layer. Starting with spin-coating technique, we also investigated dip-coating and spray-coating which could easily scale-up to industrial cost-effective applications. For the deposition of the active layer with laser-ablated particles both techniques provided a good control of the film thickness. For hybrid solar cells the morphology of the active layer is of major importance for the performance of these devices.

For the spray deposition method we are especially interested in how the morphology changes with increasing film thickness during deposition. Therefore we followed the development of the morphology of the active layer in situ with high spatial and temporal resolution. The mesoscale was probed as well as the crystallinity of the polymer and the inorganic component. The changes of the morphology of the active layer are discussed and implications for an improved processing of devices are given.
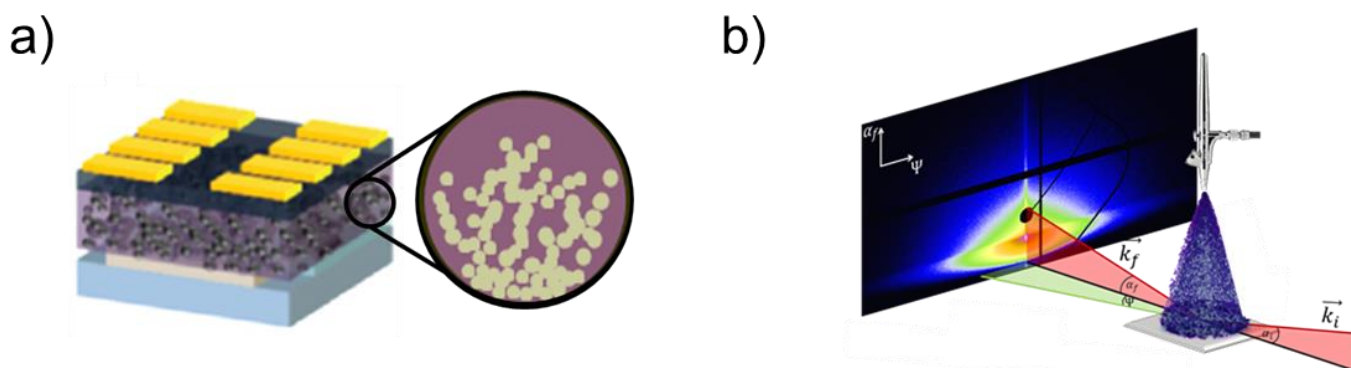


Figure 1: a) Built-up of a hybrid solar cell with a zoom-in into the active layer picturing functionalized titania nanoparticles in the polymer matrix  b) in-situ spray deposition of the active layer probed with grazing incidence small angle x-ray scattering.

Hybrid solar cells are produced by applying a new water-based processing method. The cost-effective deposition technique spray-coating allows for precise control of the film thickness whereas the morphology of the active layer is maintained. We also demonstrate further tuning of the device efficiency enabled by introducing a vertical compositional gradient in the active layer.

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42

# Silylated $Ge_{9-x}Si_x$-ZINTL Clusters as Wet Chemical Precursors for Mesoporous $Ge_{1-x}Si_x$-Films

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Hybrid solar cells combine the unique properties of inorganic semiconductors and organic polymers which result in low production costs and flexibility.[1] In contrast to approaches which yield nanoparticles or nanowires of inorganic semiconductors, routes to periodic porous materials are scarce.

Oxidative decomposition of Zintl clusters in presence of a specific template leads to homogenous thin films. So far, we succeeded in preparing germanium films with inverse opal morphology and a well-defined pore size in the range of 300 nm using solutions of the intermetallic compound $K_4Ge_9$ which contains nine-atomic clusters.[2] Moreover we used Si-Ge mixed Zintl clusters to prepare periodic porous silicon-germanium morphologies. However, this approach resulted in solubility issues.

Herein we present a type of functionalized Si-Ge Zintl clusters which show a good solubility in a broad range of common solvents such as acetonitrile, toluene and hexane. They could be used to gain access to periodic porous silicon-germanium morphologies with tunable Si:Ge ratio.

The results of this synthetic approach are shown using nuclear magnetic resonance (NMR) and mass spectrometry (MS). Furthermore, two possible routes to periodic porous morphologies are depicted.
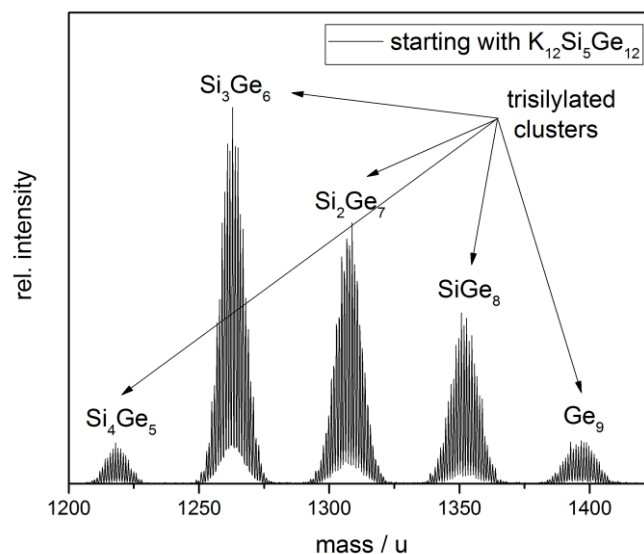


**Figure 1. Mass spectrum of [Ge9-xSix](Si(SiMe3)3)3-**

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# Screening of Cu+ZrO$_2$ as PGM-free ORR Catalysts for PEMFCs

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Low-temperature proton-exchange-membrane fuel cells (PEMFCs) are promising energy conversion devices. However, one of the hindrance in the mass commercialization is the high amount of very expensive Pt-based catalysts required at the cathode side, where the oxygen reduction reaction (ORR) takes place. In the last decade, many efforts have been made to reduce the Pt loading at the cathode or to replace it completely by Pt-group–metal (PGM) free catalysts. The best PGM-free catalysts reported so far are MCyN$_X$ (M = Fe/Cu/Co) [1]. They have acceptable ORR activity and are inexpensive. The main drawback of the aforementioned catalysts is their long-term instability in acid environment. High activity and long-term durability are the main requirements for a new catalyst. Based on our previous work with ZrO$_2$ [2][3] and recently submitted work with Fe+ZrO$_2$ based catalyst [4], we were motivated to investigate also Cu+ZrO$_2$ as a possible PGM-free ORR catalyst. Doping in ZrO$_2$ seems to be inevitable owing to limited ORR activity of pure ZrO$_2$ samples, possibly due to low amount of active sites. In addition, this motivation is also supported by literature, which reports the creation of oxygen vacancies in oxide when Cu is incorporated in ZrO$_2$ [5], which are hypothesized to be ORR active sites [6][7].

In short, soluble metal (Zr and Cu) phthalocyanines were impregnated on carbon black (graphitized Ketjenblack) followed by heat treatment. A series of samples were synthesized with different heat treatment temperatures (700-900 °C), and Cu loadings (0.1-0.5 wt.%). Structural characterization of the samples was primarily done by X-ray diffraction technique.
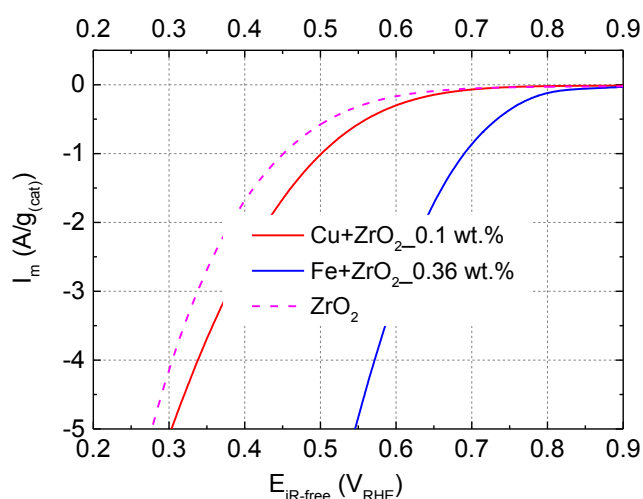


Figure 1: ORR mass activities of graphitized KB supported Cu+ZrO2, Fe+ZrO2, and ZrO2 catalysts

Furthermore, cyclic voltammetry on thin-film (70-76 µg$_{cat}$/cm²) rotating disc electrode was employed to determine the ORR activities of the samples at 20 °C in O$_2$-saturated 0.1 M HClO$_4$ electrolyte at 1600 rpm. Figure 1 shows the increase of activity for Cu+ZrO$_2$ and Fe+ZrO$_2$ catalysts compared to pure ZrO$_2$. Structural characterization viz. magnetic measurements and XPS analysis will be done to better understand the nature of the active sites. In addition, the Cu+Fe+ZrO$_2$ system will be analyzed, to check if a possible co-doping leads to a better catalyst. The sample with the activity close or higher than Fe+ZrO$_2$_0.36 wt.% (Figure 1) will be tested in a PEMFC system for its activity and durability.

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# Quantifying the Degradation Phenomena of Silicon-based Electrodes in Lithium-ion Batteries

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Silicon is an attractive candidate as anode active material for the next generation of Lithium-ion batteries with cell-level gravimetric energy densities above 300 Wh $kg^{-1}_{cell}$.[1] In contrast to state-of-the-art graphite intercalation electrodes (372 mAh $g^{-1}_C$, $LiC_6$), silicon forms an alloy with lithium, which considerably increases the theoretical specific capacity (3579 mAh $g^{-1}_{Si}$, $Li_{15}Si_4$).[2]

The practical application of silicon-based electrodes in Lithium-ion batteries is still hampered by two major drawbacks that are closely related to the extent of the lithium uptake: (i) In their fully lithiated (charged) state, the silicon particle volume increases by 280%, which leads to a severe mechanical degradation of the entire electrode upon repeated charge-discharge. (ii) Continuous volume changes inhibit the formation of a stable solid-electrolyte interphase (SEI) at the silicon particle surface, which results in an ongoing electrolyte decomposition at low potentials.[3]

Our research focusses on the identification and quantification of the degradation phenomena that occur in silicon-based electrodes during battery cycling. Hence, we employ various electrochemical and spectroscopic techniques, including impedance spectroscopy (EIS), on-line electrochemical mass spectrometry (OEMS), 19F-nuclear magnetic resonance (NMR) spectroscopy, and scanning electron microscopy (see Figure 1).[4,5]



**Figure 1: SEM cross-sectional image of a pristine silicon-graphite electrode, consisting of 20 wt% silicon, 65 wt% graphite, 7 wt% carbon fibers, and 8 wt% LiPAA polymer binder. Thickness: ~25 μm.**

In this contribution, we present selected results from our previous research on the quantification of the electrolyte decomposition in silicon-graphite//$LiFePO_4$ coin-cells in dependence on the cycling conditions. Based on this, we discuss the influence of the decomposition products and morphological changes during cycling on the tortuosity and pore volume of the silicon-based electrodes.

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# Investigation of new materials for high-efficiency polymer solar cells

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Technological advances and the rising demand for electrical energy have led to a point, at which the impact of fossil energy sources on nature is more noticeable than ever. Today, the discussion between economic and ecological interests has reached a new urgency. Improvements in the field of renewable energies are inevitable to fight the trend of global warming.

Organic photovoltaics are a potential candidate to address this problem in new ways. In contrast to silicon-based solar cells, they offer a wide range of advantages. Due to their flexibility and tunable optical properties, sun harvesting in areas not accessible to conventional solar cells could be greatly increased using organic solar cells, e.g. on windows, curved or flexible surfaces. Other advantages are the lighter weight, lower energy consumption during the production and much lower production costs. Possible fields of application are enhancements in building and mobile power generation.

In the last years, the formerly poor efficiencies of organic photovoltaics have been greatly increased. This year, organic photovoltaics have already reached an efficiency of 11,7 % [1] on a laboratory scale. However, further improvements in the device architecture and stability are needed to reach industrially relevant efficiencies.

To enhance the performance of solar cells, recent research efforts focus on identifying new highly efficient materials. One way to achieve this is the development of low band-gap polymers, which absorb light of lower energies and can therefore increase the overall absorption. One prominent representative for these kinds of polymers are PTB7 and its derivatives, which can achieve efficiencies of around 10 %. Our work focuses on the comparison between these polymers and a different one called PffBT4T-2OD, which shows an even higher efficiency of approximately 11% [2]. Applied characterization techniques include optical absorption and microscopy measurements as well as X-ray scattering methods. Exploratory solar cells link the power conversion efficiency to parameters such as the active layer composition and morphology.
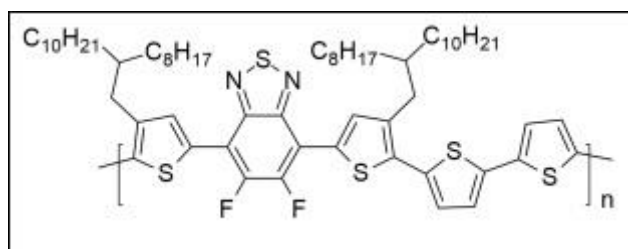


**Figure 1: Chemical Structure of PffBT4T-2OD [2]**

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# Piezo- and Pyroelectric Energy Harvesting based on PVDF for Wireless Sensor Nodes

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We report the fabrication and characterization of energy harvesters based on the piezo- and pyroelectric material polyvinylidene fluoride (PVDF). As shown in Fig. 1. (a), PVDF is composed of difluoroethane molecules, which align when an external electrical field is applied. Once the PVDF is polarized, it generates a voltage under time-varying mechanical stress (piezo-effect), as illustrated in Fig. 1 (b) or temperature (pyro-effect).

For the top and bottom electrodes that contact the $40\ \mu m$ thick PVDF-foil, spray-coated and transparent electrodes (TEs) are utilized. As illustrated in Fig. 1, the TE films are made of (c) Silver Nanowires (AgNWs), (d) poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) or a composite of these two materials. The transparency is required for the pyro-effect to allow the heat source, i.e. a conventional light bulb, to penetrate the electrode material and rapidly heat up the PVDF-foil.
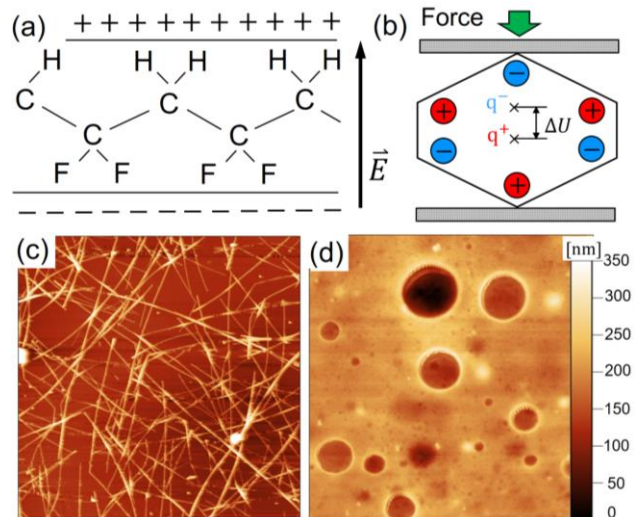


Figure 1. Schematics for (a) the polarization of PVDF and (b) a piezoelectrically active unit cell under strain. Atomic Force Microscope (AFM) images for (c) AgNWs and (d) PEDOT:PSS.
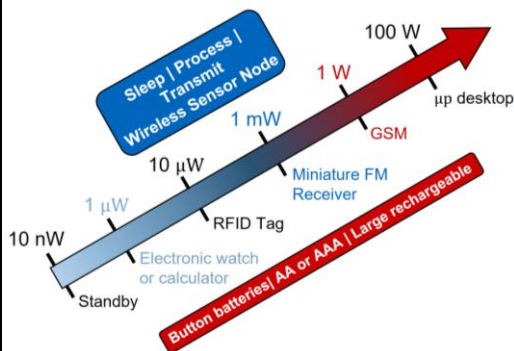


Figure 2. Power consumption for a selection of smart electronic devices.

The presented energy harvesters can for instance be used to power smart and autonomous electronics, whose power consumptions are visualized in Fig. 2. Attributed to the power output of the presented prototypes that can easily be up-scaled and lie in the sub-$\mu W$ range, a promising application is to power a Wireless Sensor Node (WSN).

The fabricated harvesters are characterized with regard to their voltage and current output as well as their optimum load resistances, as depicted in Fig. 3 (a). In order to power a WSN sketched in Fig. 3 (c), an efficient and low-power management IC that is exemplarily depicted in Fig. 3 (b) is simulated and experimentally tested.
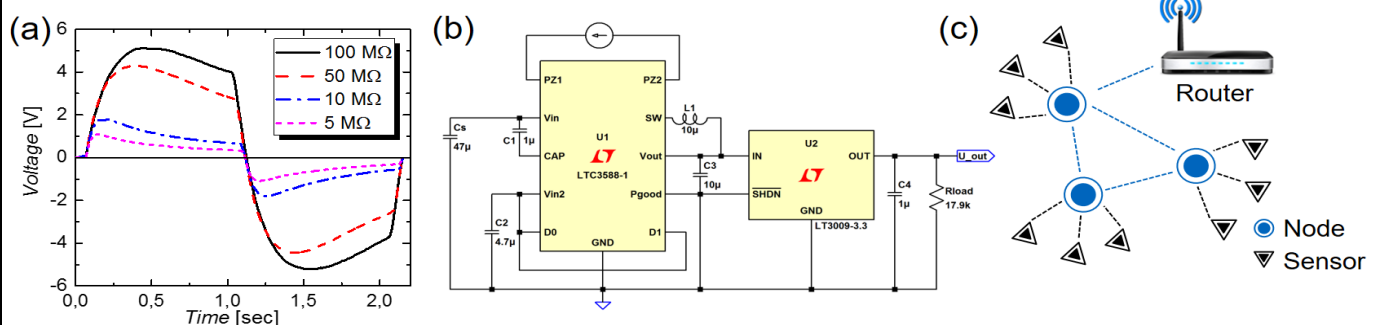


Figure 3. (a) Transient voltage response for a PVDF-based energy harvester that is subjected to heating and connected to different ohmic load resistors. (b) Sketch for a low-power management IC. (c) Schematic for a WSN.

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# Transparent silver nanowire electrodes for organic solar cells

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Organic opto-electronic devices offer the possibility of low cost, large area farbrication due to their solution-processability and low material cost. While this generally applies to the active organic materials involved, it often does not for the electrode materials. The transparent electrode is especially challenging as it needs to combine high transparency with high conductivity; we investigate the use of silver nanowire (AgNW) networks, which are spray-coated from solution, to replace the costly and brittle indium tin oxide (ITO) typically used for transparent electrodes.

Firstly, we investigated spray deposition of AgNWs and post-treatments of the resulting films. Figures 1a) and 1b) show optical microscope and SEM pictures of the films. The film thickness is controlled by the number of consecutive spray depositions and constitutes
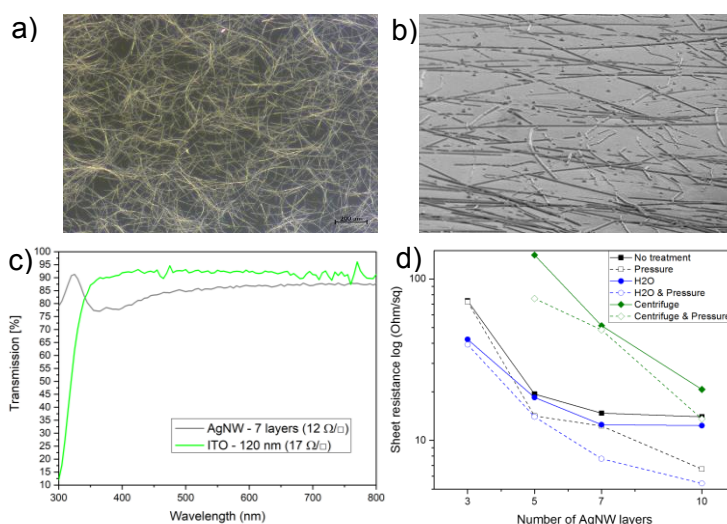


Figure 1: a) optical microscope picture, b) SEM picture of AgNW film, c) transmission of AgNW vs ITO film and d) sheet resistance vs layer thickness of AgNW films with different post-treatments.
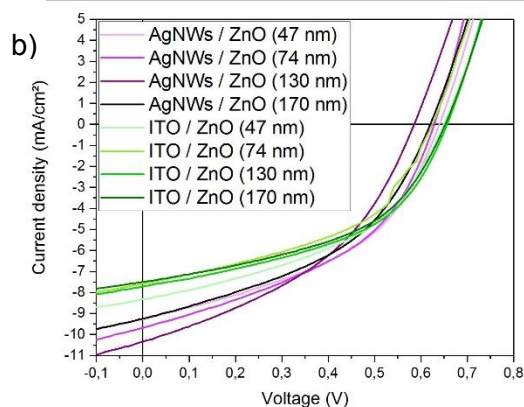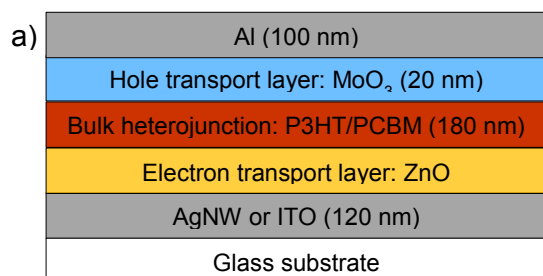


Figure 2: a) layer stack of fabricated solar cells and b) J-V characteristic of device with ITO or AgNW electrode and different ZnO thickness.

a trade-off between conductivity and transparency. Different after-treatments with water, heat or pressure can further enhance the performance of the AgNW film. An overview of the performance different thicknesses and treatments is shown in Figure 1d). An optimized layer with 7 spray runs results in a sheet resistance of $R_{sh}$= 12 Ohm/square and a transparency of 85 % at 550 nm, which is similar to the performance of ITO as shown in Figure 1c).

With a length in the order of 10 - 30 µm, the AgNW tend to form rough layers with single wires or wire bundles sticking out. These spikes can cause short circuits in thin-film devices, which typically have thicknesses in the around 250 nm. We used films made of spin coated ZnO nanoparticles as electron transport layers in order to planarize the AgNW and studied the influence on the AgNW film roughness and solar cell performance. Figure 2a) shows the layer stack of the fabricated devices and Figure 2b) compares the J-V characteristic of devices made with ITO and AgNW electrodes and different ZnO thicknesses, with the AgNW outperforming their ITO counterparts due to higher short circuit currents with power conversion efficiencies up to 3.2 %.

# Witnessing the formation of metal contacts on organic solar cells

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With a rising worldwide demand for sustainable energy, alternative sources such as solar, wind or hydropower are gaining more and more impact in the global energy supply and already contribute significantly to the energy landscape in Germany with around 31 % of the overall produced electricity for 2016 [1]. However, they typically depend on fluctuating energy sources such as wind and sunlight and are limited to static, large-scale applications. Organic photovoltaics (OPV) have received high attention in recent years as an interesting alternative to conventional solar cells. Using polymer films as active material for energy conversion has a variety of potential advantages. Photoactive polymers can be synthesized from low-cost, abundant precursor materials and enable the formation of thin, light-weight and flexible films with tunable color. The devices can be produced via roll-to-roll processing, an easily up-scalable and thereby low-cost production technique. Due to these advantages, OPV devices could be integrated into a wide range of applications, combining functionality with design in fields as diverse as mobility, architecture or clothing.

Recent research efforts focus on enhancing the photovoltaic performance to make organic solar cells feasible for industrial purposes. This has led to the development of low band-gap materials with reported power conversion efficiencies nearing 12 %. [2] However, they still show considerable efficiency losses and drastically decreased lifetimes in comparison to commercially available inorganic photovoltaics. Several issues concerning the optimal thin film morphology and architecture will need to be addressed to make organic solar cells a potential candidate for mass market applications. Our work takes a deeper look at the interface between the photoactive layers of typical organic solar cells and their metal back electrodes.

Although OPV devices consist mainly of organic materials, their electrodes are in many cases still made from metals. Thus, polymer-metal interfaces are inherently present in these solar cells. We investigate the formation of the polymer-metal interface during the deposition of metal electrodes onto photoactive films via in-situ grazing incidence small angle X-ray scattering (GISAXS). [3] This technique allows for highly time-resolved insights into the deposition behavior of the metal on the organic film, which strongly depends on the film structure. The formation processes of gold contacts on different organic layers are compared. Further characterization techniques such as electron microscopy and UV/Vis absorption measurements complete our work. Understanding the deposition behavior of metal contacts on organic thin films plays a crucial role in identifying potential ways to enhance the performance of OPV devices.

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# Inkjet and Screen Printing for an Environmental-Friendly Production of Electronic Devices

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Printing technologies are employed increasingly outside their traditional fields in the graphics industry. They offer a much less complex and more environment-friendly way to deposit functional films on recyclable substrates like paper and plastic films. The advantages of printing techniques lie in a very high throughput, very low material waste and low requirements on the substrate.

**Inkjet Printing**
Highly customizable (digital)
Non-contact method
Cheap and scalable

Small dry film thickness
Low ink viscosity

**Screen Printing**
High film thicknesses
Robust layers
Low ink requirements

Setup costs
Ink waste for small batches
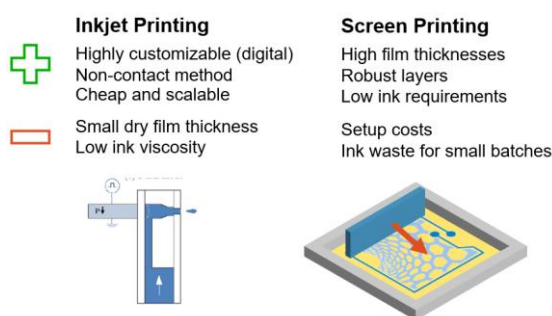
**Figure 2: Advantages and disadvantages of inkjet printing and screen printing**

We investigate inkjet printing, a digital technique without changeover costs and screen printing with its wider material selection and higher layer thicknesses. Most functional inks and pastes require post-processing like thermal curing or intense pulsed light (IPL) curing, which employs high-power broad band light pulses to specifically heat deposited thin films on temperature sensitive substrates.
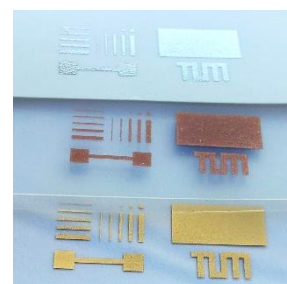
**Figure 1: Inkjet-printed Patterns on paper and PET**

We developed deposition processes for metals, graphite, and the conductive polymer PEDOT:PSS to create conductive patterns and combine them with dielectric polymers as well as semiconductive carbon nanotubes and elastic PDMS. We investigate the application of these processes to three groups of electronic devices. The main part of all electronic systems is the wiring with a conductive material. Thin, highly conductive, and non-interrupted wires that are printed on flexible or even stretchable substrate are presented. Well-defined patterns are needed for antenna structures like the NFC and UHF antennas that we produce. At last, sensors for temperature, humidity, force, pressure, and several gases will be presented that can be produced directly on the same substrate using printing techniques.
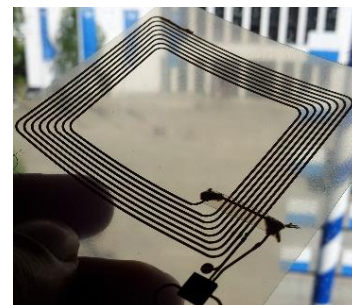
**Figure 3: Inkjeted NFC tag on PET film with SMD components**

The combination of all these components results in a sensor system consisting of one or more sensors with the sensing electronics and the communication platform. In comparison to traditional systems, the production process is much simpler: only a small number of process steps are required, environment-friendly substrates can be employed, chemical waste reduced to a minimum, and production throughput increased.
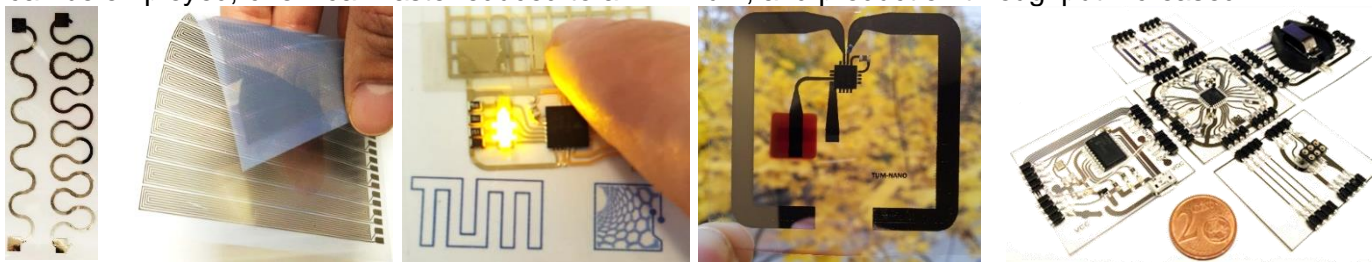
**Figure 4: Selected applications from left to right: Conductive wires on a stretchable silicone film; Thin and long electrode structures for a tamper-evident film; Inkjet- and screen printed force sensor tag with assembled LED indicators; Inkjet-printed UHF tag with organic photo-diode; Printed modular circuit board with assembled surface mount components**

# Singlet Oxygen Formation and Irreversible Side Reactions in High Energy Density Batteries

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Increasing the energy density is a major challenge in the development of next generation Li-ion or beyond Li-ion battery systems.[1] There are several interesting novel Li-ion cathode materials like lithium and manganese rich layered oxides (HE-NMC) or even entirely new cell concepts like lithium or sodium- oxygen batteries which offer superior gravimetric energy densities but still suffer from severe side reactions limiting battery life. In many of these high energy density cathode systems oxygen is released during the charge at high potentials, either as the desired cell reaction (e.g. metal oxygen batteries)[2] or as a side reaction (e.g. HE-NMC)[3].

In a recent publication, we used time and potential resolved operando electron paramagnetic resonance (EPR) spectroscopy to show that a significant fraction of the oxygen formed during the charging process of an aprotic Li-O2 cell is evolved in the form of singlet oxygen (Figure 1).[4] Singlet oxygen is a highly reactive oxygen species and a strong oxidizing agent which probably plays a central and long overlooked role in understanding the irreversible side reactions like carbon corrosion and electrolyte degradation.[4,5]

In this contribution, we present our findings regarding singlet oxygen evolution in Li-O2 cells and also discuss the role which singlet oxygen evolution might play for side reactions in novel high energy cathode materials like HE-NMC.



**Figure 1: Voltage profile and EPR signal amplitude from 4-Oxo-TEMPO formed during charge (i = 60 mA gC-1) of Li2O2 in the operando EPR cell with 0.5 M LiTFSI in diglyme containing 0.1 M 4-Oxo-TEMP as spin trap. The 4-Oxo-TEMPO radical is formed in fast chemical reaction with singlet oxygen.**

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# Modeling inhomogeneity in lithium-ion battery modules

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Inhomogeneity in a battery module denotes a gradient of a certain parameter across connected battery cells. Possible reasons for inhomogeneity in battery modules are unmatched cells showing cell-to-cell variations in capacity and impedance due to manufacturing tolerances or varying shipping conditions, defective cell contacts (i.e. due to vibrations in the car), an external heat source next to the battery module or an ineffective cooling strategy. Inhomogeneity in battery modules can lead to local temperature peaks which may result in accelerated aging or even failure of a single cell or the whole module.

The aim is to develop a model for investigating the reasons and consequences of inhomogeneity in battery modules by means of multiphysics simulation. The model should allow for simulating the transient electrical and thermal balancing behavior of connected cells while considering the physicochemical behavior of the single cells. This is achieved by coupling physicochemical, electrical and thermal models using COMSOL Multiphysics 5.2a.

Each cell is represented by a 1D physicochemical model (PCM) and a simple 3D thermal model (THM) (lumped heat capacity, anisotropic thermal conductivity). The heat generated within the PCM is passed to the THM, increasing the temperature of the respective cell. This increased temperature is coupled back to the PCM, where transport properties and reaction rates are adjusted according to the new temperature.
The transient electric balancing between connected cells is integrated by using Kirchhoff's laws (0D ELM). In order to allow for thermal balancing between the cells, thermal transport mechanisms are implemented within the THM: Thermal conduction between the neighboring connected cells over the cell connectors, thermal radiation between the surfaces of cells and cell connectors, and both, natural and forced thermal convection included by a computational fluid dynamics simulation (CFD).

The presented study investigates two parallel connected cells of different initial SOCs: SOC1=1, SOC2=0.8. The system is cycled using a 1C constant current (CC): CC-discharge, relaxation, CC-charge while being cooled by forced convection with $v_{Air}$=3 m/s.
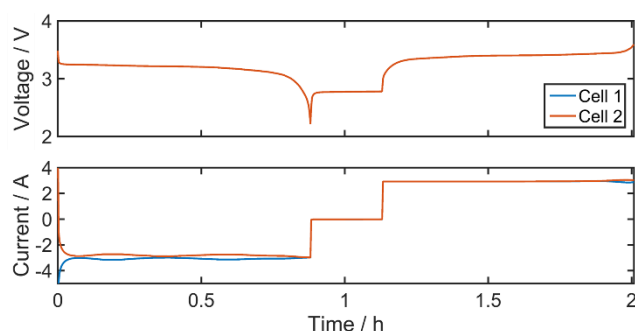


**Fig. 1: Transient electrical behavior of the two parallel connected cells: Electric potential (top) and current distribution (bottom). Cell1 has a higher initial SOC than Cell2. At the beginning of the cycle the balancing current discharges Cell1 and charges Cell2. Therefore, Cell1 shows a higher resulting negative discharge current than Cell2.**
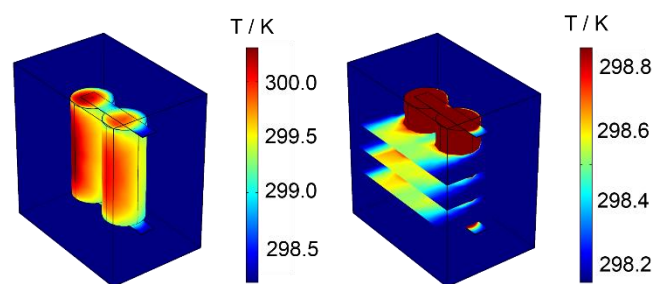


**Fig. 2: Temperature distribution within the simulated system after the CC-discharge: Temperature of the cells and cell connectors (left). Temperature of the air (right).**

Future investigations will address the aging behavior in battery modules, thermally optimized battery module design and cell matching strategies. Moreover, a program will be developed for automatic generation of coupled multiphysics models. This will allow for simulations of large battery modules.

# Anode Degradation during
# System Start-up and Shut-down in PEM Fuel Cells

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Proton Exchange Membrane Fuel Cells (PEMFC) have been the object of increasing attention since they show great promise as an alternative source of power generation in transportation applications.[1] However, to successfully substitute conventional combustion engines, competitive prices, life-time and durability have to be achieved. Cathode degradation due to carbon corrosion, is a life-time limiting factor taking place during system start-up and shut-down (SUSD), where a $H_2$/air front passes through the anode compartment.[2] Amongst others, approaches to mitigate cathode degradation are to decrease the $H_2$/air$_{anode}$ front residence time and to avoid SUSD events at elevated temperatures.[3, 4]

While those and other strategies have largely reduced SUSD induced cathode damage, Mittermeier *et al.* recently proposed that repeated SUSD cycling is also responsible for anode degradation.[4] The potential cycling between ≈0 V and ≈1 V caused by the change of gases was assumed to be the main contributor to the degradation process. While cathode deterioration can be significantly reduced by the aforementioned mitigation strategies, the impact of anode degradation might increase. In this study, SUSD induced anode degradation mechanisms are characterized and the electrochemical surface area (ECSA) loss as well as the deterioration of the carbon support are quantified. The ECSA loss at cathode and anode is shown in figure 1a and b, respectively. In addition, the potential cycling induced by $H_2$/air$_{anode}$ front is mimicked by potential cycling between 0 and 1 V in $N_2$. The potential of this method as an accelerated test to quantify anode SUSD degradation is determined.

In the second part of the study, the required decrease of the anode loading in order to comply with imminent DoE targets (2020 target: 0.125 mg$_{Pt}$cm$^{-2}$ total loading)[5] is addressed. At ultra-low anode loadings (< 0.05 mg$_{Pt}$cm$^{-2}$), a decreased Pt-particle diameter might be favorable to maintain a reasonable anode roughness factor. However, small particles are known to exhibit fast degradation rates due to dissolution, coalescence and Ostwald ripening.[1] To verify the impact of the particle size on anode degradation mechanisms and overall SUSD damage, Pt/C catalysts with different particle sizes will be synthesized and tested in SUSD and voltage cycling.



**Figure 1: Cyclic voltammograms (CVs) depicting the ECSA degradation on a) cathode (100 mVs$^{-1}$) and b) anode (200 mVs$^{-1}$) relative to the number of ageing cycles in a SUSD test conducted in a 50 cm$^2$ single-cell at 80 °C, 66 % RH, 112 kPa$_{abs}$ and at a $H_2$/air front residence time of 0.1 s. CVs were recorded at 40 °C and 150 kPa$_{abs}$ with dry $N_2$ and fully humidified $H_2$ (flows of 50 and 500 nccm, respectively).**

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# 2. Poster Presentations

# Energy Systems and Buildings

# The MISTRALWIND project – towards a remaining useful lifetime analysis and holistic asset management approach for more sustainability of wind turbine structures

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In the near future more and more onshore wind turbines will reach the end of their designed service life of twenty years. From an economic and operational perspective, it can be profitable to prolong the operational activities beyond the original design life. In particular, turbines in the megawatt class bear technical and economical reserves, which should be yielded for more sustainability of wind turbine technology. Prospectively it might be possible to operate wind turbine structures longer than thirty years with a service life optimizing operation and maintenance strategy. The MISTRALWIND project (acronym for Monitoring and Inspection of Structures of Large Wind Turbines; partners: Technical University Munich, Siemens AG, Industrieanlagen-Betriebsgesellschaft mbH) focusses its research activities on developing innovative and reliable methods and sensor systems for analyzing the remaining useful lifetime (RUL) capacities of a wind turbine structure. The paper is aimed at giving an overview of the first project results in the areas of FEM-modelling, wired and wire-less sensor technology, non-destructive testing techniques, fatigue mechanisms and integrating information from monitoring and inspection into the turbine's controller, and probabilistic models for optimized operation and maintenance strategies for wind turbines. The methods developed here can be transferred to other structural systems – e.g. civil engineering structures or aerospace structures – to optimize their operation and maintenance strategy.

# Optimization potentials of LCA results of laboratories

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Climate change and resource shortage require new construction strategies to achieve more sustainability within the building industry. The total amount of energy consumed by a building during its lifetime is called "grey energy" and implies the energy needed for its construction, utilisation and demolition. Huge effort is being put into minimisation of energy consumption during the utilisation, whereas possible energy saving potential during the construction and demolition phase is not sufficiently investigated yet.

In this thesis energy saving potentials during the construction phase and the demolition phase are identified for a reference laboratory building, which is the Center for Applied Energy Research (ZAE) in Würzburg. Two construction concepts, "ZAE classic" and "ZAE future", are presented and compared to the original concept "ZAE real" regarding the energy consumption of the building throughout its entire lifetime by a life cycle analysis (LCA).

The LCA is based on the calculation of the global warming potential (GWP) which is carried out using the online tool eLCA provided by the Federal Institute for Research on Building, Urban Affairs and Spatial Development (BBSR). A comparison of the GWP of the new concepts and the original construction allows to draw a conclusion which concept offers the most energy saving potential compared to the original construction. The thesis reveals that "ZAE future" achieves a GWP saving potential of 48,7 %, whereas the application of the "ZAE classic" concept leads to an increased GWP of 7,5 % in comparison to "ZAE real".

# DecEnSys – Decentralized Solution Approaches for Energy Systems

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Renewable energy sources gain more and more importance in many countries, especially in Europe. On the one hand, this change promises an independence from fossil fuels and nuclear power, on the other hand, it requires a restructuring of the energy systems in terms of usage, expansion and control. In contrast to large, centralized conventional power plants, renewable energy can be generated by smaller units that are built in a decentralized manner. Additionally, the fluctuating nature of renewable energy resources makes it harder to synchronize peaks in generation and demand and adds a new level of uncertainty to the power system.

These changes require the development of new methods to analyze and plan energy systems: The feedback from a city's decentralized power system needs to be taken into account while optimizing an aggregated model of a whole country, and vice versa, in order to obtain an accurate result. Furthermore, large fluctuations in the output of renewables require a high resolution with respect to time. Storage facilities can be used to offset these fluctuations, linking dispatch decisions between different time periods. Together, these requirements lead to large system models, which currently available optimization methods cannot solve easily within a reasonable timeframe. As a result, they are often sacrificed in favor of faster computation times, leading to inaccurate results.
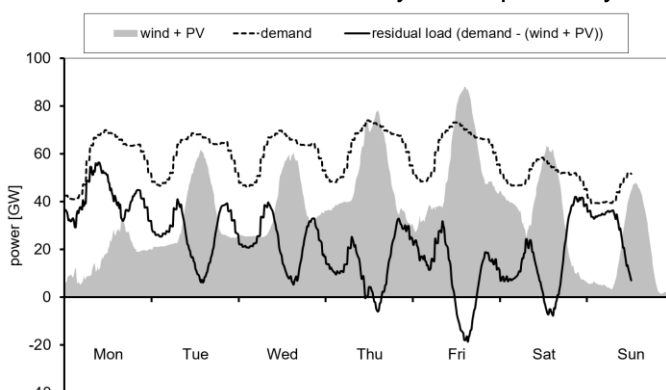


**Figure 1: Increased fluctuation and mismatch between production and demand due to renewables**

The project DecEnSys (Decomposition of energy systems for modeling decentralized power supply systems) approaches this tradeoff between accuracy and computation time from a new perspective. Decomposition techniques allow for large optimization problem to be split into smaller subproblems along the time axis as well as regionally. This not only improves computation times by reducing the problem size, the added flexibility furthermore permits to tackle each particular subproblem by a solution method suited best for its particular structure and properties. On this idea, we build an open framework, which allows to combine subproblems of different types. The framework, as well as all the system data acquired for evaluation runs will be made accessible on a suitable open-source platform.
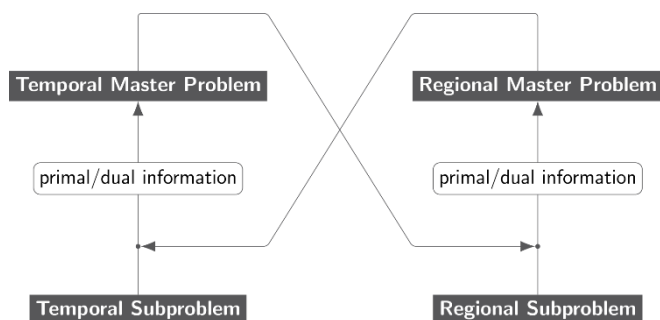


**Figure 2: Structure of the decomposition framework**

On our poster, we present the structure of the above framework as well as its application to a prototypical choice of models. We also propose modifications to well-known decomposition methods from the literature that allow us to take advantage of particular problem structures encountered in problems from the domain of power system optimization. Finally, we present some preliminary results from their application to our prototypical model set-up.

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# Open-switch faults on the machine side of a back-to-back converter in wind turbine systems

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## Motivation

One of the major contributors to failures of wind turbine systems is the back-to-back converter [1]. There are several reasons for faults in the converter (e.g. driver failure, bond wire lift off, etc.), but as a consequence usually one of the switches (IGBTs, etc.) does not close anymore [2]. This is called an *open-switch fault*. In particular for remote or off-shore sites (where maintenance or component replacement is time-consuming), it is crucial to know whether this fault forces the wind turbine system to shut down.



**Figure 1: Schematic of back-to-back converter and electrical machine**

## Methodology & results

To model such an open-switch fault, the semiconductor switches are modelled as ideal switches and the anti-parallel diodes are also assumed to be ideal, see Fig. 1. For an open-switch fault in switch $S_1$—for other switches the impact is analogue—the applicable output voltages of the inverter depend on the sign of the current $i^a$ in phase *a*. For $i^a < 0$, the whole voltage hexagon is available (like in the fault-free case); for $i^a = 0$ the area is reduced; and, for $i^a > 0$, even more, see Fig. 2. The reduced output voltage area affects the resulting currents in the electrical machine, see Fig. 3. The currents are deteriorated; e.g., the positive half-wave of $i^a$ has a reduced amplitude.

This poster will present a generic mathematical model of a back-to-back converter which allows to consider open-switch faults and to investigate the impact on the current control system, torque generation and the overall wind turbine system



**Figure 2: Applicable voltage range for different currents $i^a$ for open switch $S_1$**
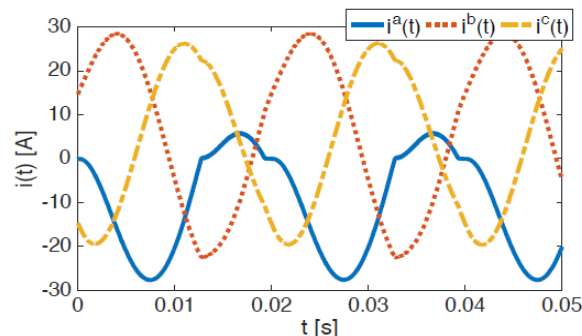


**Figure 3: Currents $i^{abc}(t)$ of the electrical machine for open switch $S_1$**

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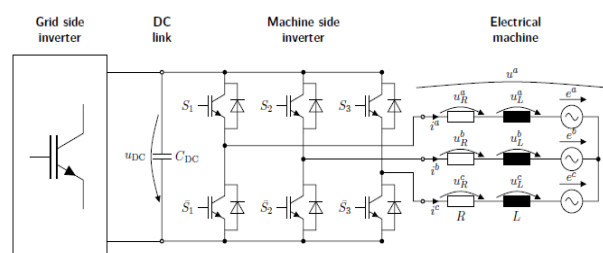
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58

# Potential use of thermo-responsive polymers as smart window surface coatings

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Today more than half of the world´s population already lives in an urban environment and this trend will even be increased to 70% by 2050 [1]. Therefore, a well-balanced energy management is necessary to keep the urban areas sustainable. In the United States over 40% of the energy consumption can be traced back to building utilities, of which cooling and heating are the main contributors [2]. Novel, ecological concepts for cooling have been proposed in the past years, mostly based on passive systems that are directly integrated in the roofs or the facades of the buildings. These systems demand autonomously 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. A promising approach for self-cooling building is sweating [3]. For example, mammals were able to life under environmental conditions of more than 25°C above their body temperature since they had the ability to sweat. With the transformation of this capability towards buildings an environmentally friendly way of autonomous cooling can be achieved.

A simple and highly efficient way to cool buildings would be to use thermo-responsive polymer thin films as smart surface coating since they undergo a phase transition at their lower critical solution temperature (LCST). Below the LCST, polymer-solvent interactions are favored and $H_2O$ molecules from the surrounding diffuse into the polymer film. However, once the LCST is exceeded, the polymer becomes more hydrophobic and water molecules are released out of the polymer film. The released water molecules evaporate and the building is cooled down by evaporative cooling. Dependent on the composition of the polymer the LCST is tunable within a broad temperature range and the absorption as well as desorption of water molecules are reversible. In order to establish such thin polymer films in smart surface coatings a fundamental understanding in the kinetics is needed. The most prominent representative of thermo-responsive polymers is poly(N-isopropylacrylamide) (PNIPAM). Therefore, we analyze a new PNIPAM-based block copolymer via neutron reflectometry. With this sophisticated technique we are able to follow in-situ the swelling behavior and determine the underlying fundamental processes.

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# Detection of Single-Phase Parameters Using Second Order Generalized Integrators for Calculation of Symmetrical Components of Highly Distorted Grids

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## Motivation

In power systems like overhead power lines, grid faults or unbalanced loads can lead to a highly distorted or unbalanced grid. In order to ensure a stable grid, distortions or unbalanced operations have to be avoided. Therefore, a decomposition of unbalanced quantities like voltages or currents in balanced quantities is necessary. This decomposition is called method of symmetrical components, which was firstly presented by Fortescue [1] and later on modified for single-phase applications as reported in e.g. [2], [3], [4], [5], [6], [7]. If the phases are distorted by harmonics or a constant offset, a decomposition is no longer possible. So, these distortions have to be detected and compensated for. Additionally, for an online detection of symmetrical components, the quadrature signal of the phase quantities are needed.

## Methodology

This poster proposes an algorithm for detecting phase parameters based on a Second Order Generalized Integrator (SOGI), which is also called Adaptive Notch Filter (ANF) for generating the quadrature signal [6], [8]. Since a SOGI needs a reference frequency to compute the quadrature signal, another disturbance is found if the reference frequency does not match the actual frequency of the phase quantity. So, for computing the symmetric components, the signal has to be analyzed with respect to frequency, harmonic and dc components. Frequency detection can be achieved by a Frequency Locked Loop (FLL) [6], [7], [8] or a Phase Locked Loop (PLL) [2], [9]. DC offset estimation was reported in [4], [10] whereas extraction of harmonics is considered in [11], [12]. Different approaches for detecting phase parameters without SOGIs are mostly based on delay blocks [5], [13].

Since this work deals with online detection of positive, negative and zero sequences, noise has to be considered as well. Therefore, this poster presents a unified method for calculating dc offset, fundamental frequency, harmonics, phase angles and amplitudes whereas a low pass filter (LFP) is included to eliminate nose effects.

## Results

Simulation results show that a single-phase quantity of any form can be split up into fundamental frequency, amplitudes of the harmonics, constant offset and phase angle. Furthermore, symmetric components are calculated using the in- and quadrature signals. These presented results are also verified by measurements.

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# Model predictive current control of doubly-fed induction machines with LC filter in wind turbine systems

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## Motivation

The doubly-fed induction machine (DFIM) is one of the most common generator topologies in large-scale wind turbine systems (WTS). Around 50% of the installed onshore WTS in Germany 2013 [1, p.31] come with this generator topology. Fig. 1 shows the components of such a WTS. It consists of turbine, gear box, DFIM, back-to-back converter, transformer and electrical filters. The stator of the DFIM is directly coupled to the electrical grid via the transformer and its rotor is connected to the back-to-back converter via an LC filter, which reduces the harmonic distortion of the rotor currents and voltages. To control the mechanical torque (or mechanical speed, resp.) and the reactive power of the DFIM, underlying rotor current control loops can be used.
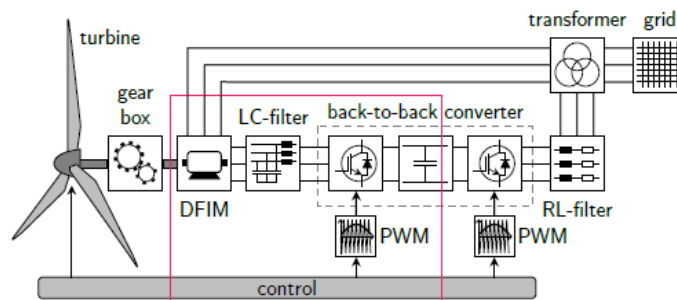


**Figure 1: Wind turbine system (WTS) with doubly-fed induction machine (DFIM).**

## Methodology

For that, this poster discusses model predictive current control with analytical solution, which (i) ensures global optimality and (ii) allows for high prediction horizons in comparison to finite-control-set model predictive control (MPC) [2],[3]. Long prediction horizons are—despite the increasing computational power of standard real-time systems—still not feasible in general but are important; both to guarantee closed-loop stability (e.g. for minimum-phase systems [4]) and to improve the control performance [5],[6]. For all MPC methods steady-state accuracy cannot be ensured in general. Therefore, to achieve steady-state accuracy, the system is augmented by an integral error feedback (IEF) term which can be included in the existing MPC theory and does not endanger closed-loop stability [7].

## Results

Simulation results illustrate the good control performance of the model predictive current controller with analytical solution (even for significant changes in the magnitude of the grid voltage). Moreover, they clearly show the improved control performance of MPC with IEF compared to MPC without IEF: Steady-state accuracy is achieved although varying disturbances act on the closed-loop system.

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# Energy-meter data analysis using Android App: An Economical Approach

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This project is ascribed to develop a relatively cost-effective module in order to analyse the electrical energy consumption through a convenient interface of android application. Although in the current age, there are smart prepaid meters serving the very purpose, the module created is merely a slight modification to the existing single phase digital energy-meter and serves as a cost-efficient model. The approach mainly consists of two major segments: one being to develop a hardware equipped to interact with android phone easily and other being android application with decent features that would analyse and present data to the costumers. The complete overview of this has been given in this paper.

The hardware basically consists of a pulse retrieving circuit. The CalLed of the energy-meter is tapped directly from the meter and fed to a microcontroller. The microcontroller counts the number of pulses received and translates it as the power consumption in kWh. This computed power consumption is projected onto a website embedded in the IC which is accessible through the android application.

The android application, extracts the power consumption data from the website. The data collected over a week is then analysed and a prediction of the monthly and yearly consumption is made using linear projections.

Following are the domains where this set-up can be utilised:
1. Smart Real time awareness for consumers to optimize consumption and reduce wastage of energy.
2. Test Bench for implementing Demand-side Control Algorithms.

The future scope for this project would be:
1. Integration of this meter onto a smart home automation environment with specific real-time energy saving solutions to the consumer.
2. Test artificial intelligence algorithms wherein smarter suggestions to the consumer can be provided based on the pattern of energy consumption specific to a consumer.
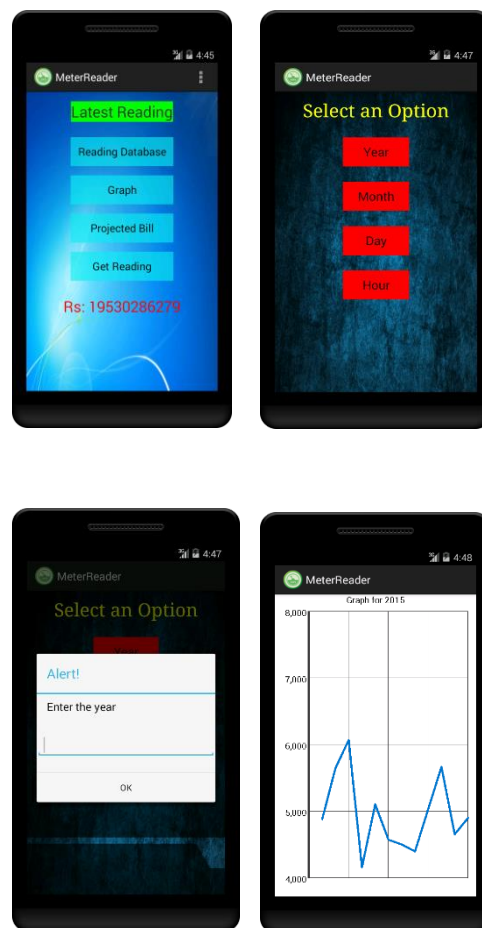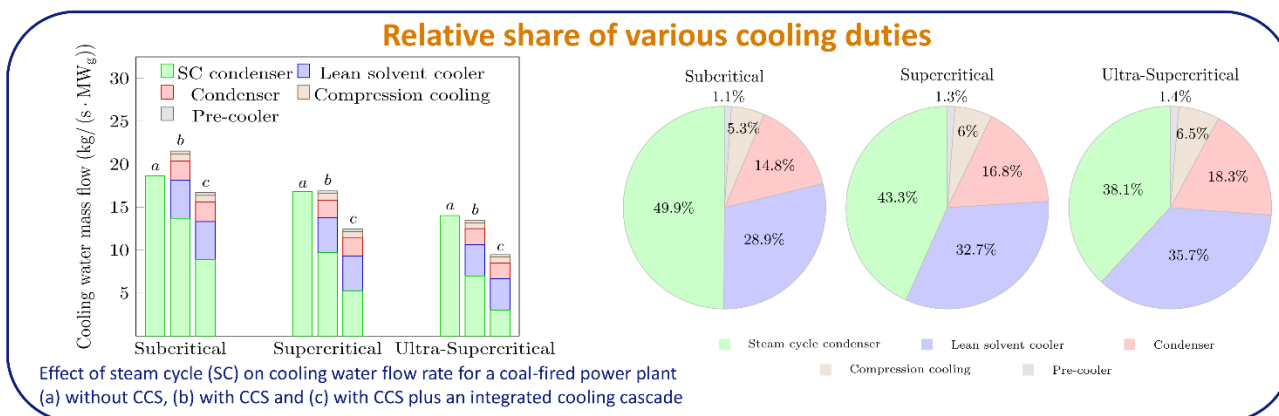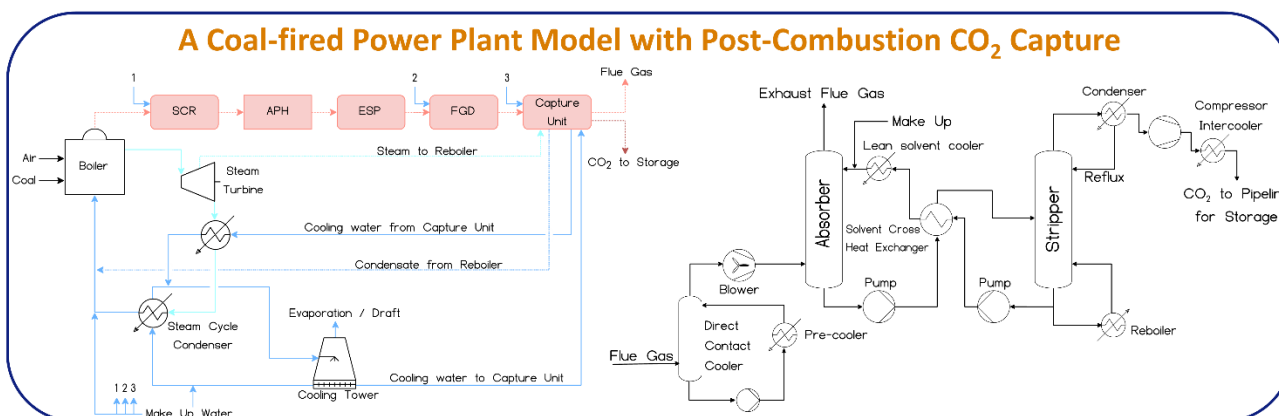


**Figure 1: The user interface in the app**

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# Evaluation of cooling requirements of post-combustion CO2 capture applied to coal-fired power plants

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## Carbon Capture in the UK: Factsheet

The UK has been committed to reduce the $CO_2$ emissions by 80% from 1990 levels by 2050.

Electricity generation from fossil fuels is one of the biggest single emission sources of $CO_2$ (25% of total) [1].

Capturing $CO_2$ from the power plants' flue gas emitted otherwise into the atmosphere can significantly reduce $CO_2$ emissions.

In conjunction with other technologies, CCS leads to a minimised overall costs of electricity supply in the long run [2].

## Water-Energy Nexus

Water usage at fossil fuel power stations is considerably high [3].

An additional CCS plant could result in a significant increase in the associated cooling requirements leading to an surge in the localised water usage.

## Objectives

Evaluating the cooling demand of an amine-based post-combustion $CO_2$ capture process integrated with a coal-fired power plant.

Presenting a breakdown of the required cooling duty by taking into account the plant's capacity, steam cycle and operating conditions and classifying the potential of cascading cooling water.

## A Coal-fired Power Plant Model with Post-Combustion $CO_2$ Capture



## Relative share of various cooling duties



Effect of steam cycle (SC) on cooling water flow rate for a coal-fired power plant (a) without CCS, (b) with CCS and (c) with CCS plus an integrated cooling cascade

## Conclusions

The results are in contrast to previous suggestions that the addition of CCS would double the water footprint.

The temperature at which cooling is required varies appreciably throughout the integrated capture process plant.

The increase in cooling duty (MW) does not necessarily lead to an increase in cooling water usage ($kg_{H_2O}$/MW).

Integration of a cooling water cascade can result in a reduction in the cooling water requirements of a decarbonised power plant.

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# Radiative Cooling in Munich

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The architectural design of new buildings is using more frequently large-scaled glass facades or similar transparent constructional components. Especially in office buildings, where visual connection to outdoor areas creates comfortable working spaces [1] and maximizes daylight in the room, simultaneously reducing the need for artificial lightning. However high glass surface area of the buildings' will result higher internal solar gains, causing higher cooling loads. At the same time, there is a huge interest to provide energy-efficient and sustainable energy supply for buildings, that needs multiple innovative ideas in the design and implementation of modern buildings.

Recent investigations focus on the passive cooling supply of a virtual single office room, with passive house related construction standard, located in Munich. Nocturnal radiative cooling is used by a flat plate collector to provide cooling power at night, that refrigerates water in a thermal energy storage (TES). Chilled water in the TES provides a heat sink by day. Then, it is used to cool down the investigated single office room with the ceiling cooling and the mechanical ventilation when there is a cooling demand at daytime. Figure 1 shows a simplified technical schematic diagram of the cooling supply concept. A sufficient cooling for the office room is crucial, where among other things the dependency of



**Figure 1: Simplified schematic of the cooling supply concept**

the collector area, the TES volume and the room area is investigated. The plant concept is simulated with the thermal building simulation tool TRNSYS 17 using Genopt to optimize the parameters of the system.

First results confirm the plausibility of such designed cooling concept which makes it possible to satisfactorily temper the room in the entire cooling period. The applied passive cooling needs, in comparison to active cooling systems (e.g. conventional compression refrigeration), only a minimal amount of electrical energy. It is shown that radiative cooling can be applied in Munich's moderate climate. Possible generation of solar heating power (even electrical power using PVT-collectors) by daytime supplying the energy demand for the whole year is investigated in a parallel study. The findings of the dependency of the plant dimensions can later be used in a combined cooling and heating system. The investigation carried out are based on a virtual room, the consideration of this study can be taken into account for buildings, residential areas and future energy concepts.



**Figure 2: Dependancy of plant dimensions to provided cooling power**

Reference:

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# New pattern of sharing bicycle rental policies promoting efficiency of urban public transportation

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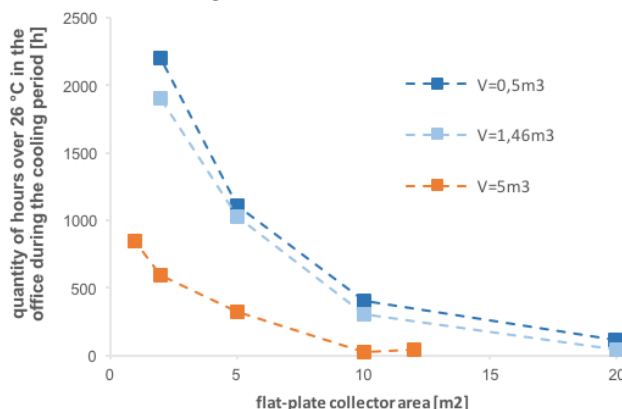
China's economy is growing rapidly in the current time, due to which the transportation industry is also growing fast. People are getting more concerned about the energy issues because of this rapid growth in the transportation industry. Development of an efficient public transportation system can be a better solution to reduce the energy consumption. The usage of bicycles is also growing to reduce the fuel consumption. Shanghai is currently the biggest user of public bicycles in the world.

This study will conduct a random sampling survey on two dwelling districts in Shanghai in 2015 and 2016 to analyze the changes in citizens' mobility options and how the usage of energy has been affected by an increase in people's affinity towards public transportation systems. This study will also analyze how the increase in the usage of public bicycles or sharing bicycles （Figure 1）will lead to an efficient utilization of public transport. It can be used as a single transport or combined with other public transportation vehicles.



**Figure 1: "Mobike" sharing bicycles**

The governmental public bicycles were good and people used to use it often but they have fixed station from which it can be picked and returned. The new mode of bicycle sharing system provides the flexibility of parking the bicycles anywhere. Due to the flexibility provided by the private companies, people are using the sharing bicycles more often. The smart bike-sharing service are based on "Sharing economy" and "Internet Technologies" which leads to strong liquidity and have eliminated the difference between places having different numbers of bicycles stations. (Figure 2)
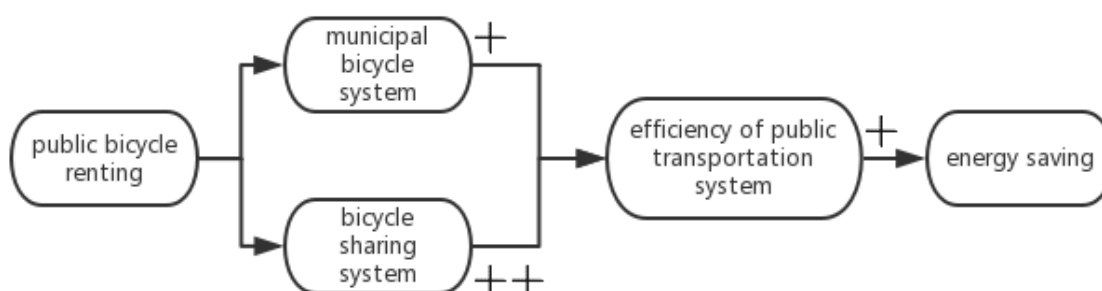


**Figure 2: structure of efficient public transportation system**

Keywords:
sharing bicycle
transportation system
energy consumption

# Energy optimization for highly saturated synchronous machines

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As electrification advances as a trend in the automotive industry to cope with stringent emission and fuel consumption requirements, energy efficiency of electrical drives becomes a central issue. Since highly anisotropic and saturated synchronous machines are widely used in these applications, due to their inherent cost and performance advantages, the development of strategies for improving their efficiency has a significant impact on the aforementioned aspects.

The Maximum Torque per Ampere (MTPA) strategy and the Maximum Torque per Volt (MTPV), which consist at minimizing the total current and voltage respectively, are used in order to maximize the machine efficiency. These two strategies are dependent on temperature, aging and the machine itself, making their application a challenging task. To deal with these dependencies, a novel numerical approach is developed by considering the effects of saturation and cross coupling in the machine through the use of the differential inductances. The solution is capable of delivering results online and its convergence rate and limits are analytically proven.

Fig.1 and 2 prove the effectiveness of the proposed method for two different synchronous machines, while showing that state-of-the-art methods fail to reach the energy optimal operation points in both cases. In Fig. 1c and 2c, it is possible to see that the proposed MTPA and MTPV approaches can lead to 15% and 42% loss reductions for Machine 1 (PMa-SynRM) and 5.8% and 2.5% for Machine 2 (RSM) at low and high speed respectively.



**1a – MTPA - PMa-SynRM**



**1b – MTPA - RSM**



**1c – MTPA – Copper loss reduction**



**2a – MTPV – PMa-SynRM**



**2b – MTPV - RSM**



**2c – MTPV – Core loss reduction**

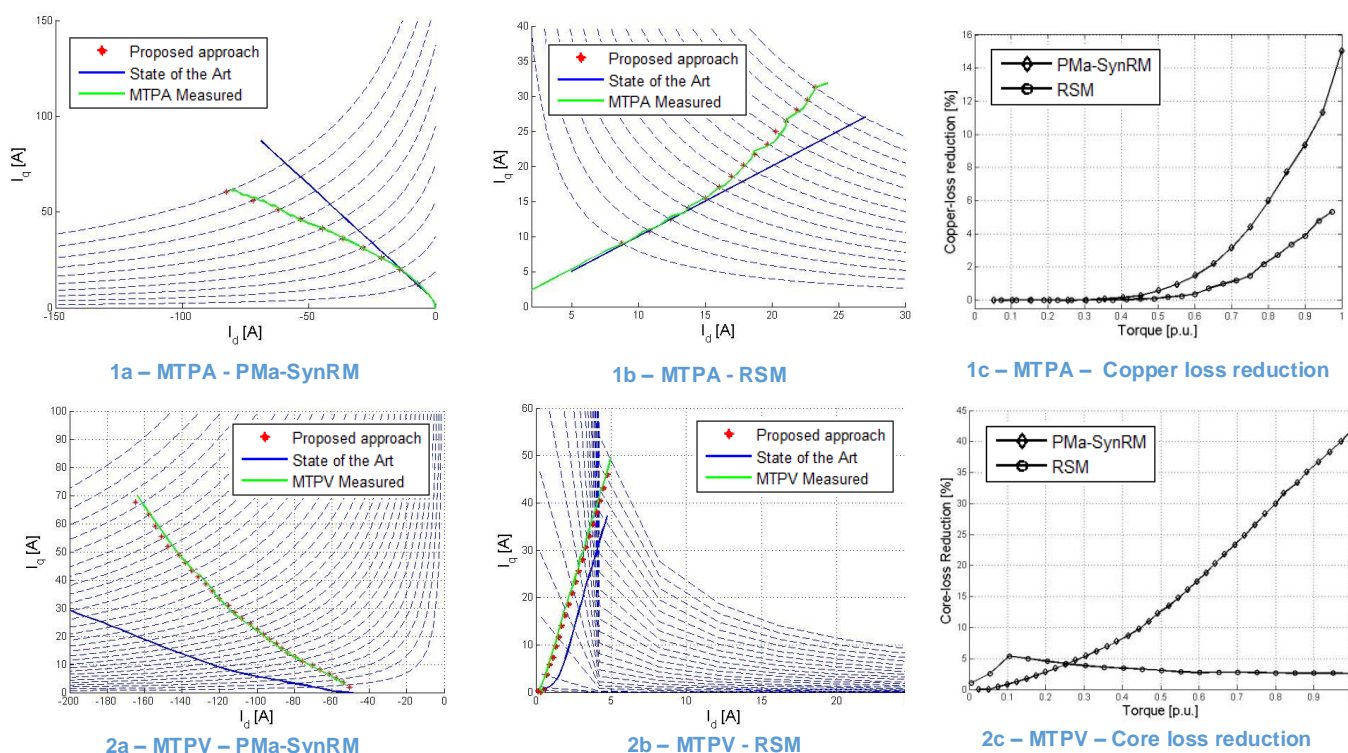**Figure 1a and 1b: Current loci for MTPA strategy; Figure 2a and 2b: Current loci for MTPV strategy; Figure 1c and 2c: Copper and Core loss reduction for MTPA and MTPV strategies.**

Bonifacio, J; Kennel, R.; "*On considering saturation and cross-coupling effects for copper loss minimization on highly anisotropic synchronous machines*"; International Conference on Electrical Machines and Systems (ICEMS'16), Chiba, Japan, Nov. 2016.

# Probabilistic GIS-based technical potential assessment of hydrothermal energy in Bavaria

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Geothermal energy is expected to play an important role in the German power transition. State-of-the-art geothermal technology is capable of providing base load power, of using heat directly, and of coupling the heat and power sectors. Although several studies have established the existence of hydrothermal resources in Southern Germany, a region that partly lies on the Molasse Basin, the amounts of power and heat that could be generated and their geographical distribution remain largely unknown. Yet, such information is crucial for the optimization of the energy system expansion and operation which relies on models with a high spatial resolution.

In this study, key reservoir parameters are used in a GIS-based Monte Carlo simulation to estimate the probable range and spatial distribution of the technical potential of hydrothermal energy in the Bavarian region. A sensitivity analysis, where the uncertainty of the geological variables is characterized using different probability distributions, is also performed allowing the uncertainty of the results to be quantified. The assessed technical potential is then aggregated on a municipal level and validated with data from existing geothermal projects.

Whereas a thorough reservoir characterization is needed before any geothermal exploration is conducted, priority should be given to areas identified with high potential and low uncertainties.

Key words: Hydrothermal energy; GIS; Monte Carlo simulation

# Open-source heating energy demand estimation at the urban scale

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Coupling local energy consumption with local energy production offers opportunities for the integration of renewable energies and $CO_2$ emissions reduction in the heating sector. Calculating the spatiotemporal heating energy demand is key to identify potential improvements in the urban energy system. Heating energy demand is influenced by building geometry, building usage, building construction materials, weather conditions and user behavior. Such building-specific information is often hardly available making a detailed thermal demand estimation at the urban scale an arduous task. We propose a methodology to generate heating energy demand profiles based on open-source data overcoming the challenges of availability of building-specific data. Additionally, the spatial and temporal dimensions are considered simultaneously and the influence of occupant behavior in the heating energy demand is also taken into account. The proposed model is used to predict the heating energy demand of a municipality in Bavaria, Germany and the results are validated against real production data of the local district heating system.

Key words: heating energy demand, open-source data, urban energy

# SimSES: Software-tool for Techno-economic Simulation of Stationary Energy Storage Systems

Holger C. Hesse[a], Daniel Kukevic[b], Maik Naumann, Nam Truong, Michael Schimpe, Andreas Jossen

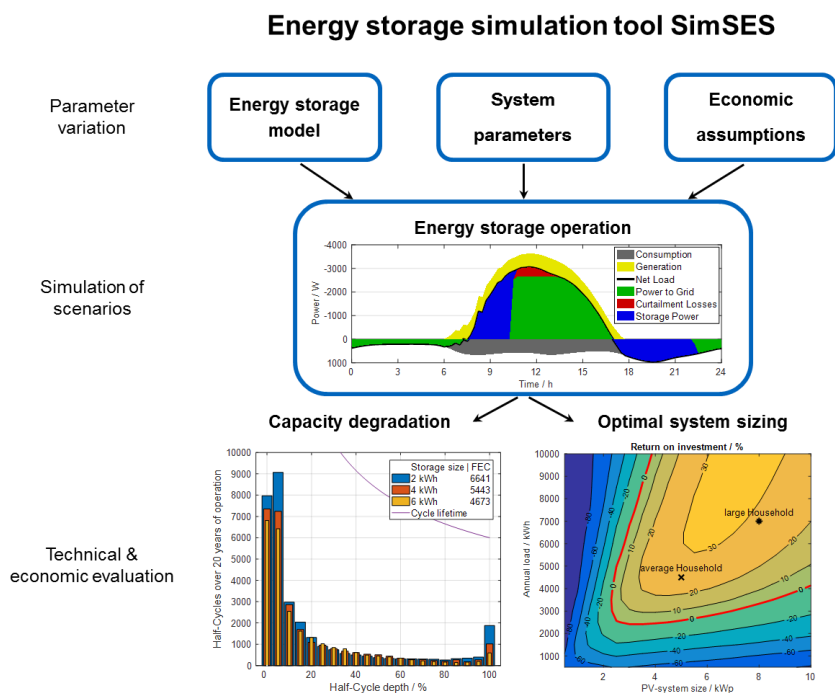[a]holger.hesse@tum.de, [b]daniel-kucevic@tum.de

**Figure 1: Structure of SImSES software tool**

Due to the new challenges in power grids and falling costs of energy storage systems, the technical and economic suitability of these technologies is presently under discussion for the various stationary applications. However, there are numerous technical degrees of freedom in the storage system design that can be optimized, such as the choice of energy storage technology or the technical sizing of the individual components. In order to be able to investigate these and other technical questions concerning stationary energy storage systems, the software-tool SimSES, has been developed at the institute of Electrical Energy Storage Technology at the Technical University of Munich.

SimSES enables a detailed techno-economic simulation and evaluation of stationary energy storage systems with the current main focus on lithium-ion batteries. Various applications of stationary energy storage systems can be simulated, such as, for example, the self-consumption maximization in households with PV systems, the grid-relieving operation by peak load reduction, the provision of control power, the arbitrage trading in the electricity market or the combination of different applications. Simulation scenarios and technical components of the energy storage system can be selected as desired. Load profile characterization enables estimation of storage degradation factors. Various aging models can be selected according to the storage technology of choice. Detailed battery models are parametrized using aging experiments conducted at the institute. In order to optimize the utilization of the energy storage in the different applications, various operating strategies are implemented. At the same time, the calculation of economic key performance indicators allows the assessment and comparison of the simulation results.

The simulation tool SimSES has already been used in various publications for the analysis of the applications "PV home energy storage system" [1-2] and "primary control reserve" [3]. In addition to the development of optimization methods for improvement of the storage operation and component sizing, the application scenarios "island grid" and "vehicle-to-grid" will be integrated in the simulation framework. The mid-term goal is to make SimSES available for non-commercial usage and further development as an open-source software.

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# Synthetic thermal load profiles for office and educational buildings

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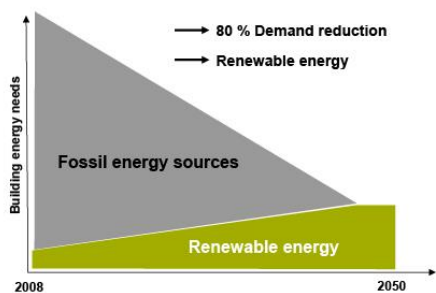
**Figure 1: Energy demand of the German building stock**

## RESEARCH APPROACH

In 2015, the German federal government presented the Energy Efficiency Strategy for Buildings. As an important pillar of the national energy and climate policy it formulates the way towards a virtually climate neutral building stock: by 2050 the primary energy demand of the building stock has to be reduced by 80 percent against 2008 through a combination of energy savings and the use of renewable energies (Figure 1) [1]. Thereby the concept includes technical and energy aspects as well as overarching aspects like the interaction between heat and electricity. The research project CleanTechCampus picks up the resulting need and aims to develop an integrated transition concept for the Garching Campus. This offers the opportunity to analyze the energy efficiency potentials of educational buildings which are intended to pose examples on the way to the climate neutral building stock.

## OBJECTIVES

Within the task to estimate the energy demand and its parameters the broad variety of the building structure at Garching Campus poses major challenges. Although the energy-system-model requires load profiles of the heat demand in a high temporal and spatial resolution a transient calculation of all buildings is neither in effort nor in variability appropriate. Due to the interactive project methodology a method for creating parametric and transferable load-profiles for non-residential buildings should be developed on the basis of non-transient energy demand calculations.

## METHOD

The main parameters of the energy demand can be identified using the non-transient calculations which were done for almost all buildings in the first part of the project. Depending on the building age class the impact of transmission losses is high for older buildings while the type of use dominates the energy demand of the younger buildings. Based on the first results the energy demand parameters in different areas of use are analyzed more deeply using transient calculations. Here, parts of the buildings were investigated separately to optimize the confirmability of the results. The gained standardized and parameterized load profiles (Figure 2) will be super-positioned up to the building scale and further varied in the different energy demand scenarios of the Garching Campus.
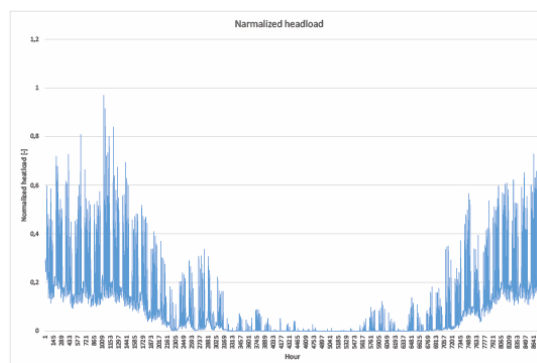


**Figure 2: Standardized heatload-profile**

## PROSPECTS:

The method will be applied to several buildings with different characteristics in order to get detailed insights into the buildings energy demand structure and the resulting efficiency potentials.

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# Integrating Demand Side Management of Residential Heating Systems in Distribution Grids

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Residential electro-thermal heating systems are promising candidates to better integrate excess electricity generation from renewable energy sources, but may also add additional stress to existing grid infrastructure during peak load times. Heat pumps in combination with storages and the thermal mass of buildings can offer a certain load-shifting potential without seriously affecting the residents' comfort. Classic grid planning strategies lack an appropriate incorporation of the flexibility such loads may offer and may often lead to overinvestments in infrastructure. There is a need to better understand the local effects of heat pumps on distribution grids and how demand-side management (DSM) mechanisms can be integrated into robust grid planning strategies.

The presented bottom-up approach creates simplified resistance and capacitance (RC) models to represent the dynamic behaviour of each building. The dynamic representation of the individual buildings enables to test DSM strategies. An uncoordinated model predictive control strategy (MPC) for each building to minimize energy consumption is compared to a distributed approach (DMPC) to respect both local goals of the buildings and the global goal of the distribution system operator (DSO) to flatten the aggregate load profile.
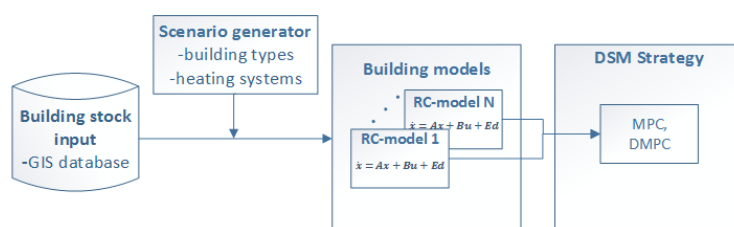


Figure 1: Workflow from model parameterisation to DSM studies.

The simulation results demonstrate how the aggregate residual load curve of all buildings can be optimized towards a grid-supportive operation to avoid overloading at the transformer. Communication infrastructure is reduced and a certain level of privacy maintained, due to the distributed communication mechanism and the parallelized optimization of the individual buildings.
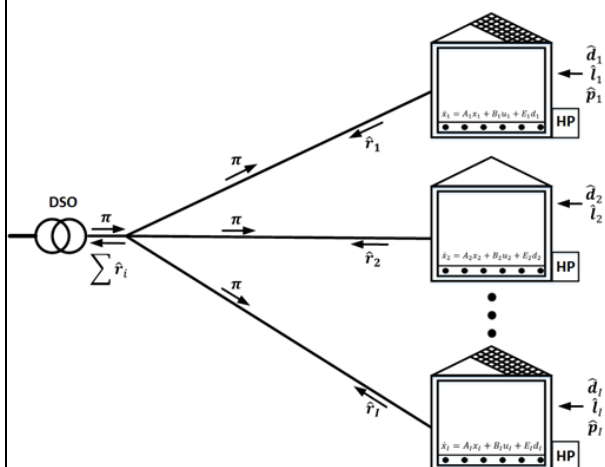


Figure 2: Communication between buildings and DSO in DMPC scheme.

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# Integration of energy storage in urban energy systems

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The changes that are occurring within the energy sector such as greater penetration of distributed generation and the increasing electrification of the heating and transportation sector result in the need for more flexible energy systems. As a powerful provider of flexibility, one can assume that electrical energy storage will play a much more significant role in future energy systems. Within this work the aim is to investigate the most important aspects of the integration of energy storage and their effect on one another to create insight about how to best integrate energy storage.

The three main aspects to consider are, a) optimal planning, b) operational strategies, and c) future markets and flexible pricing schemes.

Regarding optimal planning the objective is to develop an algorithm that calculates the optimal size and location of storage units within a given distribution grid. The difficulty in modelling electrical grids is that energy storage introduces time interdependency, and therefore it is important to have accurate predictions of local generation and loads.

Investigation into operational strategies is particularly important for residential storage, because it can be shown that coordination of energy storage units can greatly increase their utility. However to coordinate storage units there needs to be information exchange which can pose several problems. Besides the physical infrastructure required for data exchange, the issue of privacy also needs to be considered. Therefore it is valuable to minimize the actual amount of household data that is shared, whilst still managing to coordinate the households. Since the use of centralized control is not realistic because of the problem size and the amount of data exchange required, the focus is on development of distributed control, where each unit is controlled independently with minimal communication between units. A Distributed Model Predictive Control (DMPC) is developed and demonstrated, where Local Controllers (LC) communicate minimally with a Centralised Controller (CC) to coordinate the storage operation of several Residential Energy Systems (RES) with loads and PV generation. The optimization results of a 24 hour trajectory is shown in Figure 1.
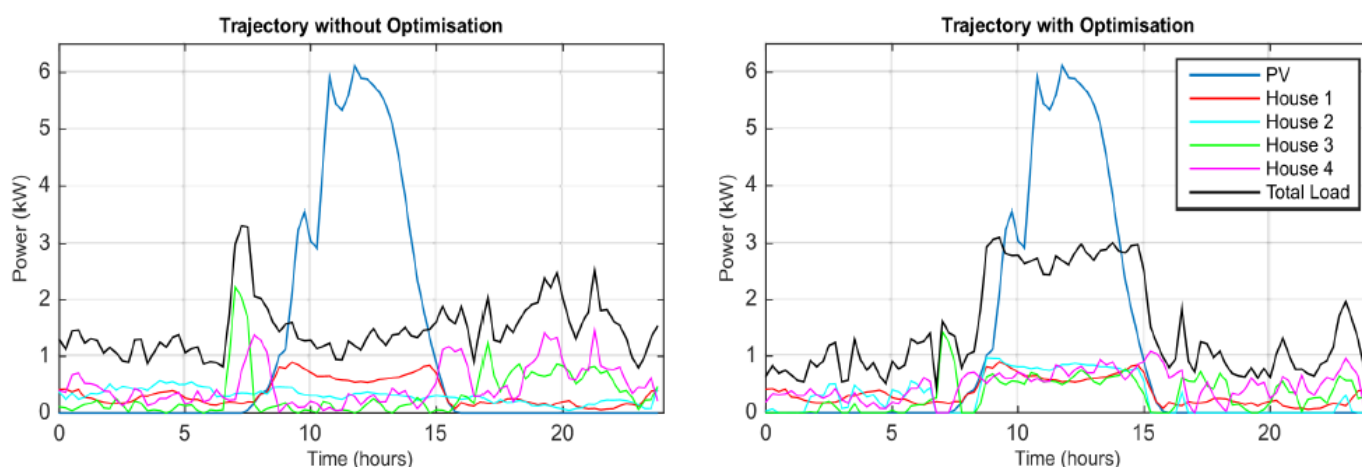
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72

# Current distribution in hybrid battery systems loaded with a dynamic drive cycle

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The design of battery applications depends strongly on the power and energy of the storage. These parameters are limited by the properties of the cell. Large storage systems comprise many small cells. Tesla, for example, uses 7.104 cylindrical 18650 cells for the 85 kWh version of its Model S. In most applications, the cells are connected in parallel and series.

The approach shown in this poster combines cells with high power (HP) and cells with high energy content (HE) to gain a further degree of freedom. In Figure 1 the used 18650 cells can be seen. A storage system with two strings was constructed. The string with HP cells uses 5 parallel 96 series (5p96s) connection, the HE string is designed as 10p96s. As the HE cells have around twice the energy content ratio of the HP cells, the energy content of the strings is 4:1. Looking at the impedance, it is the contrary. The HP cells have on cell level



**Figure 1: HP and HE battery cells**

HP cell
LG
ICR18650HB2
1.5 Ah $I_{max}$=30 A

HE cell
Panasonic
NCR18650PF
2.9 Ah $I_{max}$=10 A

around half the impedance of HE cells. On string level, the impedance of the two strings is about the same. Depending on the cell parameters impedance and capacity, the current distribution between parallel connected cells is not equal distributed. As the cells are connected in parallel, the voltages of both strings are equal, states of charge (SoC) diverges. Impedance differences lead to short term unequal currents and capacity differences lead to long term current differences [1]. This means that the C-rate (current in relation to capacity) of the HP cells is disproportionately high for dynamic load profiles and the HE cells carry the biggest share of the total current.

The HP string contains about 20 % of the total capacity. While the storage is discharged fully, 20 % comes from this string. To see the effects in a dynamic load profile, the system is loaded by a drive cycle recorded in Stuttgart (Figure 2). The storage system completes the profile five times, simulating a long drive. The HP string supplies the power in high dynamic parts. As the energy content of HP cells is low, the SoC difference between the strings becomes bigger while discharging. Therefore, the charge throughput of the HP cells is higher
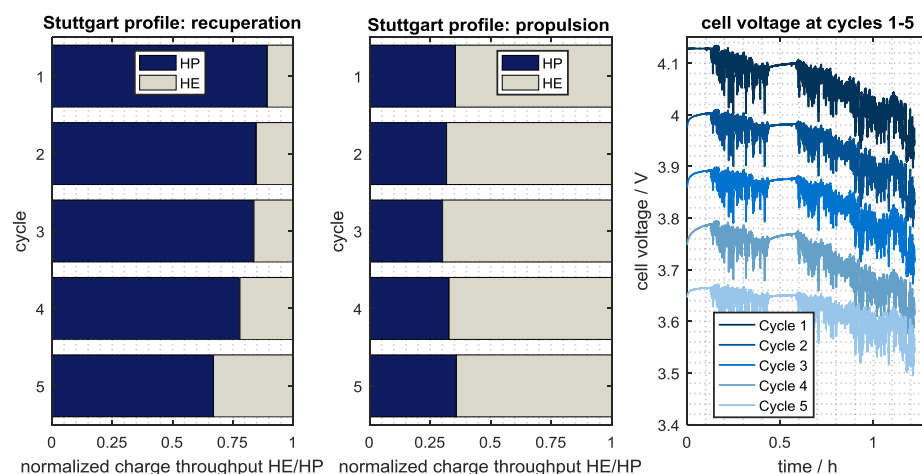


**Figure 2: Charge throughput in recuperation and propulsion case**

than the ratio of the capacity of the HP sting. HE cells are strongly limited in terms of current because high currents lead to accelerated degradation [2]. This is an indication for a longer lifetime of this cell combination. In contrast, current flow between the strings leads to about 10 % more charge throughput in total.

As HP and HE cells of the storage system are combined in 1:2 ratio, an experiment on cell level with one HP and two HE cells can emulate the performance of the system. Measurements on cell and system level are in good accordance.

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# Network Design and Yield Optimisation of Solar District Heating Systems for Urban Applications

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Multi-storey residential buildings provide high potential for solar-assisted local district heating. Current research projects focus on the utilisation of large seasonal storages to achieve a solar fraction of above 50 %. However, for retrofitting densely built-up urban areas, the feasibility of solar district heating is often restricted by the limited space available for collector arrays and heat storages. Moreover, high storage capacities come with high investment and heat production costs. These drawbacks impede the applications of seasonal storage concepts in existing urban areas and hinder the dissemination of large solar-thermal systems.

This project aims to tackle these challenges by investigating a novel solar district heating design based on distributed solar collector arrays and thermal heat storages in multi-storey residential buildings with bi-directional heat distribution capability and the intelligent interaction of these components. The study will examine the network design and yield optimisation of such a system in various urban contexts. Within the project, a real district heating network in Ingolstadt was equipped with decentralised solar thermal plants (Figure 1). These plants provide either a local use of the solar gains for domestic hot water preheating, a pure feed in to the district heating network or a combined solution. Annual solar yields between 280 and 660 kWh/m² were reached in the simulation.

Throughout the last months, an acquisition of detailed metrological data of weather conditions as well as temperatures and heat flows in the network was conducted. This allows, besides the comparison of the performance of the different plant types, the validation of the simulation models. The validation shows a good accordance of the model to the real data. Nevertheless, the solar yields of the real plants are behind expectations, as the temperature levels are higher than expected due to an unbeneficial operation of the existing network. Based on the validated models, possible improvements of the control strategy and an outlook on the solar yields during a complete year of operation are derived.

In a further step, a simulation-based test of more advanced control strategies with an intelligent distribution of the solar yields will be conducted. During this investigation, plants sizes, plant numbers and the basic configuration of the district heating system will be varied within the scope of a sensitivity analysis of the approach.

The findings of the study will show whether the intelligent interaction of small, decentralised plants can adequately compensate for the lack of storage capacity as compared to the centralized seasonal storage concepts. The outcome of the project can contribute to the realisation of renewable heating systems with low solar heat costs in combination with a decent solar fraction.
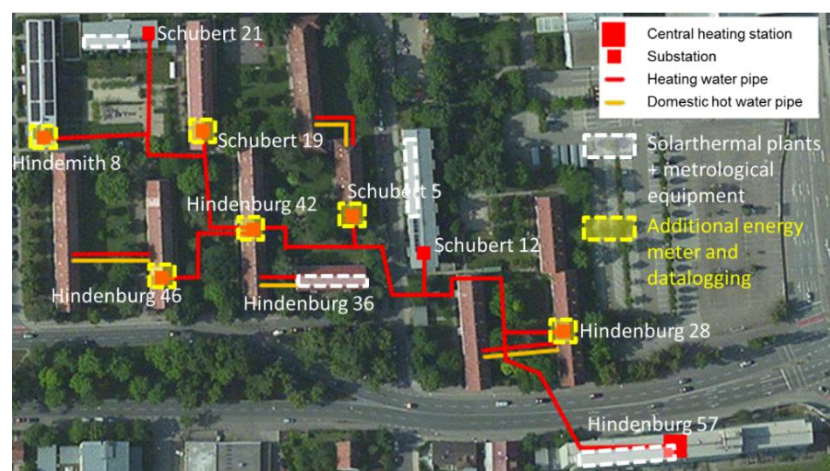


**Figure 1: Investigated district heating system with positions of solar thermal plants**

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# Technical and economic analysis of a domestic hot water system with polymeric solar thermal collectors

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The application of polymeric materials within the context of solar thermal systems promises a significant reduction of both investment and operating costs. Compared to metals, which are typically used in the solar thermal industry, polymeric materials have a reduced pressure resistance, especially in combination with high temperatures. For optimal utilization of polymeric materials, the lower pressure resistance must be compensated on system level, e.g. by means of a drain back system (DBS). The aim of this study is to evaluate the technical and economic performance of such a DBS for domestic hot water preparation in a single family home. Therefore, the Levelized Cost Of Heat (LCOH) of a typical DBS are determined and compared to a conventional solar thermal system.
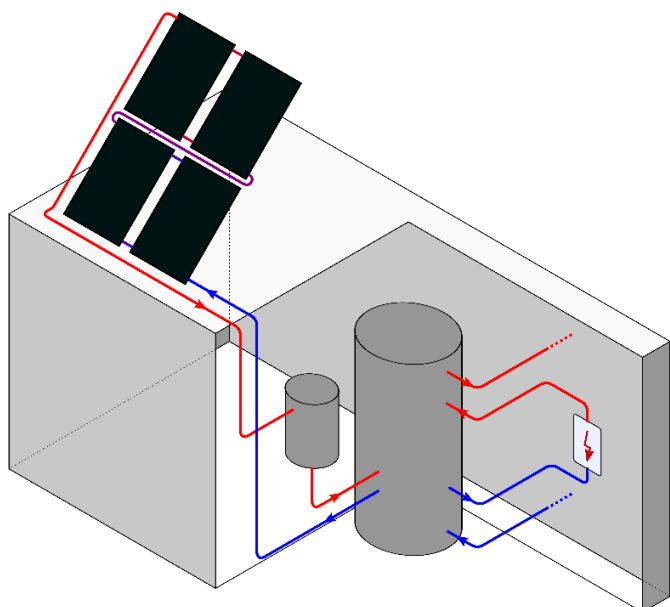
**Figure 1: Setup of the outdoor test rig**

The basis for this investigation are experimental results, which have been obtained at an outdoor system test rig at the Insitute of new Energy-Systems in Ingolstadt. A collector array made of polymeric solar thermal collectors (45°, south orientation) with an overall area of 2.3 m² is connected with a 500 l storage tank. Between the collector array and the storage tank, an additional 80 l volume is used as a drain back storage. A 9 kW backup heater heats up the storage tank in case of insufficient solar irradiation. The generated heat is consumed according to a typical load curve for single family homes (VDI 4655). A schematic setup of the test rig is shown in figure 1. The experimental results of the system test have been the basis for a numerical model, which is used to predict the annual energy demand and the annual solar yield of a typical single family home. In addition, a conventional solar thermal system was investigated with this numerical model in order to compare the annual solar thermal yield of both systems.

Due to the lower efficiency of the polymeric collectors compared to the metal collectors, more modules have to be installed in order to obtain comparable solar thermal yields. On the one hand, this yields higher installation costs, on the other hand the investment costs of polymeric collectors are approximately 30 % lower compared to the investigated metal based collectors. To quantify the different parameters of both systems, the LCOH have been determined, taking into account investment and maintenance costs as well as the different annual solar thermal yields. The results indicate that DBS with polymeric collectors can provide a cost advantage compared to conventional solar thermal systems. However, a further cost reduction both on component and system level is necessary to further disseminate polymeric DBS.

# Enhanced control and model-based condition monitoring of electric submersible pumps in geothermal energy systems

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## Motivation

Electric submersible pumps (ESP) are deployed in deep geothermal systems in order to lift geothermal fluid to the surface. High production rates and harsh environmental conditions put severe chemical, thermal and mechanical strain on the electrical and hydraulic components of the pump, leading to frequent failure and high maintenance costs [1]. This subproject of the *Geothermie-Allianz Bayern* research project aims to increase pump lifetimes by

(i) Developing a model-based condition monitoring system for early warnings of imminent faults and
(ii) Enhancing the control algorithms for improved efficiency    and robustness of the system.

As a first step, a detailed dynamical system model has been derived. Based on this model, objectives (i) and (ii) will be pursued, accompanied by simulations allowing for offline testing of the derived algorithms and visualization of the system response.

## Modeling of an ESP system

The dynamic system model of the ESP has been derived using a system theoretical approach (white-box modeling), which involves deriving the differential equations, that describe the physical processes acting inside the pump system (see Fig. 1). The system model comprises three different physical subsystems, i.e.

- hydraulic subsystem (fluid flow),
- mechanical subsystem (shaft rotation),
- electrical subsystem (current flow),

which are interconnected, since energy is exchanged. The coupled subsystems can be described mathematically using a nonlinear state-space representation. This representation allows for simulations and further analysis, e.g. by linearization of the system at specific operating points. In order to perform actual simulations, the qualitative model must be parametrized by means of real system data, such as power curves or measured parameters provided by manufactures and operators.



**Electronics**
Current dynamics
$\frac{d}{dt}\mathbf{i_s} = \mathbf{f_1}(\mathbf{i_s}, \omega, \mathbf{u_s})$

**Mechanics**
Speed dynamics
$\frac{d}{dt}\omega = f_2(\mathbf{i_s}, \omega, Q)$

**Hydraulics**
Flow dynamics
$\frac{d}{dt}Q = f_3(\omega, Q)$

**Nonlinear state-space model**
Used for simulations
$$\frac{d}{dt}\mathbf{x} = \mathbf{f}(\mathbf{x}, \mathbf{u}), \qquad \mathbf{x} = [\mathbf{i_s}, \omega, Q]^\top, \quad \mathbf{u} = \mathbf{u_s}$$
$$\mathbf{y} = \mathbf{g}(\mathbf{x}, \mathbf{u})$$

linearization

**Linear state-space model**
Used for system analysis
$$\frac{d}{dt}\Delta\mathbf{x} = \mathbf{A}\Delta\mathbf{x} + \mathbf{B}\Delta\mathbf{u},$$
$$\Delta\mathbf{y} = \mathbf{C}\Delta\mathbf{x} + \mathbf{D}\Delta\mathbf{u}$$

**Fig. 1 Derivation of a state-space model for ESP systems**

The model covers the following components: centrifugal pump, shaft (multi-mass system), 3-phase AC induction motor, power cable, sine filter and multilevel converter.

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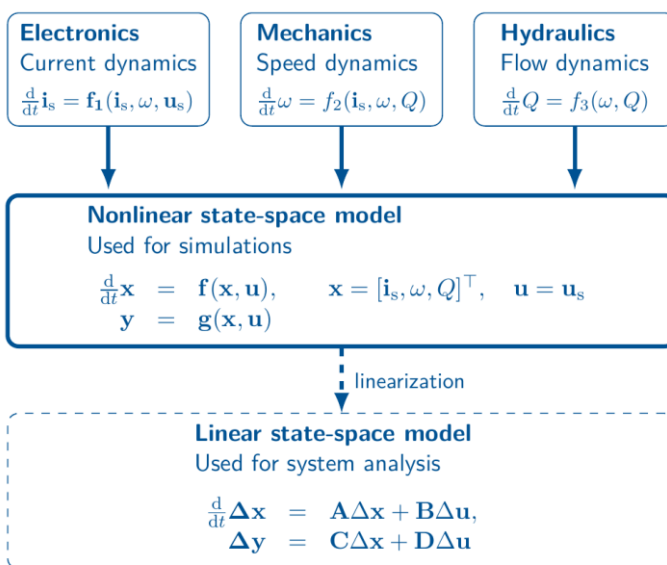
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76