Munich School of Engineering

Technische Universität München

Research Towards Innovative Energy Systems and Materials

3 rd Colloquium of the Munich School of Engineering

04.07.2013

Contents

In 2003, four of the twenty biggest companies listed in the Forbes 2000 list belonged to the oil and gas business. Nine years later this number had increased to eight. This development demonstrates the increasing importance of energy for the development of the world economy. During the last ten years the oil price rose from 20$/bbl to a 100$/bbl, mainly as result of increasing demand. Did we enter the final game of the fossil fuel age or will this age be prolonged by an unprecedented hunt for the last litre of oil and gas which will be squeezed out of mother earth? In either case, research efforts aiming at the development of alternative sources of energy and a much more efficient use of energy are necessary to guarantee economic prosperity, integrity of eco- and climate systems and the reduction of political tensions in resource rich areas of the world.

The Munich School of Engineering (MSE) promoting TUM.Energy hosts promising research projects in Bavaria which try to give an answer to the global challenges as well as to the special efforts necessary to make the "Energiewende" in Germany a long-term success. Ph.D. students and young researchers at the heart of these efforts will again give examples of their excellent work in this year's MSE-colloquium.

I would like to invite you to participate in the MSE colloquium 2013, get more insight in the work of TUM researchers, find possible collaborators and enjoy a day full of exciting presentations and discussions.

Thomas Hamacher
Director Munich School of Engineering

Center for Power Generation

The Center for Power Generation (CPG) is an interdisciplinary working group consisting of institutes from TUM with research activities in the field of energy conversion for power generation. Besides efficient and innovative power plant technologies, the research spectrum includes future systems for energy storage and power plant control as well as new and optimized techniques for the reduction of air and climate pollutants in the energy field.

Member institutes come from mechanical and electrical engineering as well as from the departments of Chemistry and Physics. Thus, a broad spectrum of expert knowledge is being brought together. One of the center's main purposes is its networking ability. Sharing information about research proposals, partner acquisition and active funding schemes is considered one of its fundamental goals by its members, thus enabling interdisciplinary cooperation.

The research project "Flexible Power Plants" which is part of "Energy Valley Bavaria" is an example for CPG's interdisciplinary research. Experimental investigations of combustion and evaporation are combined with theoretical approaches of power plant simulation and power system optimization.

To date 16 partners from 4 faculties share their expertise in the framework of CPG. New members are always welcome.

Network for Renewable Energy

The Network for Renewable Energy (NRG) is a research network in the framework of TUM.Energy within the Munich School of Engineering (MSE). NRG acts as a platform for TUM researchers working on renewable energy projects independent of their discipline.

The network is headed by Professor Müller-Buschbaum, Chair for Functional Materials, and was founded to create the opportunity to stem interdisciplinary, large-scale research projects but also to foster an active communication between different research groups.

Over the last year, the project TUM.Solar has successfully started. TUM.Solar is one of 5 key labs of the "Solar Technologies go Hybrid" program of the Bavarian State Ministry. Research is carried out within the TUM groups investigating hybrid systems of nanomaterials for more efficient use of solar energy and photo-catalysis. In regular scientific meetings exchange with the other four Bavarian universities is fostered.

The researchers forming the Network for Renewable Energy are from various departments from the TUM and associated institutes: Physics, Chemistry, Engineering, Electrical Engineering and Informatics, as well as the Centre of Life and Food Sciences Weihenstephan, the Walter-Schottky-Institut and the Bavarian Center for applied Energy Research (ZAE Bayern).

Doctoral students within the NRG use the network to find collaborators and exchange know-how and facilities. Furthermore the network coordinates visits to laboratories and aids with finding research collaborators throughout the network.

Participation in the NRG is open for all TUM researchers interested in renewable energy conversion and storage and only requires an informal email to the organizers which can be found on www.nrg.mse.tum.de.

Science Center for Electromobility

The Science Center for Electromobility (Wissenschaftszentrum Elektromobilität – WZE) is a union of multiple research institutions from five different faculties at TUM working together on further progress in the field of electromobility. A wide spectrum of research is covered ranging from fundamental research on future battery technologies to applied science developing innovative vehicle concepts as well as vehicle-to-grid applications. The successful completion of the MUTE project in the past is an excellent example for the good cooperation between all partners in the Science Center for Electromobility. The latest lighthouse project is called Visio.M. Its key target is to build up an electric car concept suitable for the mass at urban areas.

TUM CREATE is a joint research program between TUM and Nanyang Technological University (NTU) in Singapore. It is developing innovative technologies, future transportation concepts and the application of electric vehicles to match the challenging requirements of fast-growing tropical megacities. One of TUM CREATE's main project is to design and build the world's first purpose-built electric taxi.

As a member of the Munich School of Engineering (MSE) new interdisciplinary research cooperations are created regularly with the Science Center for Electromobility. Due to the flexibility of electric vehicles regarding their source of energy, there are multiple opportunities to use synergies between electric vehicles and other power sources or consumers. In order to explore and use these synergies, the Science Center for Electromobility is an important pillar of TUM's energy research for the future.

Center for Sustainable Building

The complex interdisciplinary challenges in the fields of sustainable building and energy efficiency require new comprehensive solutions. That's the main focus of the Center for Sustainable Building as a joint cooperation between the TUM chairs of Building Physics, Building Climatology and Building Services, Energy Efficient and Sustainable Design and Building as well as Energy Economics and Application Technology.

The Center for Sustainable Building provides the basis for an extensive scientific exchange between faculties – particularly the faculties of Architecture, of Civil, Geo and Environmental Engineering, of Electrical Engineering and Information Technology as well as the whole Munich School of Engineering. Due to the cross faculty composition of the Center, the expertise reaches from the consideration of sustainable urban development and sustainable building to detailed design of energy efficient façade elements and many more aspects related to energy efficiency and the use of renewable energies in buildings. The activities range from fundamental research to practical application and teaching.

With this interdisciplinary background, the Center is able to contribute to solutions for the worldwide problem of climate change: In Germany, an essential portion of primary energy is consumed by buildings, thus holding an enormous potential for energy savings in order to reach the demanded climate protection goals. This focus is incorporated in the Center's comprehensive understanding of sustainable building: Buildings should provide a comfortable, sustainable living environment and should be designed with the local conditions in mind, such as the climate, its physical and cultural environment as well as the use of regional renewable energy sources.

Munich School of Engineering (MSE)

The Munich School of Engineering (MSE) of the Technische Universität München is based on an innovative concept motivated by the demand for the de-compartmentalization of the conventional engineering disciplines: the combination of interdisciplinary research and cross-faculty teaching. The MSE is institutionalized as an Integrative Research Center with doctorate-granting rights.

TUM.Energy is a cross-faculty research initiative within the Munich School of Engineering which offers a platform for “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 faculties are working in detail on the challenges within these fields:

- 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 **Teaching Department** of the Munich School of Engineering (MSE) provides currently two degree courses with the emphasis on an interdisciplinary education in the field of engineering sciences. Talents in mathematics, natural science, and medicine get the chance to have a deep look on both, results of fundamental research in engineering and science as well as entrepreneurial viability of new technologies. This combination opens the MSE-graduates great professional opportunities in the interdisciplinary business fields of the future.

Since the winter semester of 2010/11, the MSE provides the bachelor course Engineering Science and the master course Industrial Biotechnology.

In **Engineering Science** (Bachelor of Science) students get a broad methodological and scientific training with a focus on mathematics and science subjects. In the fifth and sixth semester the concept of this course allows students to individually create their personalized specialization within engineering.

The course **Industrial Biotechnology** (Master of Science) qualifies graduates of science or engineering bachelor study programs in the field of white biotechnology. Therefore, the four semester curriculum contains subjects of a wide spectrum regarding life and food science as well as Process Engineering, Chemistry, Physics, Agronomy, Robotics and Information Technology.

Program

8.30 - 9.00 am
Registration

9.00 - 9.15 am
Opening
Thomas Hamacher, Director Munich School of Engineering

9.15 - 9.45 am
Keynote: Shale Gas Revolution
Olaf Martins, ExxonMobil

9.45 - 11.00 am
Session Chair: Hartmut Spliethoff, CPG MSE

Flexible Power and Synthesis Plant Concepts with Integrated Chemical Power Storage
Alexander Buttler, Institute for Energy Systems

Explosive Combustion of Stratified Hydrogen-Air Mixtures – Experimental Observations and Conclusions for Safety Applications
Lorenz Böck, Chair for Thermodynamics

Table-top Electron-beam Induced Plasma Chemistry
Andreas Himpsl, Chair for Experimental Physics

11.00 - 11.45 am
Poster presentation/Coffee Break

11.45 - 1.00 pm
Session Chair: Werner Lang, ZNB MSE

Processes for the Gasification of Biomass and Current Developments
Markus Ulbrich, Chair for Energy Systems

Smart Grid Simulation
Christoph Doblander, Chair for Application and Middleware Systems

Heat Consumption Analysis on a City Scale
Peter Böhme, Institute for Energy Economics and Application Technologies

1.00 - 2.30 pm
Poster presentation, Lunchbreak

2.30 - 3.45 pm
Session Chair: Peter Müller-Buschbaum, NRG MSE

Large-Scale Spray Deposition of Functional Materials for Photovoltaics
Alaa Abdellah, Institute for Nanoelectronics

Alternative Supports for Applications in Electrocatalysis: Ethanol Oxidation on Pt/TiOxCy
Celine Rüdiger, Institute of Advanced Study

Highly Conductive PEDOT:PSS as Electrode for Flexible Structured ITO-free Organic Electronics
Claudia M. Palumbiny, Chair of Functional Materials

3.45 - 4.30 pm
Poster presentation, Coffee Break

4.30 - 5.45 pm
Session Chair: Markus Lienkamp, WZE MSE

Greenhouse Gas Emissions from Induced Impacts in the Built Environment
John E. Anderson, Institute for Energy Efficient Building and Design

A Need- and Willingness-based Approach for Online Electric Vehicle Charging Control
Victor del Razo, Chair for Application and Middleware Systems

Power Systems Research – Why we Should Cooperate
Herbert Mangesius, Institute for Information-Oriented Control; Matthias Huber, Institute for Energy Economics and Application Technologies

5.45 - 6.00 pm
Summary of the Day

6.00 - 6.45 pm
Keynote: Climate Science - What Do We Know About Past, Current and Future Climate Change?
Janina Körper, Freie Universität Berlin

6.45 - 9.00 pm
Poster and Presentation Award, Colloquium Dinner

2 Oral presentations

Flexible power and synthesis plant concepts with integrated chemical power storage

Alexander Buttler[a], Hartmut Spliethoff[b]

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The German government aims to raise the share of renewable energies in gross electricity consumption to 80% by 2050 [1]. Due to the weather dependent feed-in of wind and solar power, which is not linked to the demand, a resulting excess power generation in the order of 26 TWh [2] is expected. Therefore, to balance power demand and fluctuating supply seasonal as well as hour-to-hour, storage technologies will become increasingly important. For long-term storage hydrogen produced by electrolysis is a promising storage medium due to its high energy density. In an additional step, hydrogen together with CO_2 or CO can be converted into synthetic natural gas (SNG). On the one hand this allows the full use of the natural gas network which offers storage capacity without further costs. But on the other hand this technology suffers from low storage efficiencies from power to power of 30-38% only [3] (depending on the assumed specific energy consumption of the electrolyzer and excluding energy consumption for CO_2-sequestration). However, an efficiency improvement is expected by the integration of power-to-gas technology in other industrial processes due to synergie effects. These are for example the use of the oxygen as by-product of the electrolysis process as well as the integration of the waste heat of the strongly exothermal methanation and the integration of the carbon dioxide source. The development and analysis of such innovative concepts with excess power integration (EPI) is within the focus of the overall process investigations as part of the joint research project HotVeGas II at the Institute for Energy Systems at the Technical University of Munich. The primary objective of the research project is to lay the necessary foundations for the long-term development of future, highly efficient high-temperature gasification processes with integrated hot gas purification and optional CO_2 capture and storage for IGCC power plants and processes for the development of synthetic fuel. The aim of the process simulations regarding excess power integration is to identify the potential of energy storage, load flexibility of the plant, storage efficiency and the impact of synergies on efficiency and process configuration. Various concepts of conventional power and synthesis plants with excess power integration have been developed. In a futher step they were modeled and analyzed by means of the simulation software Aspen Plus.

An example of an EPI-concept based on a small scale biomass gasification SNG synthesis plant is shown in Figure 1. In this concept the electrolysis plant is used for oxygen supply replacing the air separation unit for gasification. Additionally the H_2 from electrolysis is used to adjust the optimal gas composition of the syngas for methanation which generally has a hydrogen lack. Due to the optimal gas composition no steam addition is necessary to prevent soot formation in the methanation section and the synthesis process reaches optimum product quality without post-treatment. In comparison to the conventional power-to-gas technology a storage efficiency advantage of up to 4.6% points is calculated for this EPI-concept (see Figure 2) resulting in an efficiency of 37.3% from power and biomass to SNG and back to power. This could be shown also for an IGCC-EPI concept with a storage efficiency of 40.1% demonstrating a superior operation range from +67 MW to -253 MW of net power output/input [4].

All in all the investigations of the EPI concepts show a significant efficiency and flexibility advantage by combining power-to-gas and gasification technologies compared to stand-alone systems.

References

[1] BMWi, BMU: Das Energiekonzept der Bundesregierung 2010 und die Energiewende 2011, Oktober 2011.
[2] VDE (ETG): Energiespeicher für die Energiewende, 2012.
[3] M. Sterner, M. Jentsch, and U. Holzhammer: Energiewirtschaftliche und ökologische Bewertung eines Windgas-Angebotes, Februar 2011.
[4] A. Buttler, C. Kunze, and H. Spliethoff: IGCC–EPI: Decentralized concept of a highly load-flexible IGCC power plant for excess power integration, Applied Energy, vol. 104, pp. 869–879, 2013.
[5] ASUE: Erdgas aus Ökostrom. 2011.

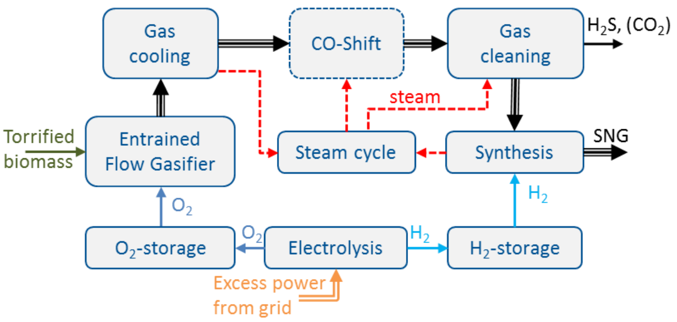

Figure 1: Simplified process scheme of a decentralized biomass-to-SNG plant with excess power integration

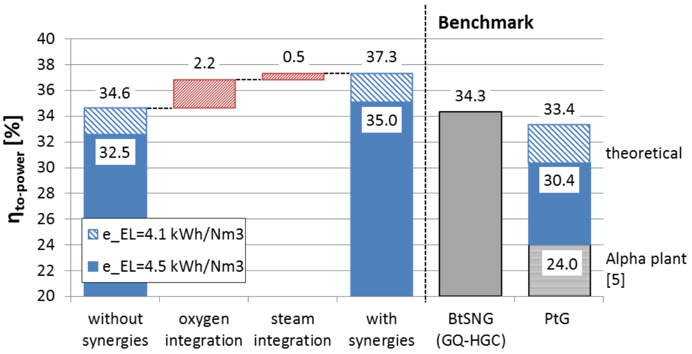

Figure 2: Storage efficiency of the biomass-to-SNG EPI concept in comparison to a conventional biomass-to-SNG (BtSNG) and power-to-gas (PtG) plant (including reconversion of the storage medias to power)

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Explosive combustion of homogeneous and inhomogeneous hydrogen-air mixtures – experimental observations and conclusions for safety applications

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Not only since the Fukushima accident in 2011, the hazard potential of hydrogen release and subsequent combustion in buildings is well-known to the public. The German Federal Ministry of Economics and Technology has therefore launched a research program on the investigation of explosive combustion of hydrogen-air mixtures in confined and semi-confined volumes. If hydrogen is spilled into ambient air in an accident scenario, a combustible hydrogen-air mixture is likely to form due to the wide ignition limits. Once the mixture is ignited by a weak ignition source, the combustion process starts as a slow deflagration with low overpressures, may transform into a fast turbulent deflagration via several accelerating mechanisms (e.g. turbulence generation by obstructions) and finally can yield a detonation. Especially the abrupt transition between the two fundamentally different combustion regimes - deflagration and detonation - is of interest. A detonation poses a major threat to the integrity of containing structure through associated high pressure loads.

Current ideas for future innovative energy systems often include hydrogen as an alternative fuel. However, the use of hydrogen obligates developers to be aware of the tremendous risks related with hydrogen combustion and explosion.

An experimental facility for the investigation of explosive combustion of hydrogen-air mixtures is operated at the Institute of Thermodynamics, Technical University of Munich. It allows for the generation of concentration gradients perpendicular to the main direction of flame propagation. Such an inhomogeneity is likely to occur in real-world accidental scenarios due to the low density of hydrogen compared to air and strongly affects the process of flame acceleration and the transition to detonation. Gaining a comprehensive understanding of these gradients' influences is of particular interest. Conventional measurement techniques (UV-sensitive time-of-arrival photodiodes and piezoelectric pressure transducers) as well as highly time-resolved optical systems (Shadowgraphy, (Color-) Schlieren, OH* chemiluminescence, High-Speed OH-PLIF) are employed.

The presentation gives an introduction on general risks related with hydrogen explosion. Thereafter, the experimental facility operated at the Institute of Thermodynamics is described and major results are presented. Conclusions are drawn concerning the particular influence of concentration gradients on the hazard potential of explosions in hydrogen-air mixtures.

The presented work is funded by the German Federal Ministry of Economics and Technology (BMWi) on the basis of a decision by the German Bundestag (project no. 1501425 and 1501338) which is gratefully acknowledged.

Figure 1: Explosion channel operated at the Institute of Thermodynamics, TUM, including high-speed optical measurement techniques.

Table-top electron-beam induced plasma chemistry

Andreas Himpsl[a], Thomas Dandl[b], Thomas Heindl[c], Andreas Ulrich[d]

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A key issue in using renewable energy is energy storage. Since most renewable energy sources such as solar cells and windmills provide electrical energy it is desirable to convert electrical energy into chemical energy, preferentially in the form of a liquid. This would allow easy storage and consumption for example also in the automotive sector. We have developed a concept which starts with the decomposition of carbon dioxide via so called radiolysis. Radiolysis of CO_2 has already been studied for a long time [1] and the results of that work can be used as a starting point for our novel approach.

Using a technology which had originally been introduced by P. Lenard in 1894 [2] and revisited since 1994 by our research group for the development of vacuum ultraviolet light sources as well as basic research in plasma physics we are able to build table-top devices which can provide power densities up to 20 MW/cm^3 induced by electron beams sent into gases at atmospheric pressure [3,4]. The key innovation is to use extremely thin (300 nm) and thermally stable as well as vacuum tight ceramic membranes as entrance windows for the electron beam. These membranes are made of a double layer of silicon nitride and silicon oxide and allow particle energies of the electrons on the order of 15 keV to be used with a transmission of beam power through the foil on the order of 90%. The low particle energy leads to the fact that the transmitted power is deposited within less than 1 mm range in the gas at atmospheric pressure. This in turn leads to very high power densities in the target gas already for very low beam currents.

An important aspect in plasma chemistry is the electron energy distribution function in the plasma. In electron beam induced plasmas it is quasi hyperbolic and reaches up to the energy at which the electrons are injected into the gas. A model calculation shows that about 85% of the electron's energy is transferred to the gas when they have an energy of more than 20 eV. This is a great advantage in comparison with discharge induced plasmas where the electrons are accelerated instead of decelerated and have a high probability to loose kinetic energy in inelastic collisions before they reach energies necessary to decompose molecules. The concept of the experiments described here is therefore to build a prototype electron beam device for plasma chemistry and to perform experiments to quantify the energy efficiency of electron beam induced chemical reactions such as the splitting of CO_2 molecules. Catalytic processes in the gas volume in contrast to catalysis on surfaces will also be studied. The power densities which are required for efficient CO_2 radiolysis have been studied by Kummler et al. [1]. It can be shown that the device described here meets the requirements for the most efficient CO_2 decomposition observed so far (so called G value of 8 corresponding to the number of molecules split per 100 eV deposited). This corresponds to an energy efficiency of about 30% which we hope to improve via catalytic effects.

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[2] P. Lenard, Ann. d. Phys. u. Chem., Neue folge **51**, Seite 15 (1894)
[3] A. Ulrich et al., Eur. Phys. J. Appl. Phys. **47**, 22815 (2009)
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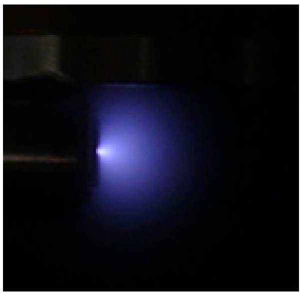
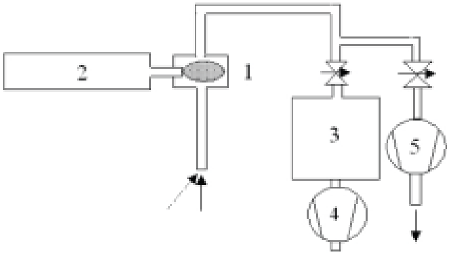
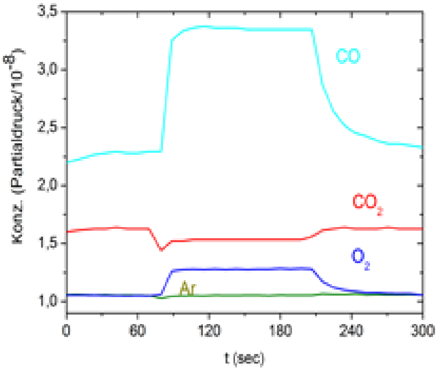


Photograph of a 12 keV electron beam stopped in nitrogen at 1 bar. The beam excited volume is on the order of 1 mm^3



Schematic drawing of a test setup for low energy electron beam driven plasma chemistry: 1 reaction chamber, 2 electron gun, 3 mass spectrometer, 4 turbo molecular pump, 5 roughing pump.



Mass spectrometer data demonstrating the decomposition of CO_2 by an increase of CO, O_2 and a decrease of the CO_2 signal when the electron beam is on (middle part). Note that the Mass spectrometer has not been calibrated.

Processes for the gasification of biomass and current developments

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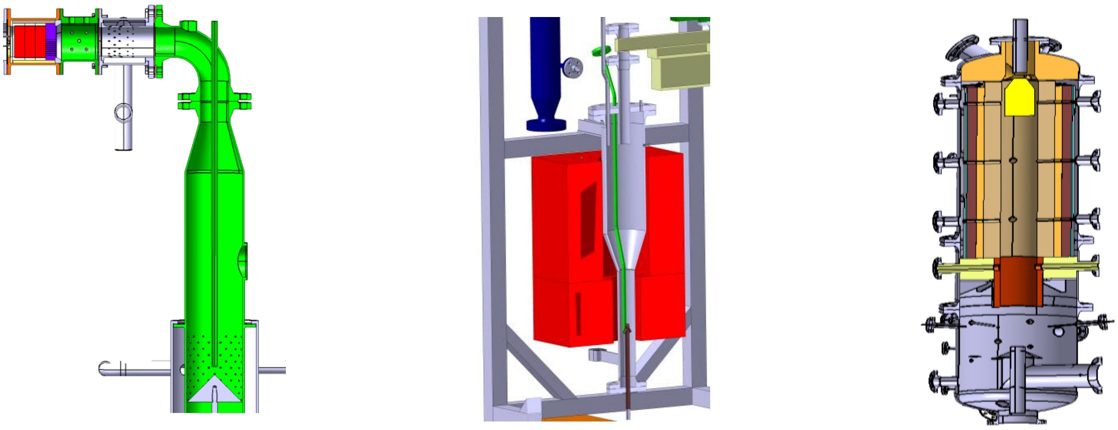
Over the last 20 years, the worldwide primary energy demand has been increasing by 2 % per year and in 2008, it ranged at app. 514 Exajoule (142.000 TWh). Whereas in Europe the increase per anno amounts to 0,7 %, the main consumers are countries in Asia, like China, with an average increase of energy demand of 7,6 % per year over the same time. Different statistics and scenarios exist of how to cover the energy demand. Apparently, fossil energy carriers will still play a very important role in the future. For some areas, coal is of importance due to the local availability. Currently, China covers 66 % of the demand with coal, the USA 24 % and Europe 19 %. Biomass is used for 6 - 10 % of the primary energy demand, thus ranging between 30 to 70 % of the realistic potential, which, obviously, differs considerably depending on the individual countries.

In 2030, renewables should contribute 22 % to power production, 67 % will be covered by fossils and 10 % by nuclear power, this distribution is comparable to the actual situation. Biomass is one of the important renewable resources for it. The main advantages of Biomass are that it is stored renewable energy and it contains carbon which can be converted into different energy carriers like synthetic gas and liquid fuels. Nevertheless the conversion into heat and power are the important application at the moment.

Countries in Northern Europe, Canada and Russia dispose of a high potential of Biomass resources mainly based on wooden biomass whereas the major potential for countries in Europe, Asia and South America lies in agricultural Biomass, which, however, causes competition with areas required for agriculture-based food. Furthermore, environmental problems originate from the change of natural areas to agricultural areas as well as the requirement of water and fertilizer for cultivation.

Although biomass is a form of stored solar energy, it is a limited resource. Compared to other renewables, it is used more flexibly for conversion into heat, power or synthetic fuels. The cost of biomass is a main economic factor and, due to its extensive use, it has strongly increased in Europe since 2008, a fact that will finally limit its potential. Consequently, only cheap biogenic residuals like very wet biomass, sewage sludge or agriculture residuals as well biomass from countries like Canada or Sweden are of interest in Europe for industrial applications and for power production by co-firing of biomass in coal power stations. For this purpose, the biomass can be "upgraded" by carbonization of the biomass. Torrefaction and hydrothermal carbonization are two processes, which are presently being developed to increase the volumetric energy density for the transport.

A number of different technologies are available to convert the biomass. Beside the combustion and the fermentation of Biomass the gasification is the most important technology to convert Biomass into a synthetic energy carrier. The different technologies of gasification and further applications will be discussed. Focused on the three technologies for biomass gasification - fixed bed, fluidized bed and entrained flow gasification and the use of it for combined heat and power and the conversion of biomass into synthetic energy carriers (e.g. substitute natural gas) and liquid are discussed.



left: fixed bed gasifier, middle: fluidized bed gasifier, right: entrained flow gasifier (source Institute Energy Systems/TUM)

Smart grid simulation

Christoph Doblander[a], Christoph Goebel[b], Hans-Arno Jacobsen[c]

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Smart grid simulation can be seen as a part of the bigger vision of the self-healing electric grid. It is also a necessary for evaluating control algorithm. To answer research questions related to both, the behavior of the communication infrastructure and the physical power grid, a new simulation tool is needed. An exemplary research question related to the communication and control of electric vehicles would be: If one mobile phone network breaks down on a cloudy day, does uncontrolled charging of electric vehicles overload the grid and if not, how far from optimal are the results of a charging control algorithm in this case. This talk will introduce starting points for the development of a scalable smart grid simulator.

Current commercial available grid simulation tool focus on the grid operator needs and are not suited for this type of research. Open source smart grid simulators are insufficient for large scale power systems with thousands of controlled devices. The first research area we plan to explore is the interdependency of the reliability of communication and the control of distributed energy resources in the smart grid. Other areas or the detail level can be adapted for future research questions.

We propose a smart grid simulator able to capture the states of the power and communication system in flexible time increments ranging from sub-seconds to hours. The level of power system granularity should include 3 phase AC power flows, fluctuating energy generators and detailed models of household energy consumption.

One of the design goals of the simulator will be providing a maximal degree of scalability and reusability. Therefor it will be easy to use for researcher wanting to evaluate new control algorithm based on realistic scenarios with minimal programming effort. Basic programming skills will suffice to extend the simulator which will facilitate modeling contributions from researchers with a background in engineering.

In the long run, our simulator could also evolve into an operational tool for power systems operators. A future usage scenario could be that the simulator is continuously fed with real-time data and computes a more realistic hour-ahead scenario in a timelier manner than currently available tools. This could be useful for contingency analysis which not only covers the electrical grid but also the underlying communication infrastructure for distributed energy resources which will become necessary to ensure the secure and reliable operation of smart grids.

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Heat consumption analysis on a city scale

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Energy consumption for room heating and warm water have a big share in total energy consumption. Data about heat consumption is often not available. It has to be estimated on the basis of building parameters. For the introduction of renewable energies and the design of district heating systems, heat consumption is estimated on a high spatial resolution. Therefore, one question is how well heat consumption can be estimated on a scale for single buildings or small groups of buildings. In addition heat consumption is often confused with heat demand. This leads to overestimated expectations about the energy saving effects of refurbishment measures.

The described investigation shows an analysis of measured heat consumption values and building parameters for 17,500 detached and semidetached buildings in a medium sized German city. Furthermore the calculated heat demand is compared to measured heat consumption on the bases of buildings with similar building parameters.

Considered building parameters are: year of construction, volume and size of the thermal envelope. They have been extracted from different sources given by the city administration. The data is combined with measured gas consumption values from the local energy supplier. The effect of the known building parameters on the measured heat consumption is analyzed by a multifactorial linear regression. Confidence intervals for estimated heat consumptions are evaluated. Based on an energy-balance-model the heat demand is calculated for every building using defined boundary conditions. Average heat demand and consumption values are compared for buildings with similar date of construction and volume.

Measured heat consumption values show a high variance. 40% of this variance can be explained by the provided building parameters. If consumption values must be estimated, the unexplained variance leads to high estimation errors. Figure 1 shows a high systematical deviation between heat demand and consumption. The deviation varies for different building clusters, clustered by age and volume.

The shown analysis gives a realistic evaluation regarding the two main reasons for city energy analysis. They are spatial highly resolved estimations of heat consumption and the effects of refurbishment incentives on the future heat consumptions.

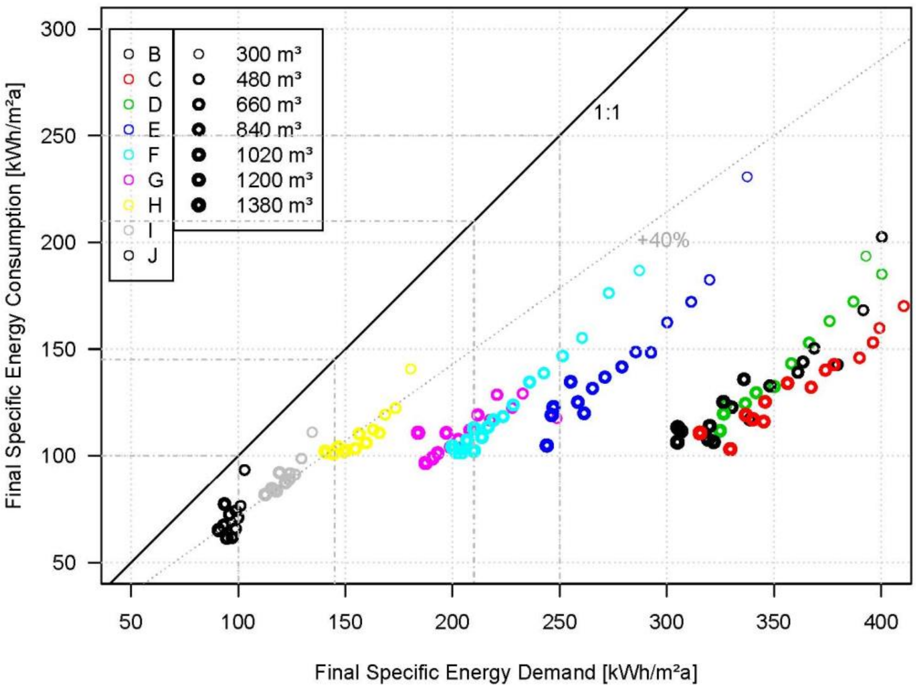

Figure 1: Final energy consumption and final energy demand of detached and semidetached buildings, which are clustered by volume (marked by thickness of the symbol) and construction-age-classes according to the Institut-für-Wohnen-und-Umwelt-building typology (marked by color).

Large-scale spray deposition of functional materials for photovoltaics

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Photovoltaic devices based on solution-processable polymer and carbon nanotube thin-films are among the most promising applications of novel organic materials. Low-cost fabrication by means of simple coating and printing techniques is one of their greatest advantages. However, in order to fully exploit the potential of polymer and carbon nanotube based electronics, large-area/low-cost processing technologies suitable for thin-film deposition on arbitrary substrate materials and geometries are necessary. One very promising deposition technique is provided by spray technology. The most significant advantages associated with the utilization of spray technology are related to its inherent compatibility with large-area industrial-scale processes.

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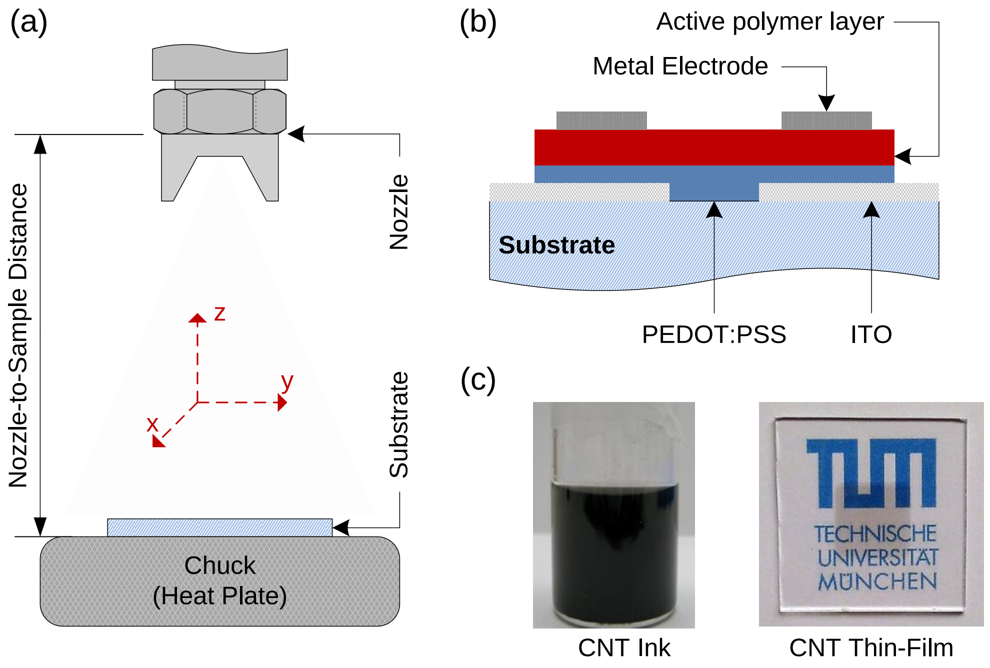

Alternative supports for applications in electrocatalysis: Ethanol oxidation on Pt/TiO_xC_y

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In commercial polymer electrolyte membrane fuel cells (PEMFC), carbon materials are used as electrocatalyst supports. They have the disadvantage to be prone to corrosion under operating conditions leading to a low durability of the fuel cells. Titanium dioxide (TiO_2) is of high interest for application as advanced electrocatalyst support material, since it is more stable than carbon in corrosive environment and especially promising for medium temperature applications (up to 250°C). Partially reduced TiO_2 has shown interesting substrate/catalyst interaction properties in UHV catalysis [1]. To expand the utilization of TiO_2 to applications in electrocatalysis the material has to be made conductive and inert towards re-oxidation.

In our group, TiO_2 is reduced by means of a carbothermal treatment in acetylene which leads to formation of oxycarbide compounds (TiO_xC_y). In a previous paper, we presented a detailed investigation of the carbothermal reduction process for the conversion of compact, anodically grown TiO_2 films on polycrystalline Ti sheets to TiO_xC_y. Anodic TiO_2 has been converted at different annealing temperatures between 750 and 1050°C, and the morphology, chemical composition and crystallographic structure of the films have been studied with scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and grazing incidence diffraction (GID). A thermodynamic model was proposed based on these investigations for the carbothermal conversion mechanism on compact anodic titania films showing that carbon and oxygen contents in the film decrease with increasing annealing temperature. The electronic properties have been investigated using electrochemical impedance spectroscopy (EIS) revealing an increase in charge transfer resistance for the ferri-/ferrocyanide redox couple with increasing annealing temperature. [2]

In the presented work, the electrocatalytic activity of Pt nanoparticles supported on planar TiO_xC_y films towards the ethanol oxidation reaction (EOR) was studied in a half cell electrochemical setup at elevated temperatures. Pt was deposited on the previously characterized TiO_xC_y films using aerosol assisted deposition (AAD) [3]. It was found that the electrocatalytic activity correlates with the annealing temperature during support preparation. The EOR performance at room temperature was enhanced for Pt deposited on TiO_xC_y films compared to Pt deposited on Glassy Carbon (GC), only if the TiO_xC_y was annealed at 750°C. This indicates that tailored TiO_xC_y can potentially replace carbon as support for fuel cell applications.

The EOR at Pt/TiO_xC_y and Pt/GC model systems was studied between room temperature and 80°C in concentrated H_3PO_4. The highest stable steady state current on Pt/GC was measured at 80°C and 0.6 V and is by a factor of 170 lower than the corresponding current on Pt/TiO_xC_y. Furthermore, the chemical and electrochemical stability of the catalyst-support systems was tested. SEM demonstrated that the degradation of catalyst and support under reaction conditions strongly depends on the properties of the underlying substrate grains. It is possible that not only the stability but also the activity towards EOR on Pt/TiO_xC_y is dependent on the orientation and individual stoichiometry of the grains of the TiO_xC_y support. This means that the identification of the grain orientations of TiO_xC_y which show high stability and activity towards the EOR can be the key for the design of a highly stable TiO_xC_y catalyst support with high activity towards the EOR at low and intermediate temperatures.

Our findings demonstrate that TiO_xC_y is a very promising potential candidate to replace carbon as a support for use in DEFCs. [4]

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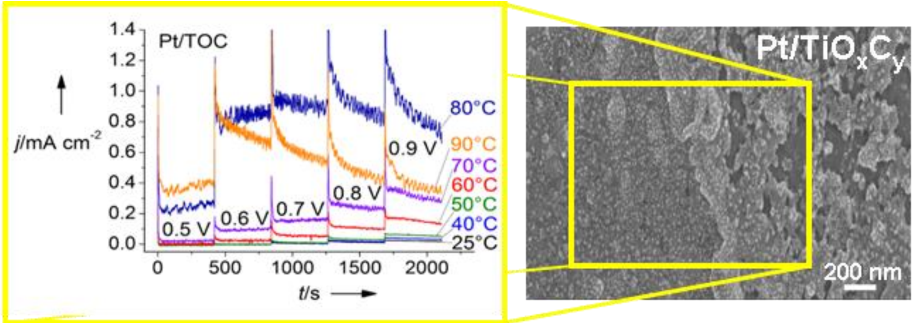

EOR current transients of Pt nanoparticles deposited on TiOxCy and SEM after electrochemical tests.

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Highly conductive PEDOT:PSS as electrode for flexible structured ITO-free organic electronics: A morphological study

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Energy resources run dry and the limited resources are controlled by only a few countries which does and will influence the world affairs even more in future. Additionally, the energy consumption of our society is steadily increasing, picturing the need for new technologies to feed up the demands and save the future of upcoming generations. In this context a new source for energy production has developed in the past years, the so-called renewable energies. They opened the path towards sustainable energy production. Furthermore, developments towards up-scaling for cheap and light-weighted materials, e. g. for displays can be observed. With this trend the demands on materials and devices changed dramatically. Materials, which are lightweight and flexible, but also cheap and can be up-scaled are desired.

Within the field of renewable energy research, solar cells based on organic materials offer a wide variety of new applications in the field of renewable energy conversion. Their transparency, translucency and especially their potential to manufacture flexible electronic devices provide numerous smart design opportunities as well as roll-to-roll mass production. However, there are still some drawbacks. The high cost of indium tin oxide (ITO) which is used as transparent electrode and its brittleness still limits the wide range of applications for electronic devices. For this purpose several attempts using metal grids, carbon nanotubes, graphene or conducting polymers have been made to respond to these needs. Among the latter is a polymer mixture called PEDOT:PSS which has very promising properties (transparency, cost-efficiency, hole conductivity and flexibility) which is widely used as selective intermediate electrode in flexible organic electronics. For replacing the ITO electrode, however, it is lacking three orders of magnitude in conductivity. We investigate a recently developed post treatment method for enhancing the conductivity of PEDOT:PSS, reaching the order of ITO conductivity. In this way the brittle ITO electrode can be replaced by the cost-efficient and flexible electrode PEDOT:PSS.

For a deeper understanding the nano-morphology is investigated with surface imaging techniques (AFM, SEM) and the inner morphology and crystallinity is addressed with scattering techniques (GISAXS and GIWAXS). The morphological changes are consequently related to the electronic changes. Furthermore, for enhancing the light harvesting in the organic thin film and hence the efficiency we introduce a novel structuring routine for PEDOT:PSS, plasticizer assisted soft embossing. Being able to control the interface between the transparent electrode and the active material, the device efficiency of OPVs under oblique light can be increased. Combining now highly conductive PEDOT:PSS as electrode with controlled structuring of the electrode, these results reveal new paths for flexible structured ITO-free solar cells of enhanced efficiency (see figure).

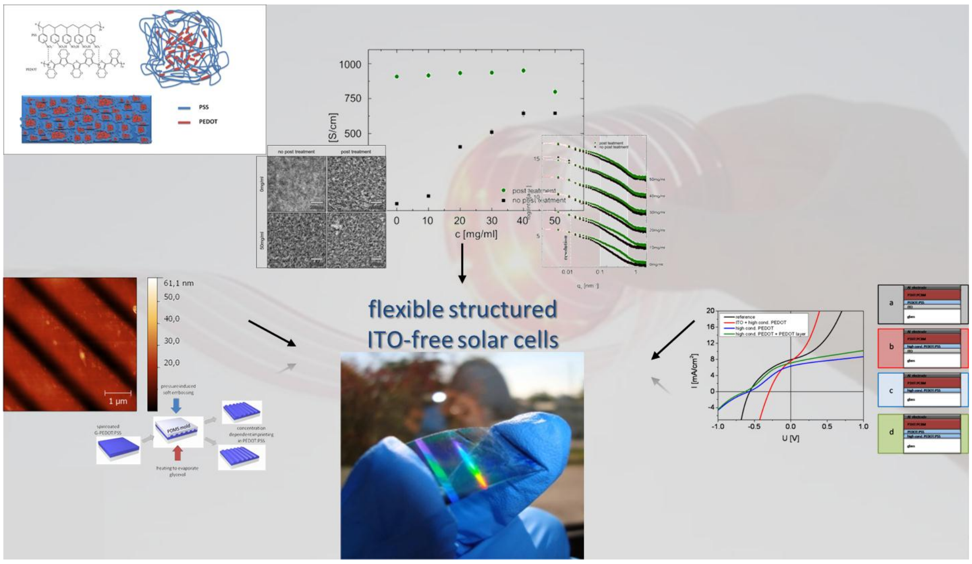

Fig.: Sketch of necessary development and processing steps to obtain a flexible polymer-based electrode.

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Greenhouse gas emissions from induced impacts in the built environment

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The paper presents the results of an expanded methodology for quantifying the energy and CO2 impacts of the built environment. Research on energy use and CO2 emissions of the built environment presently concentrates on individual buildings or entire metropolitan regions. Both of these frameworks are limiting as they do not represent actual conditions. Buildings are not isolated objects, but rather fully integrated within an urban context. Environmental assessment methods need to focus on predominate construction patterns: new construction and renovation of buildings within an existing urban framework.

The research moves the assessment of the built environment beyond the typical categories of embodied and operational impacts to include the induced impacts from the interactions of an individual building and its urban context. The induced impacts are captured in new categories of transportation, infrastructure, and consumption. Utilizing a hybrid economic input-output life-cycle assessment model developed for Germany, the quantitative assessment of direct and indirect environmental impacts is possible. The economic input-output life-cycle assessment model was created using data from the German Statistical Office and the German Environmental Office. Process based life-cycle inventory data is taken from the German Environmental Office, the European Life-cycle Database, and augmented with various software packages. Transportation data is taken from the Mobility in Germany travel survey. Infrastructure data is taken from the German Department of Transportation. Embodied and operational impacts are based on a realized building in Munich. The results illustrate the energy and CO2 impacts resulting from the five categories: embodied, operational, infrastructure, transportation, and consumption. The findings show the importance of the quantification of induced impacts in capturing all environmental outputs. The work expands the methodology and application of life-cycle assessment in the built environment in order to allow a comprehensive analysis of impacts and provides insights and recommendations for reducing energy and CO2 emissions.

A need- and willingness-based approach for online electric vehicle charging control

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The increasing penetration of distributed renewable energy (RE) generation and the use of plug-in electric vehicles (PEVs) may surpass current electricity distribution network (DN) capacities. We believe that, if managed appropriately, REs and PEVs can compensate each other and therefore reduce the impact on DNs. Although many studies about PEV charging strategies exist, few of them consider the limitations of the DN in their analysis. This presentation describes a research project (and its progress) on coordinated PEV charging considering distributed solar generation and DN limitations based on a PEV need and willingness approach. Different PEV charging strategies are briefly discussed and our proposed approach is presented. We discuss the results and advantages of our method particularly from the ICT requirements perspective. Finally we present conclusions of what has been achieved so far, challenges, areas of potential improvement and future research.

PEV charging strategies have been a popular subject in the past years with a number of optimization solutions being proposed. We are particularly interested in a solution that considers DN constraints, distributed renewable generation and online/real-time PEV management. We focus on the feasibility and applicability as the main success factors and aim at a good tradeoff between optimality and computational costs. Our objective is the design and implementation of a system that compensates for the variability of RE and demand in a DN with high penetration of solar generation. The system shall be evaluated under a realistic scenario for driving patterns, energy demand and solar incidence within a representative DN model.

The existing literature considers charging strategies implemented in a centralized or decentralized manner and apply direct or indirect (incentive-based) control. They typically formulate the control problem as an optimization problem. Our approach aims at achieving a better equilibrium between individual objectives, feasibility, optimality and computational complexity based on a distributed but hierarchical system architecture.

We consider an aggregator that controls vehicle charging in a direct and centralized manner. However, we delegate part of the computation by allowing PEVs to compute need and willingness signals based on their local objectives and constraints. With this approach we benefit from the certainty of direct control, allow PEVs to have their say, achieve a central-like complexity level and retain scalability proportional to the number of PEVs.

We show that our approach is significantly faster than performing an optimization and evaluate the distance to optimality. Furthermore, we show that the increase in complexity of PEVs objectives and constraints have no impact on the complexity of the central management scheme.

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Power systems research – why we should cooperate

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Political goals, technological progress and economic pressure challenge existing concepts for power systems. The trends to operate with narrower stability margins under increased decentralization and uncontrolled power injections, e.g. through power market activities or renewables, are drivers in the restructuring process of the existing operation scheme.

While today's architecture of operation is separated in terms of spatial and temporal scales, we expect that the future architecture requires the combination of static load flow planning and dynamic control as depicted in Fig. 1. A massive increase of interacting components necessitates the development of novel control and planning methods supporting a safe and highly automated system.

We observe the need for coordinated research from many fields, including business development, infrastructure planning, design of components, operations research, software and communications engineering, cyber security, and control theory. A first approach for bringing together various disciplines at TUM was the Workshop on Smart Grids held in 2011 in Benediktbeuern. The participating researchers conducted a survey of ongoing and planned research efforts in order to identify overlap and potential cooperation, which resulted in [1]. Amongst others we identified the following current research topics at several TUM institutes:

- Electricity markets: economic dispatch / unit commitment
- Flexibility of components: power plants, storage, loads
- Static load-flow simulation
- Novel approaches to design and verify local controller mechanisms integrated in a global electricity infrastructure
- Scalable approaches to aggregate, optimize and control thousands of components on different levels of abstraction
- Development of a new information and communication infrastructure on top of the physical system
- Cyber attacks and IT security
- Decentralized, robust control of the grid, i.e. a dynamical system of (very) high order modeled by differential-algebraic equations

In [1] we collected and documented individual research goals, interests, and expertise. We shared methods, datasets, related lectures, tools, research articles in order to create a common knowledge base.

We concluded that existing separation of research disciplines is not adequate to explore solutions to the above mentioned problem. To foster constructive exchange between the disciplines we observed the need to express criteria and relationships between problems at different levels in power systems research in a unified way. A first step could be to provide a list of requirements for an efficient, stable and safe system.

To emphasize the importance of cooperation, we highlight two specific results of our coordinated research:
- Application of methods from communication engineering to power system planning.
- Combination of static optimal dispatch with dynamic control.

These promising results motivate further joint research efforts at TUM. With this contribution we want to initiate a discussion:
- How to intensify and coordinate research cooperations at TUM?
- What is the adequate form of funding (SFB) ?
- Which role does TUM want to play in designing this new architecture?

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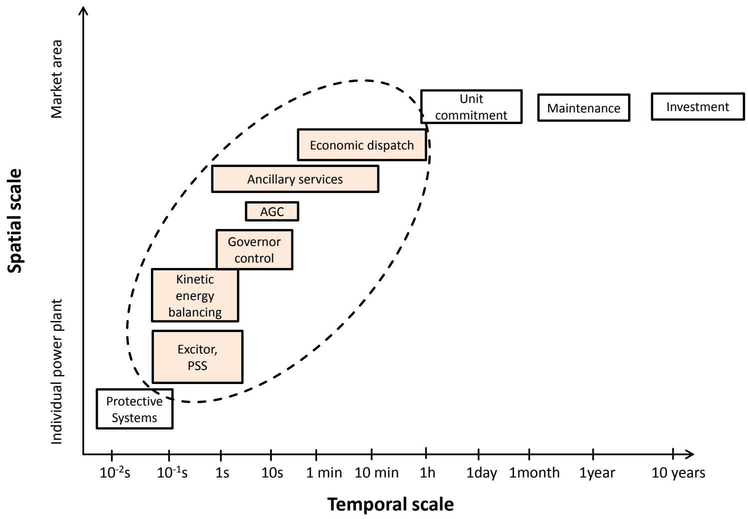

Fig.1: Temporal and spatial scales of control mechanism

Participants of Smart Grid Workshop, Benediktbeuern 2011
Faculty Graduate Center EI

3 Poster presentations

A novel FACTS stabilization scheme for photovoltaic utilization systems

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Photovoltaic-powered systems have many attractive merits such as being environmentally friendly and effective renewable green sources of electrical energy. As the conventional fossil fuel sources are depleting and the cost of energy is rising, PV energy can be considered as an alternative and viable clean source of energy. Photovoltaic solar powered systems have emerged as important solutions for energy conservation and demand-side management. However, due to their initial high costs, these systems have not yet been a viable alternative for electricity generation due to cheaper electrical energy from the utility grid. However, they have been used extensively for small applications, water pumping and air conditioning in remote, arid, and isolated areas where the utility grid is not available or too expensive to transport.

The current research on photovoltaic (PV) power sources has received much attention not only for space heating applications but also terrestrial, drives, and village and farm electricity applications. Solar cells are composed of various semiconductor materials which become electrically conductive when supplied by sunlight and thus transform directly a part of the solar radiation into electrical energy. The current –voltage (I-V) characteristic of a solar cell is nonlinear and depends on sun irradiation level and its junction temperature. The electrical load interface powered by the solar PV-array requires special design considerations because of the varying nature of the solar power generated resulting from unpredictable changes in weather conditions which affect the solar irradiation level as well as the cell junction temperature. However, the limited power conversion efficiency of existing PV arrays is still quite low; therefore, in order to achieve maximum solar energy utilization and high power efficiency, maximum power point tracking (MPPT) control techniques are needed for PV arrays. These strategies are utilized in most PV systems powered by PV arrays.

The paper presents a modulated/switched flexible DC filter compensator scheme for the DC local grid voltage stabilization of PV utilization Scheme. The novel PWM switched filter compensation scheme can be part of future integrated DC-AC smart micro grids for villages, islands, and resorts. The unified PV-DC model is based on circuit equations of the photovoltaic (PV) solar array including the effects of solar irradiation and temperature changes. The unified PV scheme has been validated using a dynamic novel two-loop error driven PID regulator to control the switching of the low cost FACTS based green plug filter compensator stabilization scheme used to stabilize the PV powered DC utilization system**.** The unified PV- powered electrical utilization system comprises the PV array, input LC filter, output capacitor filter, PMDC motor, and dynamic error driven dual loop PID controller as shown in Figure 1 and 2 below. The novel green plug filter compensator is located at common DC bus. DC motors are used to convert the electrical energy to the mechanical energy. Permanent Magnet (PM) DC motor drive systems are widely used in small PV powered applications. In this paper, a PMDC motor is powered by the PV array and stabilized using a novel flexible alternating current transmission system (FACTS) based green plug filter compensator to ensure dynamic DC bus stabilization, limited inrush current transients and ripple content in DC side voltages and currents.

In this paper, the PV energy utilization system functional model comprises the input and output filters, PID regulator, and PMDC motor. The (I-V) and (P-V) characteristic curves are presented at constant and variable temperature Tx, irradiation level Sx, and PMDC torque. Using the green plug filter and dynamic error driven dual loop PID regulator, the DC side voltages and currents are fully regulated and stabilized. The fixed gain PID regulator ensures a stabilized operation and efficient energy utilization of the PV-utilization system using the low cost green plug filter compensator. The proposed dual action PID controller ensures effective fast regulation of the pulsing patterns of the PWM - switched novel DC filter compensation scheme. The filter can be integrated with micro grid AC smart grid and fully coordinated with other FACTS based AC side stabilization schemes.

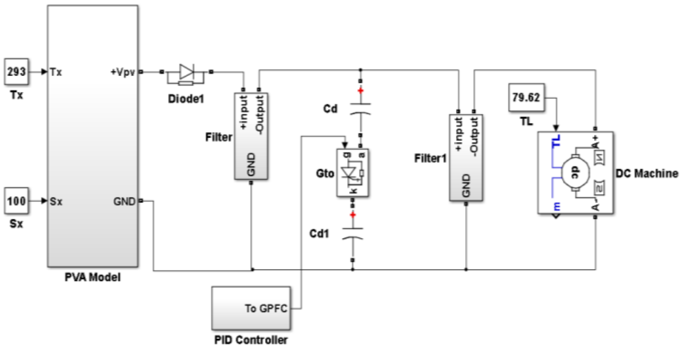

Fig.1 Unified PV-Powered Scheme

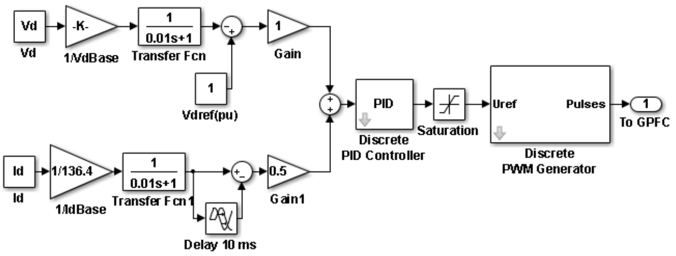

Fig.2 Dual loop error driven PID regulator for GPFC DC side filter scheme

Ordered non-oxide semiconductor networks for hybrid inorganic-polymer solar cells assembled from Zintl clusters

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Interpenetrated porous morphologies of non-oxide semiconductors have a great promise for hybrid solar cells due to a broad variation of optical and electronic characteristics in addition to a low photo-oxidation activity. We report on the recent progress in the development of bottom-up approaches to generation of such morphologies.

The formation of periodic macroporous Ge networks via self-assembly and oxidative polymerization of soluble Ge atom clusters such as the Zintl ion $[Ge_9]^{4-}$ is shown.[1] In addition, we have studied the possibility of tuning the phase composition and corresponding electronic and optical properties of the resulting materials by using soluble mixed group 14 element clusters as precursors.[2] This study involved synthesis and characterization of the new mixed clusters. The presence of Si/Ge atom clusters in the ternary intermetallic compounds $A_{12}Si_{17-x}Ge_x$ (A = K, Rb; x = 5; 9; 12) and the existence of mixed Si/Ge clusters in solution was demonstrated by powder X-ray diffraction or mass-spectrometric investigations of acetonitrile solutions of the ternary precursor phases. A structural characterization was carried out by single crystal X-ray diffraction of ammonia solvates like $Rb_4[Si_{7.8(1)}Ge_{1.2(1)}](NH_3)_5$ or $[Rb([18]crown\ 6)]_2Rb_2[(MesCu)_2(Si_{3.3(1)}Ge_{0.7(1)})](NH_3)_{12}$.[3,4]

A morphological analysis of the surface after self-assembly and oxidative polymerization reactions of Ge or mixed Si/Ge clusters on different substrates via scanning electron microscopy clearly displays the formation of ordered networks. Therefore further investigations were carried out by transmission electron microscopy, electron dispersive X-ray analysis and X-ray photoelectron spectroscopy among several examples.

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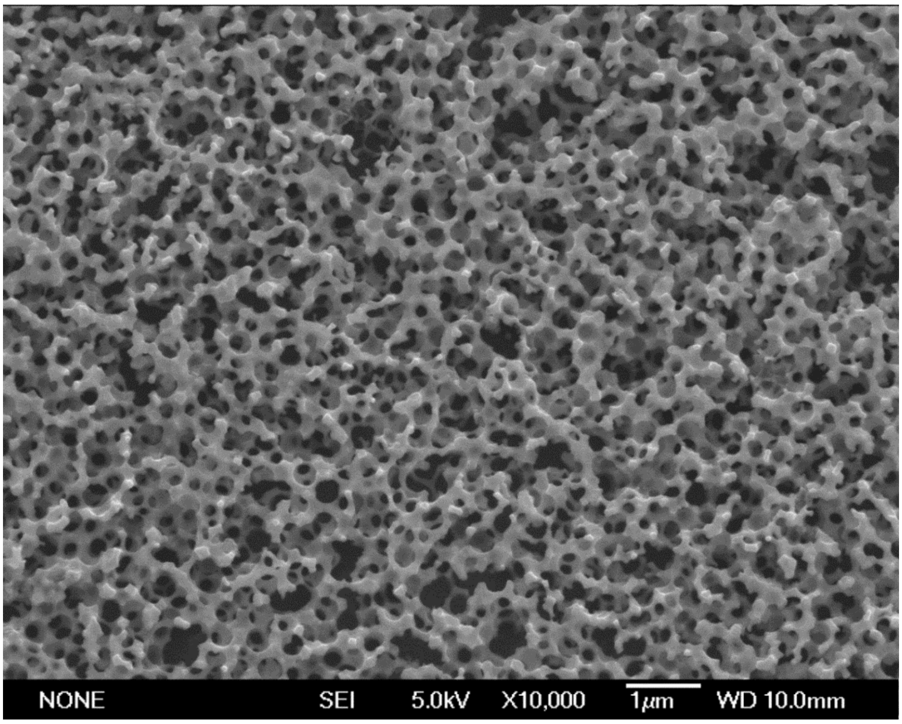

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Lithium-air battery – promises and challenges

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Secondary lithium-air cells are considered as one of the most promising upcoming electrical energy storage technologies principally because of the high theoretical specific capacity of the oxygen cathode, which would allow energy densities ≈ 3-fold larger than the ≈ 200 $Wh \cdot kg^{-1}$ currently envisaged for fully-packaged Li-ion batteries [1]. Commercialization of this battery would allow the construction of long-range full-electric vehicles. However, besides challenges related to system engineering, e.g. supply of water and carbon dioxide free oxygen, there are still fundamental issues to address.

One of the main topics concerning discharge is the development of cell materials, especially of organic electrolytes, which are stable towards oxygen reduction reaction intermediates as for example superoxide anion radicals. Therefore, we developed in our group screening tools using rotating ring disc electrode voltammetry [2], ultraviolet-visible, nuclear magnetic resonance and infrared spectroscopy to test solvents, electrolyte salts and binders towards superoxide radicals [3]. Further, we studied the influence of impurities, as for example water, during discharge [4] as well as the influence of the externally accessible surface area of non-catalyzed carbon-based electrodes [5].

During charge main challenges which have to be addressed include high charge overpotentials, which we tried to overcome using different catalysts [6], as well as the thermal reaction studied between the desired discharge product Li_2O_2 and carbon blacks commonly used as electrode materials [7]. To study products evolved during charge an online electrochemical mass spectrometer was set-up in our chair [8]. Further, electrodes pre-filled with different possible discharge products were prepared to study their charging behavior [9].

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Zinc oxide/titania nanostructured films for applications in organic photovoltaics

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The search for a solution to the world's energy provision is a challenge that gains more and more significance as we steadily use up our fossil fuels. Using the sun as an almost unlimited battery, photovoltaics became a promising candidate for a clean way to provide humanity with sufficient amounts of energy without harming the environment.

Today, most common used solar cells are silicon based. These cells are on the one hand ready for commercial use but do on the other hand have a couple of disadvantages like high and energy consuming production costs and stiffness. Due to those points in the recent years a vast field of research concerning hybrid solar cells has been developed as they show a high potential to become an important source of green energy. Hybrid solar cells consist of an inorganic electron acceptor and an organic hole-conductor. Advantages of hybrid and also organic solar cells are reduced fabrication costs, simple processing and employment of flexible substrates. However, the interest in hybrid cells is greater because of the combined advantages of the organic and inorganic materials. In the present study, a zinc oxide/titania mixture is utilized as the inorganic material in the form of nanostructures. This inorganic layer is used for an approach to fabricate Dye sensitized solar cells (DSSC), also known as Grätzel cells.

Hybrid dye sensitized solar cells conventionally prepared using titania as the inorganic material have reached power conversion efficiencies above 12 % [1]. Zinc oxide (ZnO) is a suitable candidate to be used as an alternative to titania due to their very similar optical and electronic properties. A power conversion efficiency of nearly 7 % has been reported for a ZnO based dye-sensitized solar cell that is comparable to the efficiency obtained using titania [2]. In the investigated system the advantages of both materials are tried to combine to a even better performing solar cell.

The Grätzel cells distinctive feature is a nanoporous ZnO/titania film, whose effective surface is increased by several orders of magnitude compared to a bulk film. This increase is directly transferred to the absorption of sunlight by the dye covering the titania surface and hence to the performance of the DSSC. Along this route, by tailoring an optimized morphology the overall efficiency of the solar cell can be enhanced significantly.

Zinc oxide (ZnO)/titania (TiO_2) nanostructures are synthesized on silicon substrates forming grid-like morphology. The synthesis is done by using a sol-gel mechanism coupled with an amphiphilic diblock copolymer Polystyrene-polyethylene oxide (P(S-b-EO)), acting as a template. The morphology is synthesized by using zinc acetate dihydrate (ZAD) and ethylene glycol modified titanate (EGMT) as suitable commercial ZnO respectively TiO_2 precursor on silicon (100) substrates. The morphology is varied by using different mass fractions of the two precursors and by different deposition techniques. This involves spin-coating, spray-coating, dip-coating, blade-coating and solution casting. It is tried to produce a homogenous film with a certain thickness range between 300 nm and 500 nm which is reported to be most favorable for hybrid solar cell performance. Compared to this for conventional Grätzel cells an optimum film thickness of 5–10 μm is required. DEKTAK height profilometry is used to check the thickness of the resulting films. The influences of the different coating techniques on the morphology are investigated by optical microscopy, scanning electron microscopy (SEM) as well as gracing incident wide angle x-ray scattering (GIWAXS).

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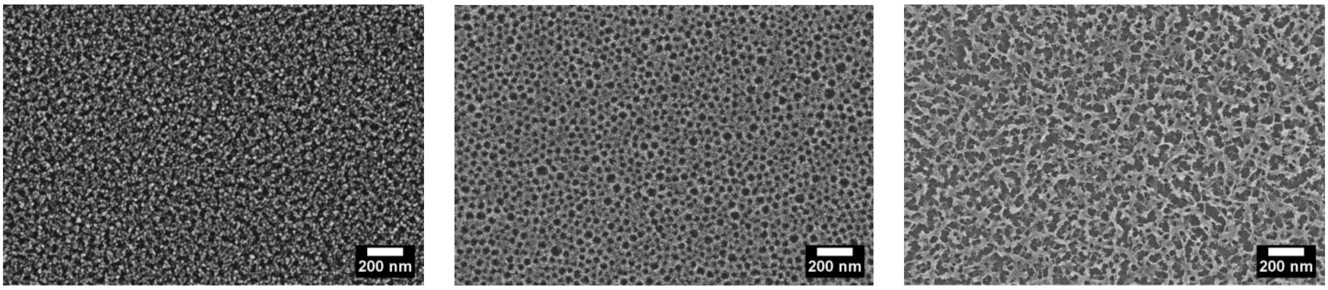

Fig.: ZnO/TiO_2 nanostructures synthesized from sol-gel technique by spin coating with increasing titania weight fraction from left to right.

Nanotubular TiO_x/C anodes for Li-ion intercalation

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Li intercalation experiments were conducted with TiO_x/C nanotubes [1] annealed in acetylene (C_2H_2) and argon (Ar) at 400°C to partially reduce the TiO_2 to TiO_x and to stabilize the reduced structure with carbon.
Anatase TiO_x nanotubes annealed in Ar were used as a reference. The nanotubes have a diameter of 100 nm and a length of 1μm.

The intercalation of lithium (Li) in the TiO_x/C tubes appears at more positive potentials compared to the one for TiO_x nanotubes. The reversible capacity of anatase TiO_x/C at a low rate of 0.3C (50 mAg^{-1}) is as high as 320$mAhg^{-1}$, which is far above the theoretical value where $Li_{0.5}TiO_2$ (168mAh/g) is formed as the Li-rich phase [2], whereas that of anatase TiO_x amounts to 141 $mAhg^{-1}$ only.
At a high rate of 6.0C (1 Ag^{-1}), still capacities of 155 $mAhg^{-1}$ are

observed for TiO_x/C, which demonstrates the high rate capability of the material.

Composite electrodes of conductive titania nanotubes coated with silicon (Si) via chemical vapor deposition (CVD) were produced and studied in terms of their Li intercalation characteristics. Both components show Li-intercalation capacities close to their theoretical values of 168 mAh/g ($Li_{0.5}TiO_2$) and 4200 mAh/g ($Li_{22}Si_5$) [3] resulting in 340 mAh/g capacity for the composite containing 4.7wt.% Si.
High capacity retention upon cycling was achieved owing to the good adhesion of the thin Si coating and the formation of a stable solid electrolyte interface (SEI) in ethylene-carbonate (EC), dimethyl-carbonate (DMC), vinylene-carbonate (VC) electrolyte with 1M $LiPF_6$.

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P(S-*b*-EO)-based polymer electrolytes for energy storage devices

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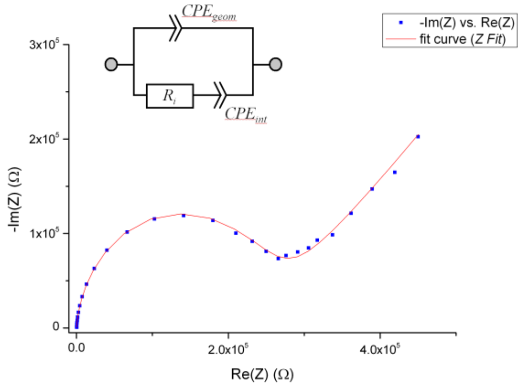
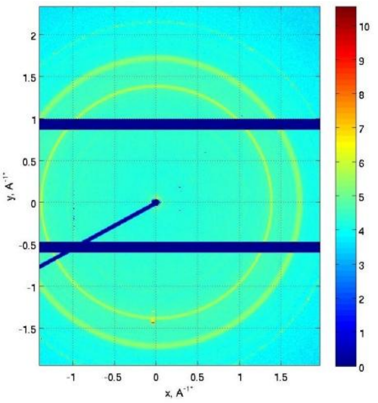
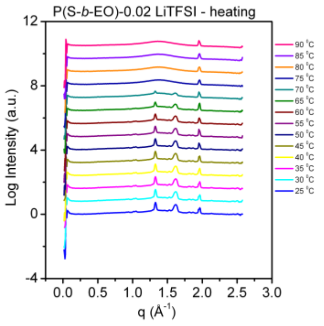
The challenges of the future energy market promote the need for new and more powerful energy storage devices. While promising new concepts like lithium air batteries are still in an early stage of development, some more conventional concepts still have potential yet to be explored and disadvantages for some applications yet to be overcome. Lithium batteries with polymer electrolytes combine the high energy densities and capacities of Li-ion batteries with better safety standards, mechanical stability and flexibility. Exploring the nano-scale regarding polymer film thickness opens up new possibilities in terms of design, application and integration of rechargeable batteries. However, ionic conductivity in polymers is limited, especially in the crystalline phase.

Poly(ethylene oxide) in the amorphous phase is suited to transport lithium ions. To prevent crystallization also at room temperature, lithium salts such as LiTFSI can be added. The amorphous phase comes along with a lack of mechanical stability, though. In our group, the conflict between conductivity and mechanical stability is addressed by the use of block copolymers consisting of lithium conducting soft poly(ethylene oxide) domains and mechanically stable glassy polystyrene domains.

The conductivity of the polymer electrolyte in a thin film format is determined by impedance spectroscopy. For these measurements, thin films of the diblock copolymer polystyrene-polyethylene oxide P(S-*b*-EO) mixed with LiTFSI salt are sandwiched between two gold electrodes and encased in an air-tight cell that enables contacting the electrodes. By fitting of the resulting impedance curves using suitable equivalent circuits, the ionic conductivity of the polymer can be derived. The measurements are carried out at different temperatures and different salt concentrations in order to investigate the effect of these parameters on the conductivity. In addition to the conductivity measurements, the inner structure of the polymer in bulk format is investigated by wide angle (WAXS) and small angle X-ray scattering (SAXS). This technique allows for the determination of crystalline structures and therefore further investigation of the effects of temperature and salt concentration on the inner morphology of the polymer. The combination of these methods facilitates the optimization of the composition and properties of P(S-*b*-EO)-based polymer electrolytes containing lithium salt and provides an insight into the mechanisms responsible for the conduction of lithium ions in these systems.







Top Left: *Impedance Plot with fit curve and corresponding equivalent circuit using constant phase elements (CPE) instead of ideal capacitances.*

Top Right: *2D WAXS image. The high intensity rings correspond to crystalline phases in the polymer.*

Bottom Right: *WAXS scattering intensity curves at different temperatures during heating.*

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Decomposition methods for large-scale optimization of power systems

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Variable renewable power sources are being integrated into power systems across the world. This restructuring process requires extensions of most parts of the power system infrastructure: generation, transmission, as well as storage capacity. Joint optimization of infrastructure extension and operation is a powerful method to identify technical solutions with minimal economic costs. This optimization problem is often formulated in a simplified linear problem [1]. Even though the resulting linear programs can be passed to standard solvers, a challenge arises from the large dimensionality of the problems, especially if a high temporal and spatial resolution is desired.

These challenges are addressed in joint efforts by our two research groups, with complementary expertise in power system optimization and communication theory. We believe that applications of communications theory to modern power networks go way beyond the obvious exchange of grid related information, such as measurements or control commands. Instead, we conjecture that communications and power networks share some interesting structural similarities leading to analogies in the associated optimization problems. For both, power and communication networks, distributed solutions, based on optimization theory and decomposition methods, were introduced and are developed independently, see [2,3] for an overview and further references.

As a first result, we investigated the potential of decomposition techniques for the specific problem of joint optimization of system extensions and operation. As there are no systematic methods to find the best suited under the many decompositions possible, our experience in successful application of decomposition methods in communication networks was very helpful. We propose a primal decomposition to split the optimization into the problem of finding the cost-optimal grid extensions and the subproblem of optimizing the operation for given infrastructure extensions, which exhibits a network flow optimization structure that is frequently observed in communication networks [2]. By doing so, the grid operation can be optimized for each time interval separately, which leads to a significantly lower overall computational complexity and allows for parallelized implementation.

As the network structure and the production costs are identical for each time interval, the demand is the only difference. By using the dual LP formulation the relaxed demand constraint appears in the objective and the set of feasible solutions is identical for every time interval. A solution of a LP can be found at one of the finitely many extreme points. Therefore, every extreme point is a solution for a set of infinitely many possible objectives. The solution of a different time interval that has similar demands, can serve as an good initial guess. Although interior point methods are superior in many applications, we propose to use the simplex algorithm that heuristically computes a series of extreme points until a solution is identified by an optimality check. By initializing the simplex algorithm with solutions of a different time interval we are able to drastically reduce the number of extreme points to be computed. At best, the only cost is the optimality check for the intial guess if it is successful.

It remains to compute the optimal system extensions, which is a non-linear problem. A solution can be computed efficiently by polyhedral approximation of the problem, which is frequently applied for network utility maximization [4]. The solution of the approximated problem, i. e., a possible grid extensions, defines the network layout for the subproblems. The solution of the subproblems allows for a refinement of the approximation. By variation of the aggregation level we are able to gradually adjust a trade-off between number of subproblems to be computed and size of the approximated problem. For the colloquium, we intend to present a general overview on our research efforts as well as specific details on the methods developed for large-scale optimization of power grid extensions and operation.

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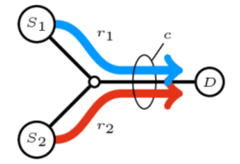


Network Utility Maximization

S_1, S_2	sources
D	destination
$U_i(r_i)$	utility function
r_i	rate emitted by S_i
c	link capacity

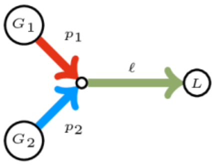
primal problem:

$$\begin{array}{ll} \underset{r_1, r_2}{\text{maximize}} & U_1(r_1) + U_2(r_2) \\ \text{subject to} & r_1 + r_2 = c \end{array}$$

dual problem:

$$\underset{\lambda}{\text{minimize}} \quad \lambda c - U_1^*(\lambda) - U_2^*(\lambda)$$

interpretation: dual variable λ is the price sources are charged for using the link



Optimal Power Flow

G_1, G_2	generators
L	load
$C_i(p_i)$	cost function
p_i	power output of G_i
ℓ	total system load

primal problem:

$$\begin{array}{ll} \underset{p_1, p_2}{\text{minimize}} & C_1(p_1) + C_2(p_2) \\ \text{subject to} & p_1 + p_2 = \ell \end{array}$$

dual problem:

$$\underset{\mu}{\text{maximize}} \quad \mu \ell - C_1^*(\mu) - C_2^*(\mu)$$

interpretation: dual variable μ is the price paid to generators for inducing power

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Experimental determination of transport parameters for binary electrolyte for use in numerical simulations

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Advanced numerical simulation tools are important for both the improvement of existing battery systems such as Li-ion batteries as well as the development of superior battery systems such as Li-air batteries. Computational methods can provide insight into physical and chemical aspects of battery systems, which is not or hardly achievable via experiments. The optimization of future battery designs is another important field of application for computer-based methods. For such numerical simulations, reproducibility and reliability are key issues, which depend on appropriate physical models, boundary conditions, and accurately determined transport parameters, among other things. Standard models as well as various computational approaches for electrolyte solutions can be found in the literature, whereas accurate and reliable transport parameters are scarce. For example, two situations are frequently encountered: either the potential range of such transport parameters provided in the literature is very broad or parameters are not reliable due to the fact that, e.g., important experimental procedures related to their determination are not specified. Therefore, it is the goal of this project to develop accurate and at the same time as simple as possible experimental procedures for determining transport parameters (including a geometrical parameterization of porous media) required for predictive numerical simulations.

The electrolyte solution filling a porous medium is modeled by the concentrated solution theory homogenized over a Representative Elementary Volume (REV) as presented, e.g., in [1]. A finite element method is developed for solving the resulting system of equations. As a result of the concentrated solution theory, a binary electrolyte can be characterized by three independent transport parameters: i) conductivity of electrolyte, ii) effective diffusion coefficient of binary electrolyte solution and iii) transference number of reacting ionic species. As usually done, the variation of the molar activity coefficient dependent on the concentration is neglected. Due to the homogenization procedure over a REV, two additional geometrical parameters are required: iv) porosity and v) tortuosity of the respective porous medium (see Fig. 1 for a depiction of an exemplary porous medium used as separator). Accurate values of all of these parameters are essential for enabling reliable numerical simulations of the complete systems consisting of electrolytes and porous media.

The experimental setup for the determination of the transport parameters comprises a battery test cell as depicted in Fig. 2. Fig. 1 shows the microstructure of the porous separator Celgard® 2500, which is located between the two electrodes in the present setup. The electrodes are composed of Lithium foils. Lithium perchlorate ($LiClO_4$) is used as the electrolyte solution. The conductivity of the electrolyte is determined by a conduction cell, the effective diffusion coefficient by the restricted diffusion method as proposed in [2], and the transference number by potentiostatic polarization as addressed in [3]. The porosity of a porous medium is a given parameter in this case, whereas the tortuosity is identified as a result of the ratio of the determined conductivities with and without porous separator, respectively. Alternative experimental methods proposed in the literature are also tested and checked against the aforementioned approaches. In the end, the results obtained from numerical simulations utilizing the experimentally determined parameters are compared to the results obtained from limiting-current experiments.

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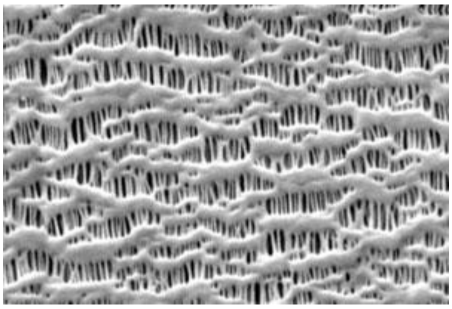

Figure 1: SEM Surface Photomicrograph Celgard® 2500 [4].

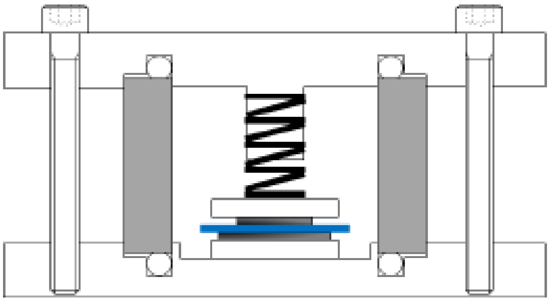

Figure 2: Schematic representation of an experimental test cell.

Controlling distributed flexible loads and energy storage to supply salancing power

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The integration of non-dispatchable generation from renewable resources with random power output, in particular wind and solar, requires a paradigm shift from load-following supply to supply-following load. Flexible loads, e.g., plug-in electric vehicles (PEVs) and heating, ventilation, and air conditioning (HVAC) systems, can be controlled to shift load on different time scales without compromising their primary use. Controlling these energy resources using information and communication technology (ICT) could turn out to be less expensive than deploying dedicated energy storage, but is to some extent restricted by dynamic user behavior. Stationary small-scale energy storage, for instance flow batteries, represents another option for realizing more energy storage capacity at arbitrary locations in the power grid. Their fast response capability and spatial distribution makes distributed flexible loads and energy storage ideal candidates for addressing various renewable integration challenges. They could help to improve voltage control in power distribution systems and reduce the peak-to-average ratio of power demand thereby enabling a more efficient use of existing power grid assets. They could also be used to supply balancing power which is needed to guarantee the secure operation of power systems. To realize this potential, academia and industry have to address challenging issues, including the technical and economical evaluation of these resources, the exploration of new control and optimization techniques, and the development and evaluation of ICT systems that meet the requirements imposed by the necessary control tasks. In addition to executing the control task including all required communication, optimization and input/output, such systems would have to be highly reliable and scalable.

This talk/poster will present our latest research results on supplying balancing power using fleets of PEVs and generic energy storage. We are particularly interested in scenarios where aggregators control these resources directly to participate in existing power markets. This turns out to be a highly demanding task, both from the communication and optimization point of view. We evaluate the potential of this scenario, propose pragmatic control and optimization techniques, and outline the vision of advanced ICT systems that could help to realize scalable and reliable resource control. Our evaluations are based on actual operational processes of power system operators, power market data, renewable power generation data, and simulations of dynamic resource behavior, e.g., driving patterns of vehicles.

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Analysis of predictions and clusters for a sustainable energy monitoring model

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The aim of this work was to generate a sustainable energy monitoring model by generating predictions and clusters out of a given data set. This should help to predict and to reduce energy costs for the end customer.

The data set comes from a test environment at the Technische Universität München, which collected the data from 29th of August 2011 to 28th of August 2012. In the environment the sensor system measures: air temperature, surface temperature, humidity, electricity, CO2, noise, radiation, heat flow and illumination. Also weather data from outside the environment were used.

To evaluate the data in the software weka [1] a so called ARFF file was generated. In weka there are several algorithms that are eligible for the generated data set. In a first step, we tested these different algorithms for predictions. The Bagging algorithm with a M5P classifier gave the best results (see table below). The Bagging selects an example from the training set [2]. When the algorithm finds a better solution the example will be replaced by this [2]. The optimizing data is a numeric value [2]. That means that the "voting" will be done by calculating the average from a bag and the value with less difference to this average value will be chosen. The settings were modified to get these results [2]. The M5P is an optimized algorithm of the M5 algorithm from Quinlan and builds a decision or regression tree [3,4]. A minimum of instances were set to four, number of iterations were set to 15, and a seed of four was used.

In a second step, we analyzed different eligible cluster methods that are available in weka. Clusters could not be identified because of a local minimum in the data set. In a further step the attributes could be analyzed more deeply.

In a third step, sustainability was considered. The Brundtland report definition (also known as UN) is used to evaluate the sustainability [5]. There are the areas social, economic, and environmental. These areas are used as a kind of filter. Sustainability will be the result when all three fit together.

Finally we created a sustainable model of the energy monitoring system. This is shown in the figure below.

Future work will be to validate the model on other environments to prove the results. Further the model could be used for simulations to prove e.g. if a new building is sustainable before it is constructed.

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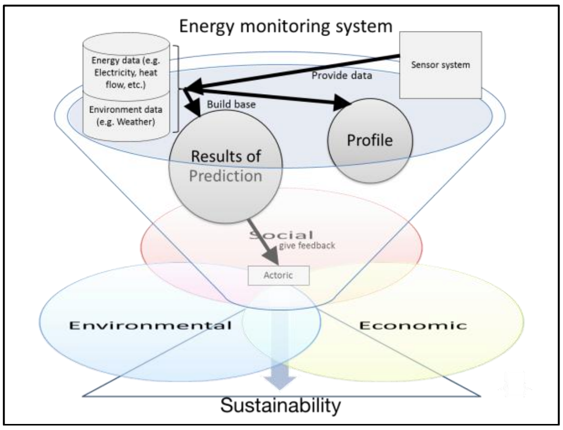
Prediction for	**Correlation coefficient**	**Mean absolute error**	**Root mean square error**	**Root absolute error in percent**	**Root relative square error in percent**
M5P default settings	0,9998	0,0061	0,0116	1,1702	1,7615
M5P Minimum Instances 7.0	0,9998	0,0061	0,0116	1,1703	1,7613
M5Rules	0,9998	0,0071	0,0126	1,3562	1,9105
Attribute Selected Classifier, M5P	0,9998	0,0061	0,0116	1,1627	1,1759
Bagging M5P	**0,9999**	0,0048	0,0093	0,9257	1,4052
M5P Minimum Instances 4, Seed 4, Iterations 15	**0,9999**	**0,0045**	**0,0085**	**0,8629**	**1,2947**
CVParameter Selection, M5Rules	0,9998	0,071	0,0126	1,3562	1,9105
MultiScheme M5Rules	0,9998	0,0071	0,0126	1,3562	1,9105

Selected results from the classificaiton (Source: Own work)



Sustainable model of the energy monitoring systems with the help of results of predictions (Source: Own work)

Combustion low calorific natural gases in gas engines: reciprocating and turbines

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Potential gas resources of shale gas in central Europe, for example in Poland, estimated to be up to more than 3000 billion Nm3. These gases have a similar composition to the currently operating in Poland in the amount of more than 4 billion Nm3 / a calorie Low Calorific Gas Natural Gases (LCNG). These gases contain essentially as flammable gases methane, a few percent higher hydrocarbons like C2H6, C3H8, and significant amounts of inert gases especially N2 (up to more than 50% N2) and sometimes CO2. Removal of nitrogen from natural gas that is: transport gas to nitrogen removal plant and the recipient, cryogenic process raise the cost per unit of energy of gas up to 15%.

Before transporting gas LCNG to energy systems based on reciprocating engines and gas turbines need to explain how far the molar gas shale gases (LCNG) may differ from the composition of the gas used to power on the market today reciprocating engines and gas turbines powered by conventional H-gas. The main problems are:

a) whether shale gases must be treated, or how much should be cleaned with nitrogen gas shale,

b) whether LCNG may be burning in power machines: engines and gas turbines directly in the natural molar composition of the high thermodynamic efficiency and low emission of pollutants?

In this paper, it will be shown that the basic thermodynamic properties of shale gases (LCNG gases are used as model gas) are significantly different from H-gas gas particularly in the property and affecting the propagation of flame stability. They presented the results of research on industrial engines installed on mine gas powered LCNG: NOx , CxHy , thermodynamic efficiency η_t Will be presented to the calculation of basic thermodynamic shale gases as for instance methane number MN, laminar flame velocity, as well as numerical simulations of the flow of combustion in the both types of power machines.

For reciprocating gas engines, the most important is the resistance to knocking combustion. It depends on the degree of compression and the size and shape of the combustion chamber, the excess air coefficient λ. Will show the results of the combustion of these gases in the premix engines equipped with a pre-chamber for easy ignition of gases containing especially high amounts of nitrogen. Shale gas incineration (LCNG) for gas engines can be implemented with greater efficiency η_t. MNLCNG as methane number is higher than MNH-gas so it is possible that operating on higher compression ratio ε.

For gas turbines powered LCNG (or shale gases) most important is the stability of the flame. It depends primarily on the degree of swirl number of stream premix mixture air-gas. Swirling should be as intense as flae is good stability, but can not be too strong due to the generation of the higher flow resistance of post flame gases through the combustion chamber of the gas turbine. As we know, to higher resistance to flow through the combustion chamber has a very large impact on the decrease of the thermodynamic efficiency of the gas turbine η_t.

Presented the results of research in the laboratory of experimental stands flame stability in swirl flow and the emission of toxic compounds in correlation to the nitrogen content and the calorific value of the gas. Burning shale (LCNG) gases in gas turbines should be done with greater efficiency, as naturally to these gases adiabatic flame temperature is lower.

The effect of fluorination in manipulating the nanomorphology in PTB7:$PC_{71}BM$ bulk heterojunction system

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Due to continuous encouraging improvement in device performance, polymer-based photovoltaics have drawn tremendous attention in both basic research and application fields during the last decade. Polymer-based photovoltaics is considered as one of the most promising candidate as a potential source of renewable energy. More than 10% power conversion efficiency has been reported in literature and 12% has been announced by Heliatek in Dresden at the beginning of this year. [1] A typical polymer-based solar cell is an active layer sandwiched between two electrodes with different work function. [2] The active layer normally is created through spin-coating process, and the solution is made of blended electron donor and electron acceptor materials as bulk heterojunction system. Therefore, the self-assembly nanomorphology is of great interest due to the exciton diffusion length is limited within 10-20 nm. By changing the used materials, solvent, solvent additive, as well as post-treatment method, dramatic changes can be observed in the film morphology, which directly leads to different device performance. Although efficiency has reached 12%, knowledge is still limited in how to further effectively improve performance of organic photovoltaics. Thus it is necessary to have a detailed investigation to address the relationship between morphology and device performance.

Here, the up-to-date highest efficient bulk heterojunction system PTB7 with varied fluorine content and the fullerene derivative $PC_{70}BM$ are thoroughly investigated. It is known that the amount of fluorine along the polymer chain strongly influences the film formation and therefore the solar cell performance. Additionally, the effect of solvent additive 1,8-diiodooctane (DIO) on differently fluorinated films is explored. To address the relation between the morphology and efficiency completely, a series of measurements have been done. The film surface structure is investigated by optical microscopy and AFM. The inner film structures, crystal orientation as well as the crystallinity are probed by advanced scattering techniques such as GISAXS and GIWAXS. By integrating all the data, the three-dimensional morphology of the active layer is detected. Consequently, the different morphologies introduced by varying the fluorine content and the addition of DIO are determined and compared with the corresponding solar cell performance of these systems. [3]

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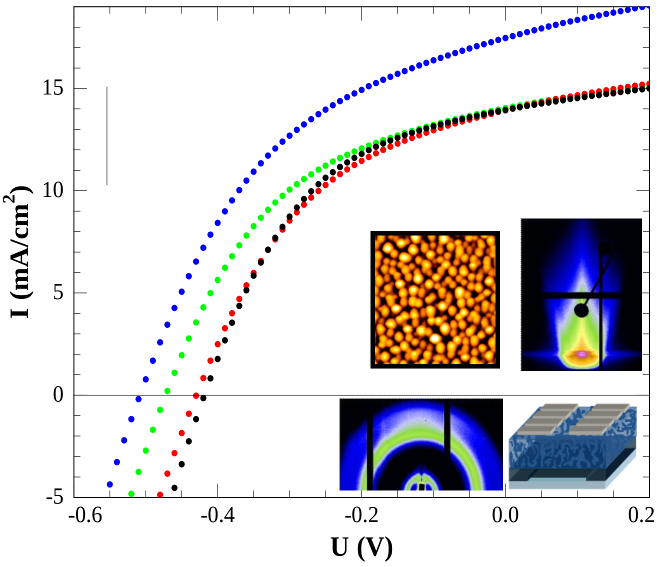

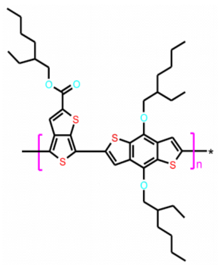

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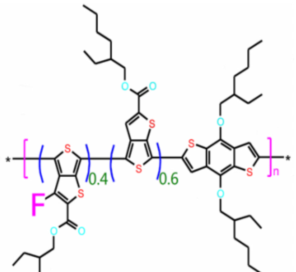

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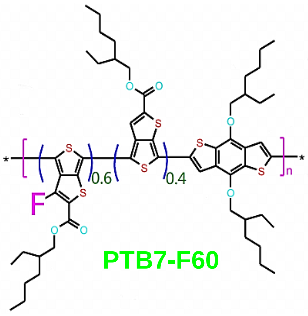

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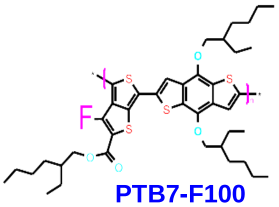

PTB7-F100

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Laser ablation ICP-MS for spatially resolved element analysis

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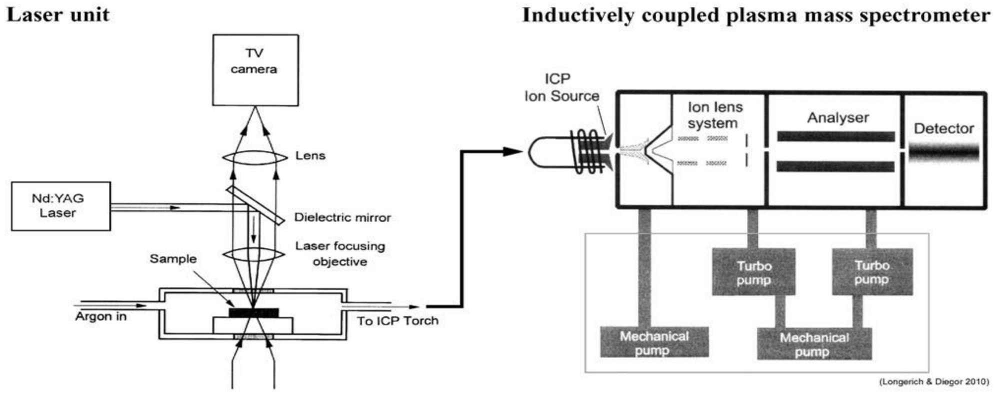
In combustion processes in a power plant, the optimization of energy production is of paramount importance. Corrosion effects and combustion residues also affect operating efficiency. The combustion residues mainly consist of silicates and aluminates. Additionally, they contain chlorides, sulfates and various heavy metals, strongly dependent on the coal used and the reaction conditions.

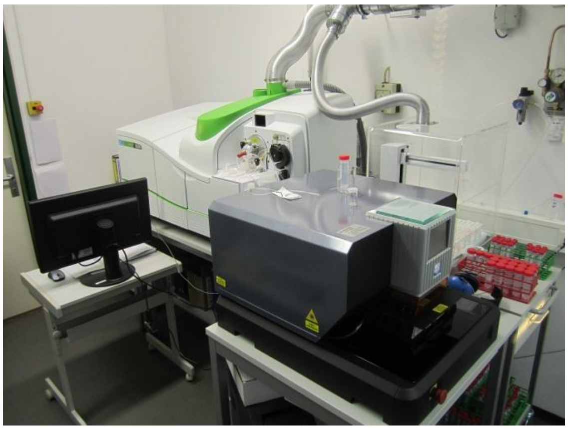
This poster introduces an analytical method, Laser Ablation Mass Spectrometry with Induced Coupled Plasma Ionisation (LA-ICP-MS) which enables the investigation of such combustion residues. The main advantages of this method are the small amount of specimen material required and a minimal specimen preparation. The specimen can be embedded in an organic matrix and pressed into tablets or, if the solid specimen is on a substrate, it can be analyzed directly. Specimen up to 10 x 10 cm^2 will find room in the measuring cell. The laser systematically removes material from the specimen surface. If the distribution of particular elements on the surface is of interest, a spatially resolved evaluation is also possible. The laser spot can be varied from 5 up to 300 µm which defines the spatial resolution. The depth of material removal is about 20 µm. The material is transferred to the ICP-MS with helium as a carrier gas. The ICP-MS is a highly sensitive analytical instrument and is able to quantify a broad range of elements.

In collaboration with the Institute for Energy Systems at the TU München, first measurements have been performed in a project on the gasification of solid fuel.

This is only one example in a broad field of possible applications.



(Longerich & Diegor 2010)



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Systematic investigation on ternary bulk heterojunction solar cells based on PTB7:PC$_{70}$BM

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Organic solar cells hold great promise for future applications in photovoltaics as they have several advantages, like the potentially lower production costs, much lower weight and flexibility in comparison to inorganic solar cells. In the present investigation the new, high efficient chlorobenzene based PTB7:PC70BM bulk heterojunction system are prepared and investigated with the addition of different third components. These kind of ternary systems have shown a promising result, which combines the advantages of the host material as well as the third component, and therefore improves the final power conversion efficiency. The inner structure of the ternary blend films is probed with grazing incidence small and wide angle X-ray scattering (GISAXS / GIWAXS). The surface morphology is investigated with atomic force microscopy (AFM) and scanning electron microscopy (SEM). Via integrating GISAXS, GIWAXS, AFM and SEM data, the inner 3D structure of the ternary films is obtained. As a consequence, the correlation between the nano-morphology of the films and the efficiency of the polymer- based solar cells is addressable.

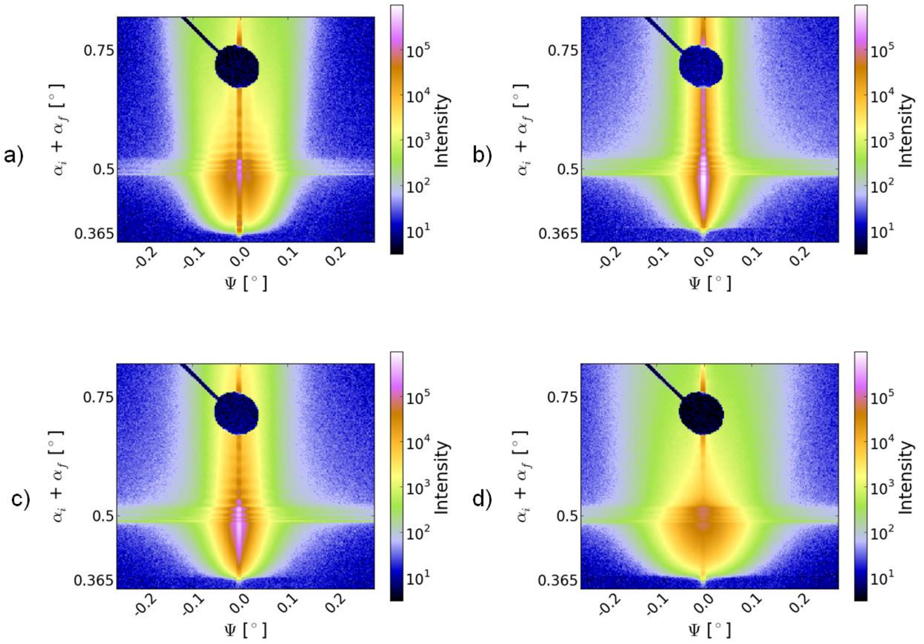

Fig. 1: 2D GISAXS data of a PTB7:PC$_{70}$BM film with different DIO concentrations: a) 0, b) 3, c) 6 and d) 9 vol %, taken at the P03 beamline at DESY Hamburg. Changes of vertical and lateral scattering pattern are observed. By increasing the concentration from 0 % to 3 % the scattering pattern gets more defined to the center. Further addition of DIO (c and d) leads to a broader and less defined scattering pattern.

Mechanisms of intercalation processes in anode and cathode materials for batteries

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Electromobility is essential in order to achieve sustainable transportation. The design and construction of electric vehicles are quite different from that of conventional cars. Progress is needed in the areas of Energy Conversion and Storage Fundamentals, Electric Vehicle Concepts and Energy Supply as well as Infrastructure. The Sino-German Network on Electromobility performs joint research in these areas in collaboration between several German and Chinese University, with the German efforts funded by BMBF. One key component in electromobility is battery technology.. For this application batteries should have a high energy and power density combined with a long lifetime and a competitive price. Further improvement of state-of-the-art lithium ion batteries would require extensive enhancement and will not reduce the production costs remarkably due to the Li scarcity. Batteries based on the intercalation of ions with higher valences of more common elements like Mg present a possible alternative. So far the intercalation kinetics of such ions is significantly worse than that of Li ions, and the energy density is less. Thus it is necessary to develop new materials with improved intercalation mechanisms, and to come to an improved understanding of the electrochemical processes during ion insertion on a nanoscopic level. These efforts are one focus of the activities in the Sino-German Network on Electromobility and are discussed in this contribution,

V_2O_5 based nanostructured materials represent potentially suitable host structures for Mg^{2+} intercalation. Different synthesis methods for V_2O_5 based nanostructured materials will be presented in this work. With the help of sonochemistry VO_x nanobundles can be produced [1] (Fig. 1). Another method to synthesise VO_x nanofibres like the ones in Fig. 2 is based on electrochemical growth by oxidation [2].

These large surface area materials are used for the preparation of novel electrodes for the cathode side based on [3] that will be electrochemically tested.

Scanning probe technique imaging with atomic resolution will be applied in order to achieve a deeper mechanistic understanding of the insertion processes and the formation of solid electrolyte interfaces. These studies are performed on model anodes and cathodes like highly oriented pyrolythic graphite (HOPG) and V_2O_5 single crystals, but also on the new materials. This should further validate their suitability for Mg^{2+} intercalaction. The results will be compared with Li^+ intercalation as a reference system.

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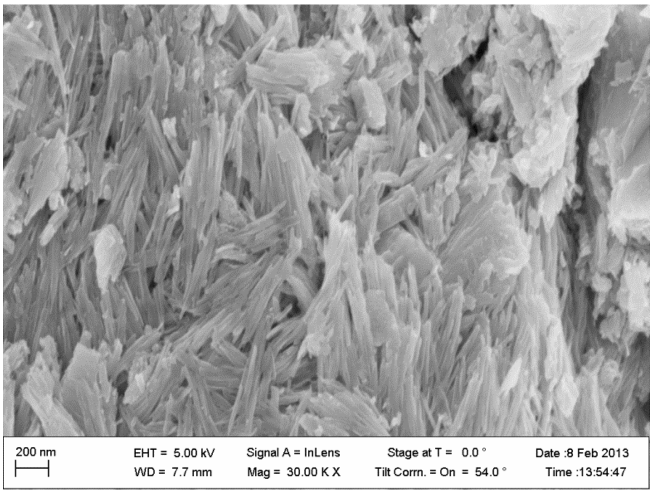

Fig. 1: SEM image of sonochemically synthesized VO_x nanobundles

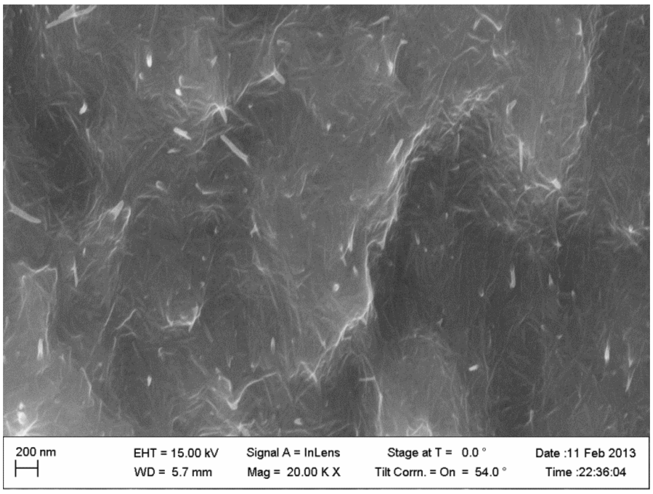

Fig. 2: SEM image of electrochemically synthesized VO_x nanofibres

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Cost of electric vehicles – example of Singapore

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Electric vehicles are known to be more energy efficient than their conventional counterparts. More specifically, the electric powertrain has a higher efficiency than the powertrain of a combustion engine vehicle [e.g. 2]. In addition, electric cars can be more environmentally friendly than cars with conventional powertrains (gasoline, diesel, natural gas), depending on the energy source which is used to produce the electricity. Further, electric vehicles have additional advantages: they are locally emission-free, which can help to reduce traffic-related air pollution in urban areas, and they are relatively silent so that they can contribute to reduce noise pollution in cities in order to improve their quality of life.

Despite these advantages, today's electric cars have some drawbacks: long charging times together with a relatively low range as well as high purchase prices. With an average annual mileage of 19,000 km for private cars [1] on an island of approximately 45 by 25 km, the range is probably not the most important problem to be solved in Singapore. Hence, this poster summarises the Total Cost of Ownership (TCO) of electric cars in Singapore. Costs for purchasing and operating a car in Singapore have been calculated in detail for five different types of powertrains, and the return when reselling the car has been taken into consideration. A special focus is on the vehicle taxation in Singapore and on the battery cost. Cost for charging infrastructure has also been taken into account.

The results show that large savings on fuel (energy) expenses are possible for the energy-efficient private electric cars. However, they are still quite expensive today compared to private conventional cars, at least for the case of Singapore. One reason therefore is the special vehicle tax structure which is imposed by the Singaporean government to control the number of vehicles on the road in order to limit traffic volume and congestion [3]. Hence, changes of the vehicle tax structure at short-term as well as technological improvements at long-term, for example on the battery technology, can help to make electric cars cost-competitive in the future. Further research needs to be performed in order to compare the situation of private cars in Singapore to Munich and other cities worldwide.

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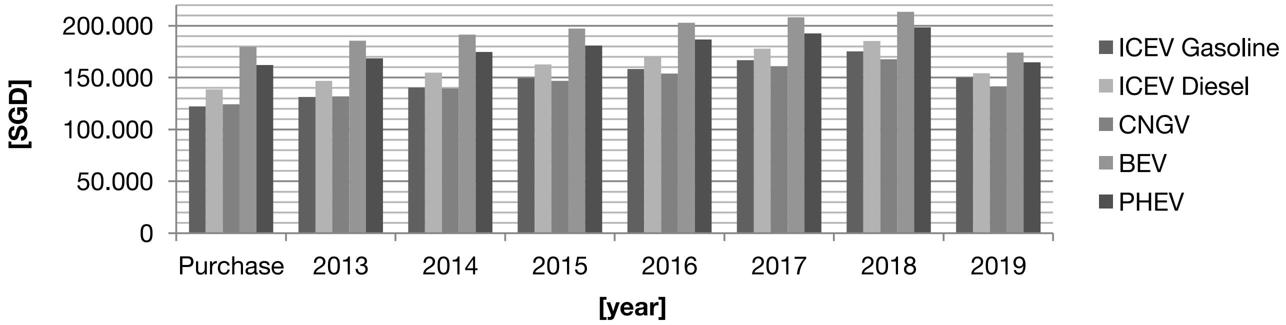
Example: comparison of the 7-year TCO of a private car in Singapore for 5 different powertrains



ICEV: Internal Combustion Engine Vehicle; CNGV: Compressed Natural Gas Vehicle; BEV: Battery Electric Vehicle; PHEV: Plug-In Hybrid Electric Vehicle

Annual mileage: 19,000 km [1]

Investigation of low GWP hydrofluoroolefins as potential working fluids in ORC

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Organic Rankine Cycles (ORC) use organic fluids instead of water as working media in conventional Clausius-Rankine processes. This enables the conversion of low temperature heat sources into electricity. The working fluids, i.e. different refrigerants, with a variety of thermodynamic properties are of great interest for Organic Rankine Cycles operating with different heat sources. However, most of the currently used working fluids have destructive effects on the environment, e.g. depletion of the ozone layer or global warming. To reduce the environmental effects, refrigerants have been progressed from CFC, HCFC to HFC in the past decades.

Hydrofluoroolefins (HFOs) have emerged in recent years as the fourth generation of refrigerant which are considered to be one of the most promising replacements for third generation refrigerants like hydrofluorochlorides (HFCs) as it possesses considerably lower effects on environment. This work will present a study concerning the thermodynamic performances of various HFOs as working fluids in Organic Rankine Cycles (ORC). The thermodynamic properties of the HFOs are estimated using Peng-Robinson equation of state in combination with group contribution methods. Simulations are carried out in Matlab, in which pinch points are specified in both heating and condensing components. Based on the first and second law of thermodynamics ORC-systems are studied. System performances under various operating conditions are mainly characterized by corresponding system efficiencies.

Figure 1 shows the component configuration of a standard ORC-system. The heat source is represented here by thermal water of geothermal wells. By varying the inlet temperature of the heat source from 120 to 200 °C an optimal inlet temperature can be obtained at a fixed system pressure for each working fluid. Taking the optimal inlet temperature into account the sum of exergy loss and exergy destruction in the economizer and the evaporator can be minimized, leading to the highest exergy efficiency. The influence of the system pressure on the plant performance is also investigated by increasing the operating pressure of the ORC-system from 15 to 30 bar at a fixed inlet temperature.

Taking the working fluid R1225yeE as an example the resulting system efficiencies, varying with the inlet temperature of the heat source and system pressure, are summarized in figure 2. At a fixed system pressure the system efficiency increases significantly with an increasing inlet temperature of the heat source until it reaches a peak at an intermediate inlet temperature of the heat source. Further on, only a small increase in the system efficiency is observed. Depending on the level of the inlet temperature of the heat source the system pressure influences the system efficiencies in different ways. At a lower inlet temperature (≤130°C) the system efficiencies reach maxima at intermediate system pressures (15 or 17.5 bar). On the other hand, at a higher inlet temperature (>130°C) the system efficiencies increase monotonically with increasing system pressures.

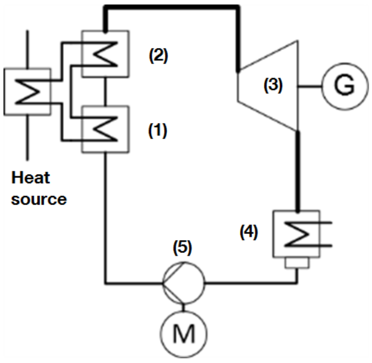

Figure 1 *Standard ORC model: (1) Economizer; (2) Evaporator; (3) Expander; (4) Condenser; (5) pump.*

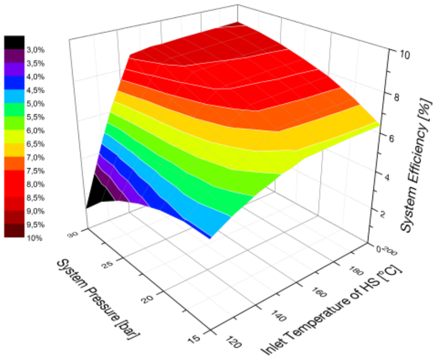

Figure 2 *System efficiencies of R1225yeE varying with the inlet temperature of heat source and system pressure.*

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Photochemical processes of solar water splitting

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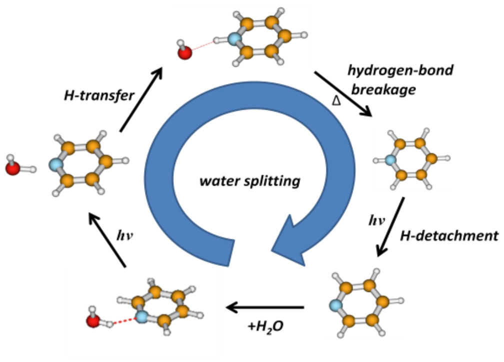
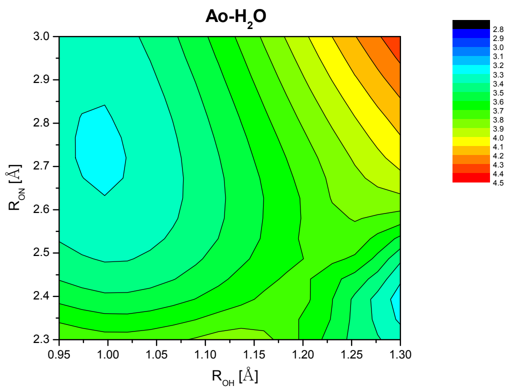
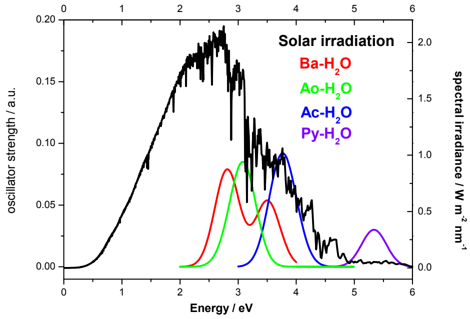
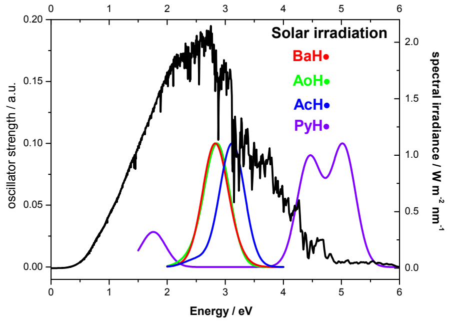
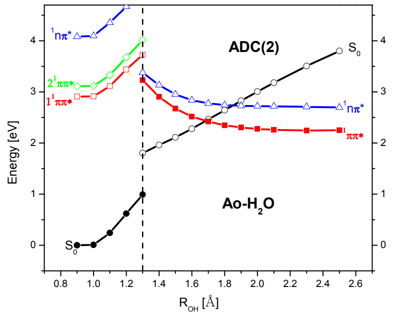
The photochemistry of a two-step solar water splitting process has been investigated with electronic structure caluclations. Organic chromophores, which have same reactive points, heterocyclic nitrogen, are used as catalyzers. In the chromophore-water complex, a proton transfers from water to chromophores overcoming a small barrier and leading to biradical products after the hydrogen-bond system absorbs a first photon. The resulting radical pair may dissociate to yield chromophore-hydride and hydroxyl radicals. In the second step, a repulsive excited state leads to the photodetachment of the hydrogen atom when a second photon is absorbed by chromophore-hydride radical. Overall, the H_2O molecule can thus be dissociated into H· and OH· radicals by the absorption of two photons and solar energy is stored in neutral radicals.

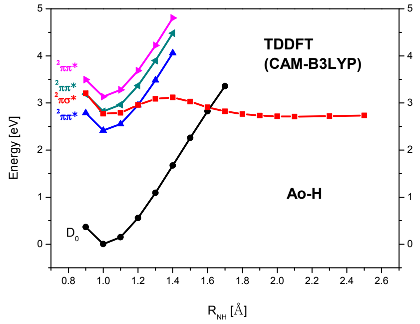












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The use of coupled oscillator models for the analysis of electric power system behavior

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The process of restructuring electric power systems has given new impetus for research on novel methods and analysis tools that possibly lead to new technologies that allow improving current power system's performance and stability characteristics. In this context coupled oscillator models have recently been introduced as promising modeling approach. In specific, a relation between mathematical tools from research in physics of complex systems and self-organization and classical models representing electric power system dynamics has been established. Our main goal here is to present this innovative connection, discuss its main assumptions and the use for electric power system studies; furthermore we present own work that exhibits novel dynamic phenomena and patterning similar to observations in real power systems. Our results highlight the importance for original research that treats dynamical systems and numerical methods for their simulation in a combined way.

In today's electric power systems generators are dynamically coupled with each other through an electrical network across large geographical distances. While in practice PDE-like behavior and propagation phenomena result from that setting, in theory the system is formally described as ODE subject to algebraic constraints (DAE), and in dynamical studies the latter part is often eliminated. The simplest dynamical model used in power system studies, the so-called classical generator model, can be related to the simplest model in coupled-oscillator studies, the so-called classical Kuramoto model using a singular perturbation approach. In specific, it can be shown, that equilibria of the Kuramoto-type model are (topologically) equivalent to equilibria of a DAE-type power system model, whenever solutions exist.

This opens the way to novel approaches in the computation of stability regions on the basis of convergence analysis of a Kuramoto-type dynamical system contrasting existing techniques which rely on static optimization. Moreover, convergence results can be given that purely base on electric network and generator parameters, which therefore yield appealing physical interpretations for factors determining the region of attraction.

On the basis of existing results we present a spatially embedded Kuramoto-type model representing power system dynamics close to steady state. While synchronization (convergence) to a steady state where coupling between generators vanishes takes place – as in cases where classical Kuramoto-type approximations are adopted – here a (bounded) growth of coupling strength after convergence to equilibrium is observed, see Fig. 1. This novel phenomenon has oscillatory characteristics with spontaneous peaks, and it does not depend on a specific discretization of time in our numerical simulations, but rather on the number of generators and maximal power transfer between pairs of them. This surprising phenomenon has strong similarity to exotic behaviors of numerical methods applied to singular perturbation problems. When diffusion of strong local coupling gradients is considered, patterning as observed in real power systems occurs, see Fig. 2. In order to acquire a deeper understanding of this behavior interdisciplinary research towards "numerics of complex systems" seems to be promising.

Figure 1: global coupling strength (rad/sec) over time: oscillation (green) and first peak (red) developing from synchronized solution.

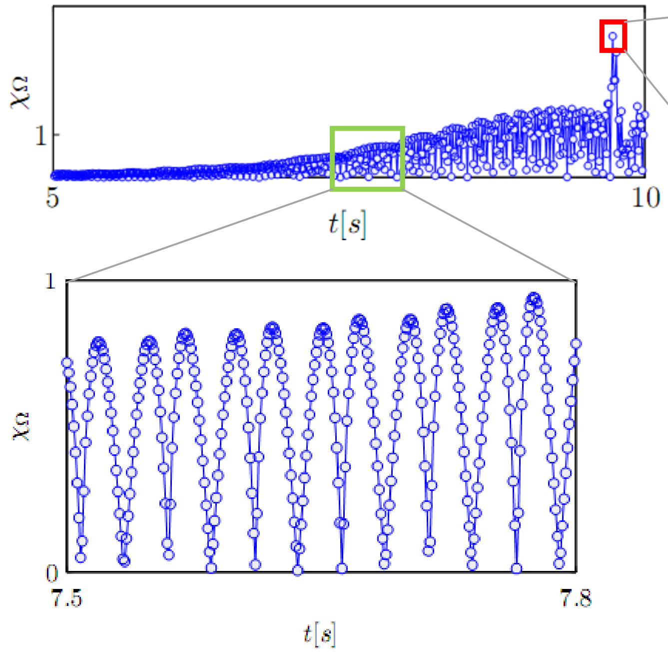
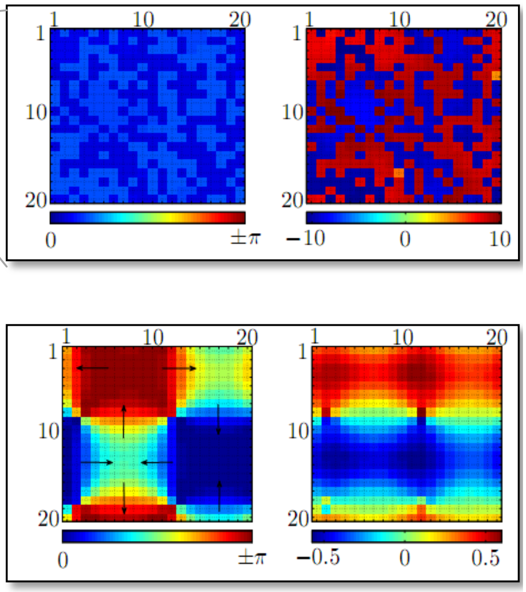


Figure 2: phase angles (left) and local coupling strength (right) at 20 x 20 generators, without (top) and with diffusion (down).



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Electrocatalytical studies for PEM fuel cells

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In this contribution, we present our recent results about electrocatalytical studies for polymer electrolyte membrane fuel cells (PEMFCs).

The aim of today's PEMFC research is to develop electrocatalysts with improved activity, durability and reduced or substituted content of platinum.

Here, oxide (e.g. ZrO_2) and carbide (e.g. TaC) based materials offer high potential as new non-noble metal electrocatalysts due to the absence of costly Pt and high corrosion resistance.

Figure 1 shows polarization curves of synthesized ZrO_2 supported on carbon, TaC and partial oxidized TaC electrocatalysts for the oxygen reduction reaction (ORR). The experiments were conducted in a three electrode RDE (rotation disk electrode) setup with 1600 rpm (rotation per minute) in 0.1 M $HClO_4$ electrolyte at 20 °C.

The ORR activities increased according to TaC < partial oxidized TaC << ZrO_2/C. The partial oxidation for TaC helped to improve the ORR activity.

More work is necessary to evaluate this type of ORR electrocatalysts for PEMFC application, especially investigations in 50 cm^2 single cells under operation conditions and structural characterization to identify the active reaction center.

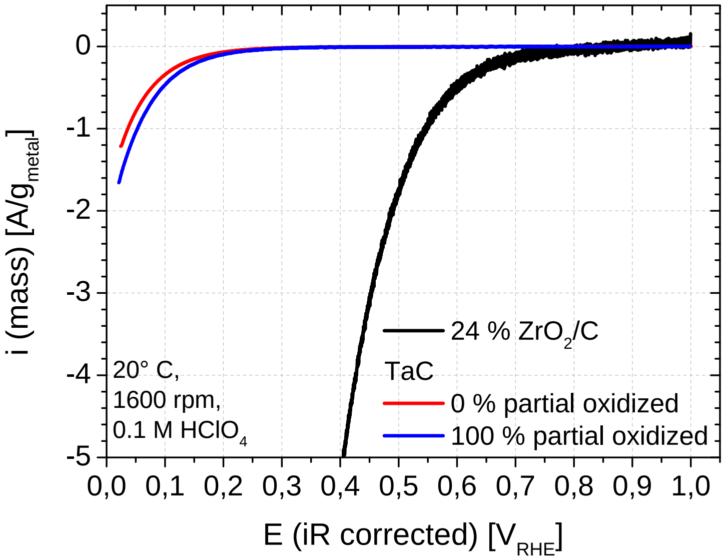

Figure 1 ORR polarization curves of various non-noble metal electrocatalysts in O_2 saturated 0.1 M $HClO_4$ electrolyte at 20 °C. Black: 24 wt. % ZrO2 supported on carbon, red: TaC, blue: 100 % partial oxidized TaC.

An evolutionary approach to the role of heritage-inspired solutions in hot and arid climate, the case of Egypt

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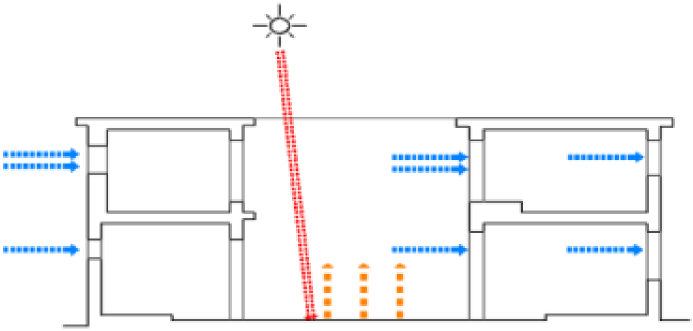
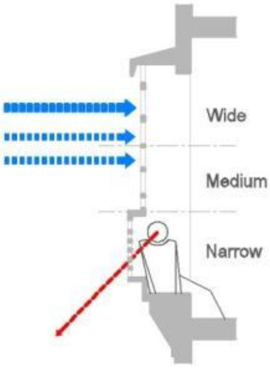
In most of architectural revivalist experiments emphasis was placed on the stylistic features and typologies as embedded values and little emphasis was placed upon functional, climatic and ecological aspects. However, greater values lie in the functional capacity of regional architecture in general. Nevertheless, a sort of inferiority complex against the new and imported methods and the invasive advancement of active climate control systems are major challenges vernacularism encounters. By means of available contemporary design tools and simulation programs more progressive methods and evolutionary actions can take place. This research aims to deal with the building as a self-sufficient passive modifier of climate extremes. The empirical part of the study targets a formulation of a design strategy that adopts an integrated passive method of design. The internal courtyard, fenestration and shading devices as basic elements of the proposed passive system and the interrelation between them shall be examined. The experiments shall also integrate all levels of details that might affect the performance of the system such as the surrounding masses and air flow pattern around the building.

In addition to the anticipated positive results on the ecological level and in terms of energy performance, the study propose that such an evolutionary approach can add a new dimension of dynamism to the historical features, which might change the ingrained perception of these features as mere images from the past. The result could be an emphasis on cultural authenticity and increased self-consciousness.



The Internal Courtyard as a climate modifier (Author)



Traditional Fenestration System (Author)

Nanostructured zinc oxide thin films towards solar energy applications

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Photovoltaic devices generate electricity directly from sunlight using a clever combination of semiconductors. Such solar powered devices can be used to power anything from small electronics such as calculators and mobile phones to huge facilities like houses and large industries.

Solar cells are mainly made using either pure inorganic materials like crystalline silicon or with organic materials like polymers and small molecules. Recently, hybrid solar cells have been proposed which aspire to combine the advantages of both inorganic and organic materials. While pure inorganic based cells are more efficient at converting sunlight to electricity, they generally have higher manufacturing costs and their performance deteriorates at high temperatures. Hybrid and organic cells typically have lower efficiencies, but are flexible and less costly to manufacture.

To create a hybrid solar cell, one needs a highly structured inorganic template of transparent conducting oxides like ZnO (electron acceptor). Such a nanostructured film is combined with an absorber layer consisting of a soluble conjugated polymer (electron donor). Incident light generates tightly bound electron-hole pairs, or exitons, on the polymer which diffuse and separate at ZnO/polymer interfaces. Holes are transported along the polymer network to the anode, and electrons along the ZnO network to the cathode and electricity is generated. Structuring is needed to form the largest possible interface between the inorganic-organic materials for efficient charge extraction and avoiding recombination.

A structured ZnO thin film is interesting for photovoltaics because it is a n-type semiconductor having a large direct band gap of 3.3 eV (at room temperature). Therefore it is transparent to visible light. With the high binding energy excitons of 60 meV it also finds applications in light emitting diodes (LEDs). ZnO is easily available, inexpensive, environmentally friendly and nontoxic. Zinc oxide has been widely used in both, organic solar cells as well as hybrid solar cells. A ZnO nanodot or nanorod array finds applications as an anti-reflection coating, a highly-structured transparent conductive oxide, a textured active part of the p-n-junction or as a light scattering element at the back-contact. Moreover, subwavelength ZnO nanorod arrays can display, due to the so-called "moth eye" effect, a reduced reflectivity and induce light trapping.

In this contribution, we will discuss the morphology, optical properties and crystallinity of some nanostructured ZnO thin films using techniques such as scanning electron microscopy, grazing incidence small angle X-ray scattering, photoluminescence, UV-VIS spectroscopy and X-ray diffraction and X-ray reflectivity.

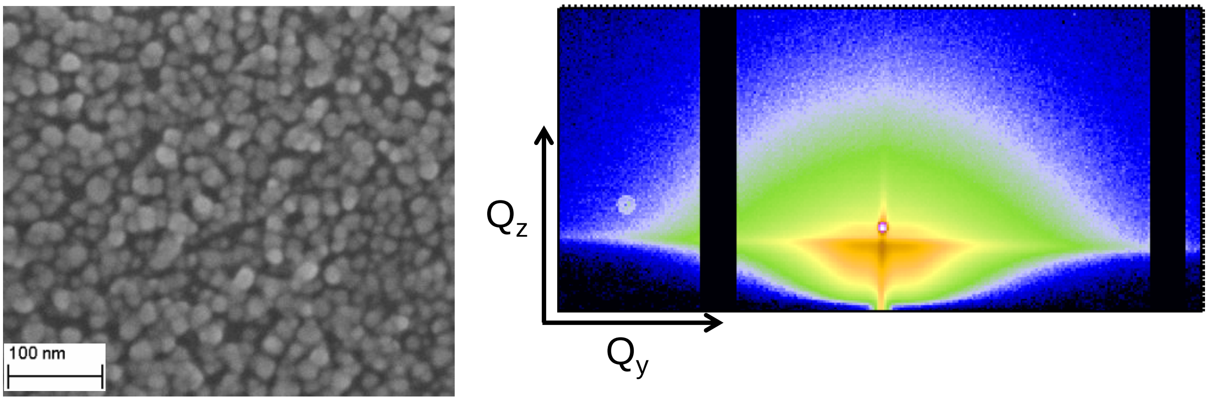

Fig. 1: SEM image of a ZnO nanostructured film in real space (left) and its GISAXS image in reciprocal space (right).

Nanoimprint technologies for organic and hybrid solar cells

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Nanoimprinting and printing techniques in general play a crucial role in nanofabrication since they offer the capability of large area patterning while simultaneously holding overall process time shorter compared to any other conventional nanolithography techniques. Nanoimprint lithography (NIL) can be used for structuring thin organic (e.g. P3HT) layers, thus allowing the realization of ordered organic solar cells or for patterning electrodes in order to enhance the optical coupling. In this work we concentrate on nanotransfer printing (nTP) and NIL as scalable, purely mechanical, lithographic techniques to fabricate ordered metallic and semiconducting nanostructures for photovoltaic applications. Improvements that can be expected from patterning have been simulated using a Drift-Diffusion approach.

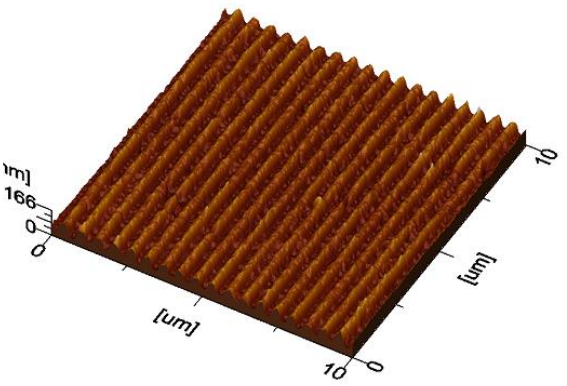

Figure 1

AFM image of a nanoimprinted P3HT polymeric layer down to 35nm feature sizes.

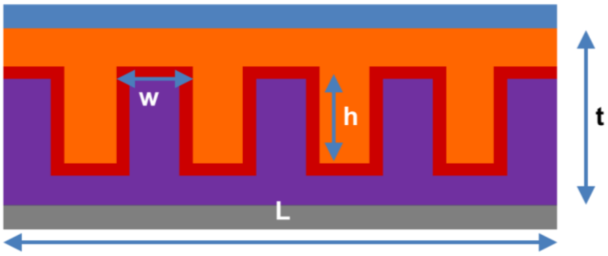

Figure 2

Schematic cross-section of a structured heterojunction organic solar cell. Structures with different widths (w) and heights (h) were theoretically investigated and their simulated efficiencies, open circuit voltages (V_{oc}) and short-circuit currents (I_{sc}) were extracted.

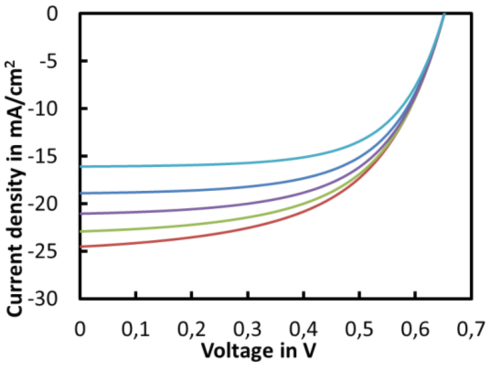

Figure 3

Simulated IV-characteristics of a structured solar cell as shown in Fig. 2 where the height (h) has been varied (between 100 and 200 nm) and the width (w) fixed at 80 nm.

Hybrid solar cells based on TiO_2-nanoparticles and water soluble polymer

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High expectations within the area of renewable energies are set on photovoltaic. Currently, solar cells are based on inorganic semiconductors, most of them made of silicon. A disadvantage of the silicon photovoltaic technology is the use of expensive materials and energy demanding production process, which can be overcome by using organic materials. These organic materials have the advantage of high absorption, an efficient roll-to-roll production technique and the possibility to fabricate flexible and lightweight solar cells. [1] Therefore, organic solar cells are eminently suited for applications such as mobile devices, the integration into flexible carriers like clothes or sunshades and, due to the possible transparency in the visible light, for applications on windows.

Combining the advantages of inorganic materials, namely high conductivity, with the film-forming properties of organic materials is addressed in using so called hybrid solar cells.

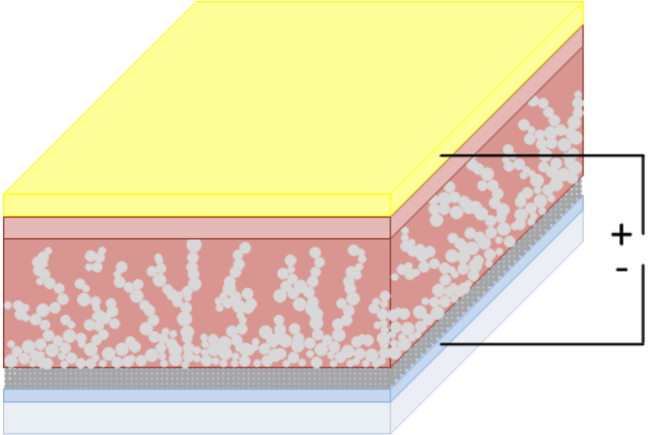
For hybrid solar cells based on titanium dioxide (TiO_2) as acceptor in combination with the widely used poly(3-hexylthiophene) (P3HT) as donor, efficiencies of up to 2.8 % are reported using a porous structure. [2]

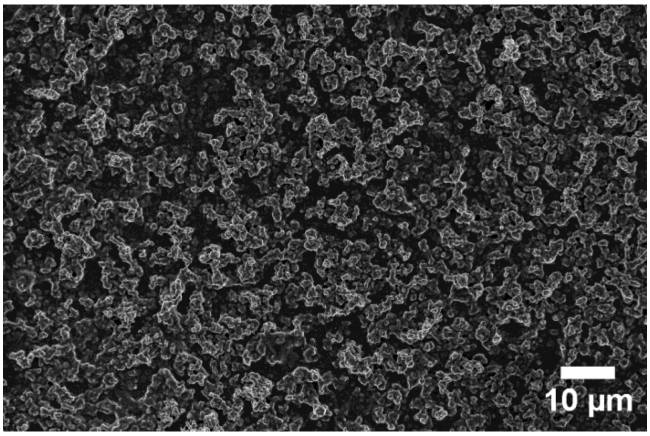
For solar cells a large interface between donor and acceptor material is needed. This is addressed by using particles with sizes in the nanometer range. A disadvantage in using P3HT is the need of toxic organic solvents like chlorobenzene.

In the present study solar cells based on TiO_2-nanoparticles as acceptor material and poly[3-potassium-6-hexanoate)thiophene-2,5-diyl] (P3P6T) as donor are under investigation. Due to the hydrophilic potassium carboxylate salt side chain, P3P6T is water soluble, which leads the polymer to be interesting for an eco-friendly processing. [3] Baeten et al. have shown that it is possible to build fully water-processable hybrid solar cells using this polymer in combination with metal oxide nanorods. [4]

In the present study, solar cells are produced in two ways, spin coating and solution casting respectively. The effect of different electron blocking layers is studied and the solar cells are measured under AM 1.5 conditions. The surface morphology is studied by scanning electron microscopy (SEM) and optical microscopy. The optical properties are investigated using UV-Vis-spectroscopy.

[1] Fraunhofer-Institut für Solare Energiesysteme ISE, press information 17/10 of June, 17th 2010
[2] A. Abrusci et al., *Energy & Environmental Science* 4 (2011) 3051-3058
[3] G.K.V.V. Thalluri et al., *Solar Energy Materials & Solar cells* 95 (2011) 3262-3268
[4] L. Baeten et al., *Solar Energy Materials & Solar cells* 107 (2012) 230-235





Left: principle setup of a hybrid solar cell
Right: Scanning electron microscopy (SEM) picture of the active layer

Distributed/hierarchical optimization for a scalable power system operation in smart grids

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The current power system operation is facing new challenges. The integration of intermittent renewable energy sources, has forced a paradigm shift. The traditional concept of only scheduling supply to follow demand does not longer provide a viable solution. Instead, there is a growing interest in the concept of demand following supply. However unlike supply, which is composed of tens or at most hundreds of large devices, demand is composed of millions of small devices. One of the main challenges for future power system operation is achieving a scalable and reliable control of these millions of devices to follow supply.

Many of the power system operation tasks involve an optimization problem. We can identify several problems: Unit commitment, economic dispatch, and optimal power flow, the definition of steady-state security regions, reactive power flow optimization, and optimal load shedding, optimal reconfiguration of the electric distribution network and uncertainty analysis. The traditional approach is to solve these problems in a centralized optimization. However, this is not scalable to millions of devices. The computation and communication costs make it impracticable.

There are two main approaches to address the scalability challenge in optimization: Distributed and hierarchical optimization.

Distributed optimization follows the divide and conquer strategy. In this strategy a large optimization problem is divided into smaller subproblems that are easier to solve. These subproblems follow a protocol which guarantees that the solution of the original optimization problem is achieved.

Hierarchical optimization, on the other hand, follows the simplify and conquer strategy. In this approach the original problem is reformulated into a simpler problem. Although this problem is easier to solve, a lot of the system details are lost in the simplification. This leads to a suboptimal solution of the original problem. Nevertheless, this method is preferred due to its simplicity.

Our research focuses on the design and implementation of distributed and hierarchical computation techniques for power system operation. Beyond the question of methods and requirements, this work aims to define the trade-off between these approaches and a centralized implementation.

Zinc oxide nanostructured films for applications in organic photovoltaics

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The role played by the inorganic nanostructures in the field of energy conversion has dramatically intensified by the contribution from the hybrid photovoltaic devices such as light emitting diodes, organic thin film transistors and solar cells. Solar energy serves as the most abundant source for green electricity which has triggered the fabrication of photovoltaic devices in the past two decades for the generation of electric power to answer the increasing demand. Organic as well as hybrid solar cells have been studied which promise reduced fabrication costs, simple processing and employment of flexible substrates. However, hybrid solar cells are of greater interest as they provide the benefits associated with both the organic and the inorganic material. In this regard, an approach towards fabrication of dye sensitized Grätzel cells using zinc oxide is made in the present study.

Hybrid dye sensitized solar cells conventionally prepared using titania as the inorganic material have reached power conversion efficiencies above 12 % [1]. Zinc oxide (ZnO) is a suitable candidate to be used as an alternative to titania due to their very similar optical and electronic properties. A power conversion efficiency of nearly 7 % has been reported for a ZnO based dye-sensitized solar cell which is comparable to the efficiency obtained using titania [2].

Two crucial parameters which decide the performance of such a photovoltaic device are the morphology and thickness of the inorganic layer. In this study, the so-called sol-gel technique is employed to synthesize nanostructured morphology of the ZnO films. The sol-gel chemistry is assisted by a structure-directing amphiphilic diblock copolymer, known as, poly(styrene-*block*-4-vinylpyridine). A "good-poor" solvent pair induced microphase separation in the polymer leads to the formation of micelles with polystyrene block as the core and the 4-vinylpyridine block as the corona of such micelles. A suitable commercial precursor for ZnO, namely, zinc acetate dihydrate is then incorporated in the hydrophilic 4-vinylpyridine block. By varying the weight fraction of the different solvents and the ZnO precursor, different morphologies are obtained out of which the foam-like network structure is selected due to its large surface-to-volume ratio and high capacity to retain material within itself. The high mechanical stability of such morphology also helps in up-scaling the thickness of the film for final device fabrication. Scanning electron microscopy (SEM) is used to investigate the resulting morphologies of the films. Since SEM only provides surface sensitive information, grazing incidence small angle x-ray scattering (GISAXS) is used to probe the morphology buried in the volume of the films.

For conventional Grätzel cells, an optimum film thickness of 5 – 10 µm is required. Several means are undertaken in the present study to meet the optimum thickness. Among these, blade coating and spraying are the most promising methods for significantly improving the film thickness over multiple blade coats and sprays. DEKTAK height profilometry is used to check the thickness of the resulting films.

Another very important parameter which decides the charge transport and mobility in the films is the crystallinity. To ensure sufficient crystallinity of ZnO, a high temperature thermal treatment is performed. Crystallinity of the films is then verified using x-ray diffraction (XRD) measurements. XRD studies have confirmed that ZnO crystallizes in hexagonal wurtzite phase upon the temperature treatment.

[1] Yella et al., *Science.*, 334, 629-634 (**2011**)

[2] Sacco et al., *Phys. Chem. Chem. Phys.*, 14, 16203-16208 (**2012**)

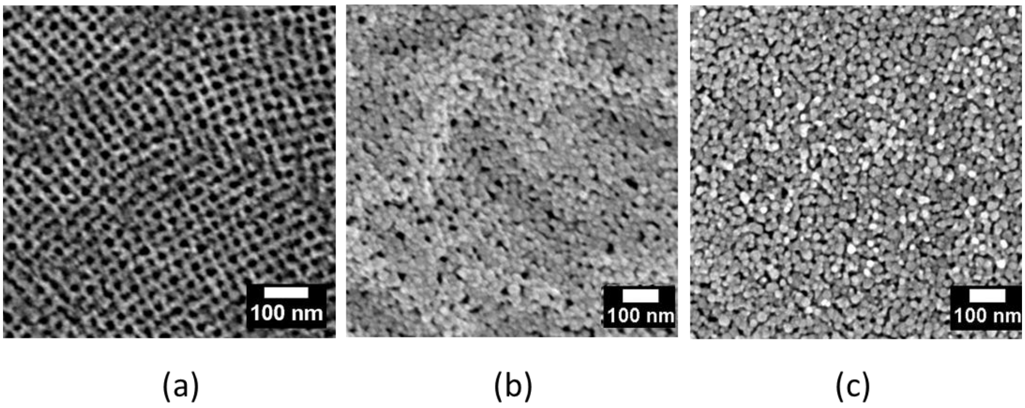

Fig.: ZnO nanostructures synthesized from sol-gel technique by spin coating (a), spray deposition (b) and blade coating (c).

First-principles kinetic modelling for organic solar cell optimisation

Christoph Schober[a,*], Harald Oberhofer[b,*], Jochen Blumberger[c,†], and Karsten Reuter[d,*]

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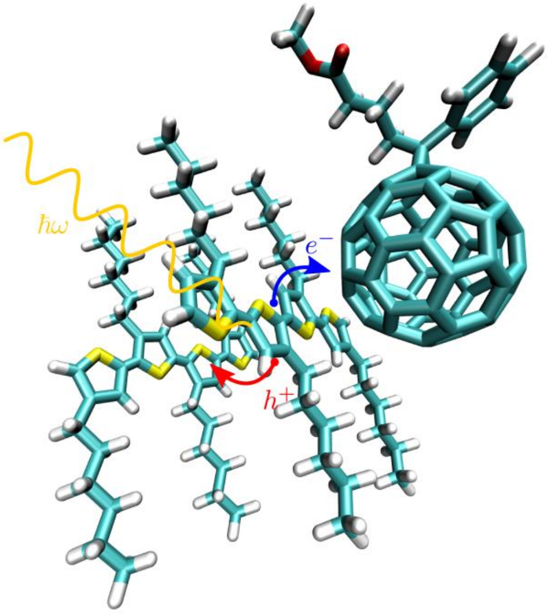
Organic solar cells are envisaged as a promising alternative to silicon based solar cells. They are cheap and easy to produce, light and flexible, and easily deployed on walls or roofs. Unfortunately, these advantages currently come at the price of small photo-electric conversion efficiencies. To help overcome this deficiency we use advanced density functional theory (DFT) based methods to investigate the electron- and hole-conducting properties of organic solar cell components such as nano-crystals of modified Fullerene molecules (PCBM) as well as the amorphous melt of semi-conducting organic polymers (P3HT). The aim is to combine data from these simulations into a comprehensive model of the cell. Of special interest here is the relationship between the microscopic structure and the macroscopically observed efficiency.

A popular model describes charge transport as 'hopping' of localised charges (electrons or holes) between different sites. These movements have been successfully described by rate theories, such as the Marcus theory, in some materials. In order to form a localised state (polaron), the local reorganisation energy λ has to be sufficiently large to result in a barrier between two localised states. It can be shown that the electronic coupling matrix H_{ab} needs to be smaller than $3\lambda/8$ in order for this condition to be met. First calculations for different directions in Fullerene and PCBM nano-crystals showed that this is not true for all crystal directions, even less so when the zero point energy of the charge transfer mode is taken into account. This leads to the conclusion that hopping models are not applicable for those systems.



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Applied neutron methods in Li-battery research

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The increasing interest in regenerative energies also brought a new focus in the research of energy storage and battery applications. Especially rechargeable Li-ion-batteries are widely investigated in many fields, reaching from portable energy devices to automotive power sources or temporary storages for regenerative energies.

The ExZellTUM research project (funded by the BMBF) has been created to investigate all processes and steps involved in the production of such Li-ion-batteries in the automotive sector. As a partner in this project the FRM II neutron sources major aim is the development of new methods to investigate such Li-ion-batteries using neutron radiation.
A great interest in studies with Li-ion-batteries is dedicated to the changes of the batteries and battery materials during operation. These changes often lead to capacity loss or other system failures and an understanding of these factors is a key for successful battery development.

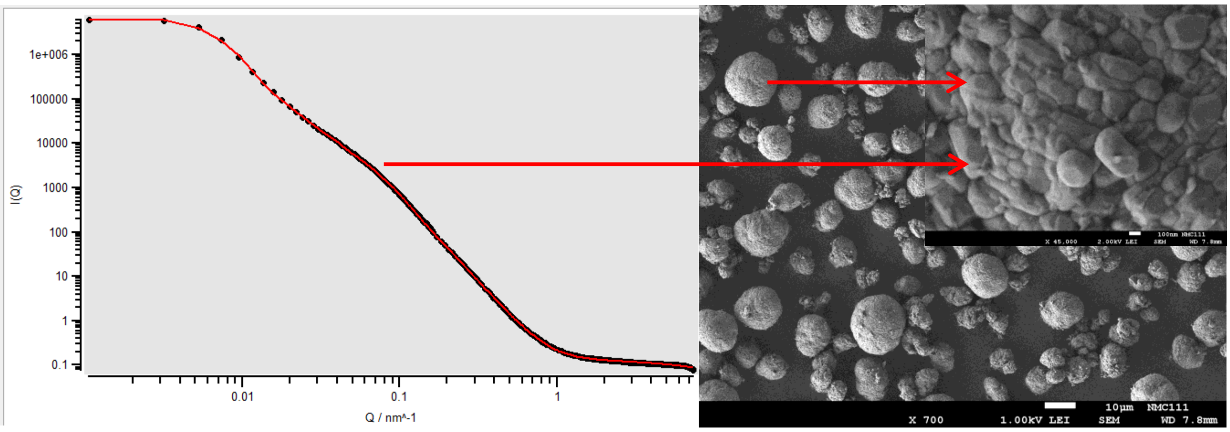
For most analytics that are used to characterize changes of battery materials though only post-mortem studies are possible, i.e. the Li-ion-batteries have to be disassembled prior to the measurements. Because of the complexity of battery cells and many unwanted reactions of the materials inside with air or moisture it would be very helpful to have experimental methods at hand for Li-ion-batteries without the need for disassembly.

Neutron radiation on the contrary is capable of easily penetrating most casings or hulls due to its weak interaction with matter and thus can enable us to gain insight into Li-ion-batteries without the need to disassemble the cells prior to the experiment.

At FRM II we have successfully developed various methods to investigate Li-ion-batteries in their operating state.

With the use of neutron diffraction (ND) methods at the STRESS-SPEC instrument it is possible to obtain information on the phase composition and the spatial distribution of the phases inside of Li-ion-batteries. By measuring only specific regions of the diffraction data we can also monitor continuous changes i.e. while charging the batteries in an in-situ experiment.

With specially designed thin (<1mm) Li-ion-battery cells it is also possible to use small angle neutron scattering (SANS) to obtain information about size and shape of particles in the range between 1-300 nm with the SANS-1 instrument.
Both methods, ND and SANS can also be used in conjunction and thus yield a complementary information about size, shape, particle distribution, phase composition and many other aspects over a broad range of size-domains, ranging from changes in interatomic distances to inner- and inter-particle shapes up to particle agglomerates.



SANS data (left image) obtained for cathode material REM images showing the particle size dimensions.

A systematic approach to energy efficiency retrofit solutions for existing office buildings

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The general problem addressed in this project is the integration of decision support tools and building design. This problem has been narrowed down to decision support for the specific type of building design decision, in this case, the selection and integration of energy efficiency measures which is applicable during the early phases of the building retrofit design process (feasibility study, conceptual design). The focus is on the energy efficiency retrofits of commercial office buildings.

The central goal of the doctoral research is the development of a decision support methodology to support decision-makers in choosing the most adequate energy efficiency retrofit solutions for existing commercial office buildings. The model could be used to help decision-makers with the selection and integration of energy saving building components in the early phases of an office building retrofit project, and it could also be used by the maintenance team of a real estate company with office buildings to do pre-retrofit evaluations of possible solutions to reduce the energy intensity of buildings.

In this study, the energy efficiency retrofit of an office building is regarded as a set of single actions that are expected to improve the sustainability of a building. A new systematic approach is presented to help a design team, or the maintenance team of a real estate company to find the most adequate energy efficiency solutions in the early phases of a retrofit project. The problem is attributed to a multi-objective optimization and evaluation problem characterized by the existence of multiple and competing objectives and a large number of possibilities.

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Fabrication of sponge-like titania nanostructures by the combination of sol-gel synthesis and spin coating

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Nanostructured titania thin films have drawn a great deal of attention in different fields of application such as photovoltaics, photocatalysis, and gas sensing. The main advantages are related to their chemical and optical stability, no toxicity and low cost, as well as a strong hydrophilicity. Titania, especially its anatase polymorph, has resulted in a fast upward trend in the field of dye-sensitized solar cell (DSSCs). For solar cell applications, a high surface area is desirable for the morphology influencing the light absorbance and the recombination probabilities of the photo-generated electrons and holes. Sponge-like titania nanostructures are particularly promising due to their morphology with a high surface area and an interconnected network.

Several techniques have been developed to fabricate sponge-like titania nanostructure like chemical vapor deposition, a hydrothermal method, electrodeposition, and sol-gel synthesis. A very promising route is the application of the sol-gel chemistry in combination with amphiphilic block copolymer templates. In this approach, relatively low temperature is needed; the reactants can be mixed uniformly at the molecular level; the micro-phase separation could takes place through a so-called good-poor solvent pair, which induces a large specific surface area, narrow size distribution and high order of pores after the removing of the templates. Meanwhile, many methods have been applied to get titania thin films, such as spray pyrolysis, magnetron sputtering, and spin coating from solution. In the last method the film thickness is controllable via the concentration and viscosity of the solution and the used spin coating parameters.

In this work, the titania nanostructures are obtained from the sol-gel synthesis in combination with block copolymer templating and then spin coating (see figure). The Titanium tetraisopropoxide (TTIP) is the titanium source, by changing the amount of which the size of pores can be tuned-the more TTIP the bigger pore size; the structure-directing agent is the amphiphilic diblock copolymer of P(S-b-4VP). Through the coordination bond between its P4VP block and the TTIP, titania nanostructures can be synthesized within the copolymer. Compared to the titania film using another structure-directing agent P(S-b-EO), the pores of P(S-b-4VP)-induced titania film are equally ordered but smaller. The surface morphology is probed with scanning electron microscopy (SEM). The polymorph is investigated by UV/Vis spectroscopy and Photoluminescence. In addition, in solid-state DSSC the titania network structure needs to be covered with a dye layer, thus the adhesive ability of titania with respect to the dye is crucial, which links closely with its hydrophilicity. The hydrophlicity is characterized by water contact angle measurements.

In summary, sponge-like titania nanostructures are achieved. The films are homogeneous with the size of pores being determined by the amount of TTIP and the structure-directing agent. Anatase phase is present in the films. The hydrophilicity of the films is improved by UV light irradiation and oxygen plasma.

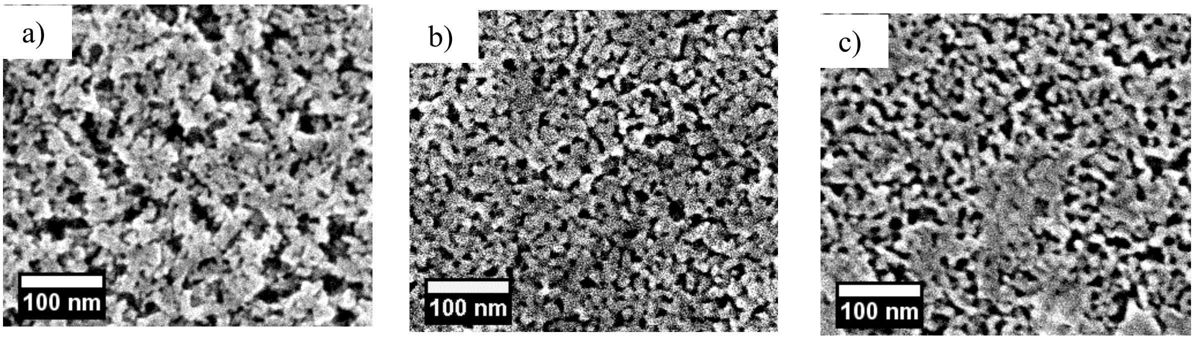

Figure: SEM image of sponge-like titania nanostructures prepared by the same reactant weight ratios but two different structure-directing agents: a) P(S-b-EO) and b) P(S-b-4VP); the same structure-directing agents but two different reactant weight ratios(THF/DMF:TTIP:HCL): b) 0.935:0.06:0.005 and c) 0.92:0.075:0.05

Munich School of Engineering Technische Universität München

HER/HOR at Pd nanoparticles on Ru(0001) substrates

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For energy conversion *e.g.* in fuel cells, catalyst materials play a crucial role. In the last years, nanostructured catalysts have been intensely studied not only due to their optimised surface area/material ratio, but also because the catalytic activity of nanoparticles can drastically change compared to bulk material. Both Pd and Pt particles on Au(111) substrates show an enhanced chemical activity compared to bulk Pd or Pt for the hydrogen related reactions. One parameter controlling the catalytic activity of Pd and Pt is the lattice strain that is present e.g. in pseudomorphic monolayers grown on single crystal substrates like Au, Pt, or Ru [1,2,3]. Additionally, the reduction of the diameter of monolayer thick Pd islands on Au substrates results in a furthermore enhanced chemical reactivity indicating additional influencing parameters such as substrate effects [3,4,5].

In this work, the electrochemical reactivity of Pd nanoparticles on Ru(0001) single crystal substrates was studied by analysing the hydrogen evolution reaction (HER) and the hydrogen oxidation reaction (HOR).
Heteroepitaxially grown Ru(0001) films on YSZ buffered Si(111) were used as substrates [6]. The electrochemical characterisation of the substrates proofed the high crystal quality with HER exchange current densities as known for conventional Ru(0001) single crystals [3].
The Pd particles/nano-islands were deposited electrochemically from 6.25 mM $Pd(NO_3)_2$ in 1 M H_2SO_4. By application of different potentials and deposition times the Pd coverage was varied from fully closed films down to the sub-monolayer ranges. The dimensions of the nanoparticles *i.e.* diameter and height were determined by STM. The reactivity of the Pd particles on Ru(0001) regarding HER/HOR was studied by electrochemical measurements in hydrogen-saturated 1 M H_2SO_4. The influence of the Pd particle size on the electrochemical activity will be discussed.

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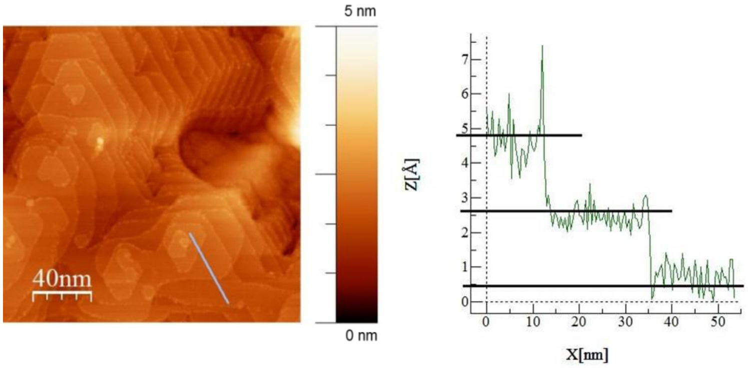
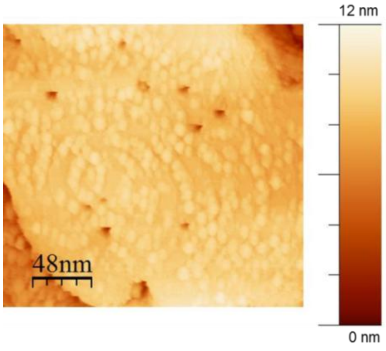


STM image of the Ru(0001) substrates used for this studies. The step height corresponds well to the half lattice constant of Ru in c-axis direction



STM image of a Ru(0001) sample after electrochemical deposition of Pd

Foam-like structures of titania films for application in hybrid photovoltaic cells

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Due to a high surface to volume ratio and their bicontinuous morphology, foam-like nanostructures are becoming more interesting in photovoltaic cells, for example in hybrid solar cells and dye-sensitized solar cells (DSSC). The nanoporous titania layers are responsible for the electron transport and for directing the dye layer structure. In our studies, the morphology of the titania films is investigated with respect to a possible incorporation into hybrid solar cells. The amphiphilic block copolymer polystyrene-block-poly(ethylene oxide), denoted (PS-b-PEO), has attracted particular interest as a structure-directing agent with benefits such as controllable pore size. The titania films are prepared by a sol-gel process. During this process, PS-b-PEO is dissolved in 1,4-dioxane, next HCl is added as a bad solvent for the PS blocks, and titanium tetraisopropoxide (TTIP) is put as titania precursor. Via this route we have a very high level of control over the final morphology.

The deposition methods are spin-coating and spray pyrolysis. Due to its low costs and the capability of a continuous flow process for making solar cells, spray pyrolysis is a industrial relevant method, which can also generate thick meso- and macroporous morphologies in case of metal oxide films. Our approach is to compare these two deposition methods, spin-coating and spray pyrolysis. During the preparation of the sol-gel process, the solution is sprayed on the silicon wafer, which was heated at 150 °C (pressure of nitrogen was kept at 2 mbar). Simultaneously, we deposited titania films by spin-coating under ambient condition (temperature, 18.9 °C; relative humidity, 30%; rotation speed at 2000 rmp). After this deposition process, the samples were calcined at 400 °C for 4 hours under an insert atmosphere with a ramping rate of 375 °C/h.

Titanium dioxide films were measured by scanning electron microscopy (SEM) as shown in figure 1 and 2. The films contain a large number of small-sized structures. However, mesopores are homogeneously distributed in the film. It was observed that the average diameter of the pores is changing by different weight ratios of 1,4-dioxan, HCl and TTIP. The size of the pores increases slightly by decreasing the weight ratio of TTIP. In case of the preparation route based on spray pyrolysis, TiO_2 films still have a foam-like nanostructure and thicker films can be obtained by increasing the spraying time. To determine the optical and the optoelectronic properties UV/Vis spectroscopy is used, which shows that crystallization of TiO_2 is identical for both preparation routes. The water contact angle of the TiO_2 films also investigated. After 40 minutes of oxygen plasma treatment, the water contact angle has reduced drastically from 19.65° to 3.5°. The etching effect of the O_2 plasma was not observed in this work.

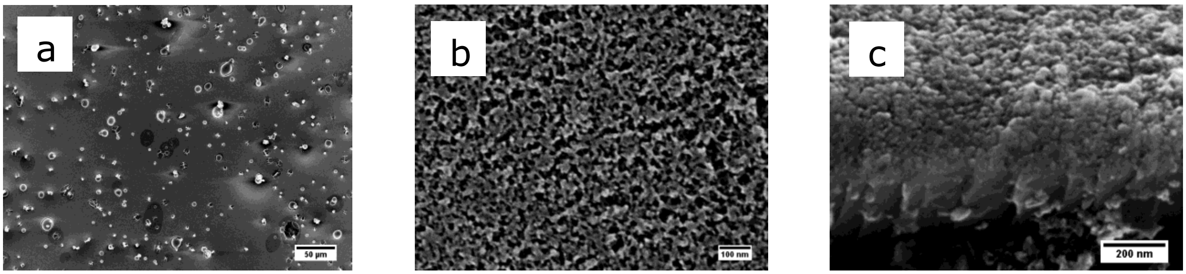

Figure 1: Top view scanning electron micrographs of films prepared via spray pyrolysis.(a) sample before calcination; (b) sample after calcination; (c) cross section of sample after calcination.

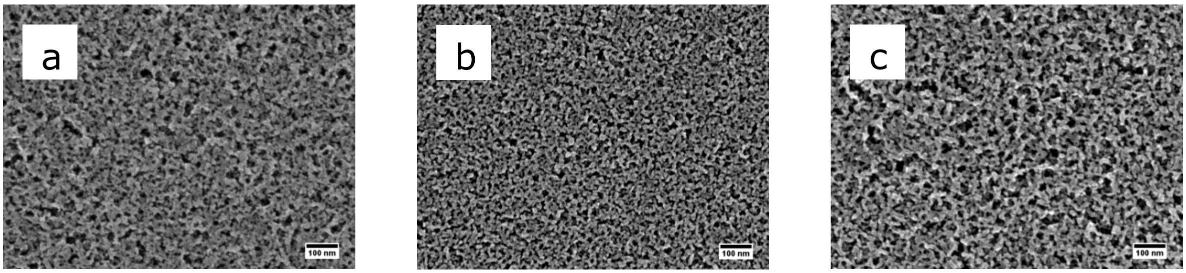

Figure 2: Top view scanning electron micrographs of films with different weight ratios prepared via spin-coating: a) $W_{1,4\text{-Dioxan}}:W_{HCl}:W_{TTIP}=0.92:0.01:0.07$; b) $W_{1,4\text{-Dioxan}}:W_{HCl}:W_{TTIP}=0.93:0.01:0.06$; c) $W_{1,4\text{-Dioxan}}:W_{HCl}:W_{TTIP}=0.94:0.01:0.05$

Energy conversion & storage: Fundamental insights in electrocatalysis

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In order to improve the performance of energy storage and energy conversion devices, new paths have to be explored. Learning from nature, developing new materials and morphologies is our strategy to address the challenges in energy research.

A major disadvantage of carbon supports, which are used in many commercial catalyst systems, is that they are prone to corrosion. Titania is more corrosion resistant compared to carbon and hence a promising material for medium and high temperature applications, such as the direct conversion of ethanol in proton exchange membrane fuel cells (PEMFC). However, the application of titania in electrocatalysis is limited due to its poor conductivity. An enhancement in the conductivity can be achieved by a high temperature carbothermal reduction treatment which converts titanium dioxide (TiO_2) into titanium oxycarbide (TiO_xC_y). A detailed investigation of the carbothermal reduction process has been carried out by studying compact anodic TiO_2 films after treatment at different temperatures and a thermodynamic model is proposed [1]. To test the applicability of compact TiO_xC_y as a support material for electrocatalysis, aerosol assisted deposition (AAD) of platinum on compact TiO_xC_y films has been performed and its electrocatalytic activity for ethanol oxidation was investigated at room and intermediate temperatures [2].
High surface area TiO_xC_y nanotubes and powders are currently synthesized for application in direct ethanol fuel cells.

The carbothermal treatment, as implemented in our group, can as well be used to tailor the band gap of titania for photo-electrocatalytic applications. First results of a current project on the application of TiO_xC_y nano-structures for photo-electrocatalytic water splitting will be presented.

A great deal of interest has been developed in the recent years towards enzyme catalysis for energy conversion. In order to obtain a fundamental understanding of the oxygen reduction reaction in electrocatalysis, investigations of enzymes directly immobilized on electrode surfaces are of great value. Combination of interfacial bioelectrochemistry and scanning probe microscopy (SPM) offers an excellent tool to investigate the electrochemical activity of redox enzymes on model electrode surfaces as it is capable of in-situ mapping of the direct electron transfer (DET) between a single redox molecule and the electrode. The immobilization of the oxygen reduction catalysing enzyme, laccase, on the electrode surface has been achieved using mixed monolayers of two different thiols on a Au(111) surface. One of these thiols, called linker, exhibits a functional group similar to the natural substrate of the enzyme. This guarantees a proper enzyme orientation and DET to the active center of the immobilized enzyme. In order to improve the enzymes' accessibility to these linkers they are embedded in a matrix of shorter thiols which leads to an increased distance between the linker molecules. It has been found that enzymes show activity when the thiol monolayers is homogeneously mixed, whereas no activity is observed when the thiol molecules attach in two separated phases.

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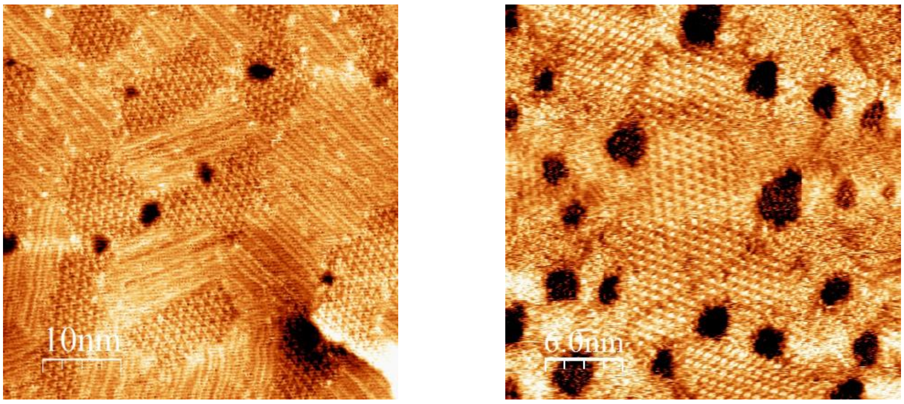

Electrochemical Scanning Tunneling Microscopy images of a mixed thiol monolayer on Au(111).
Left: phase separation, right: mixed phase

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Hybrid solar cells based on zinc oxide nanostructures

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Mesoporous zinc oxide (ZnO) structures in the form of thin films have been investigated in the present work. The promising electronic and optical property of ZnO leads to its wide scale applications from which the area of hybrid photovoltaics interests us. In a hybrid solar cell, ZnO acts as the inorganic electron acceptor in combination with a backfilling hole-conducting organic polymer (P3HT).

The main focus of this project is to synthesize mesoporous ZnO network morphologies in the form of thin films. The mesoporous network provides large surface-to-volume ratio to enhance light harvesting capacity and the interconnected network reduces the probability of electron-hole recombination in addition. The synthesis of such thin films is carried out via a sol-gel technique.

An amphiphilic diblock copolymer, poly (styrene-block-acrylic acid) is used as a template in which a suitable commercial precursor of ZnO is incorporated. The task is to find a proper morphology of ZnO network by varying the weight fractions of the solvent system used along with the weight fraction of the ZnO precursor. Structural characterization of the thin films is obtained by scanning electron microscopy (SEM), atomic force microscopy (AFM), and grazing incidence small angle neutron scattering (GISANS). Thickness of the films is investigated by white light interferometry and height profilometry. Optical properties of the films are studied by UV/Vis spectroscopy and photoluminescence.

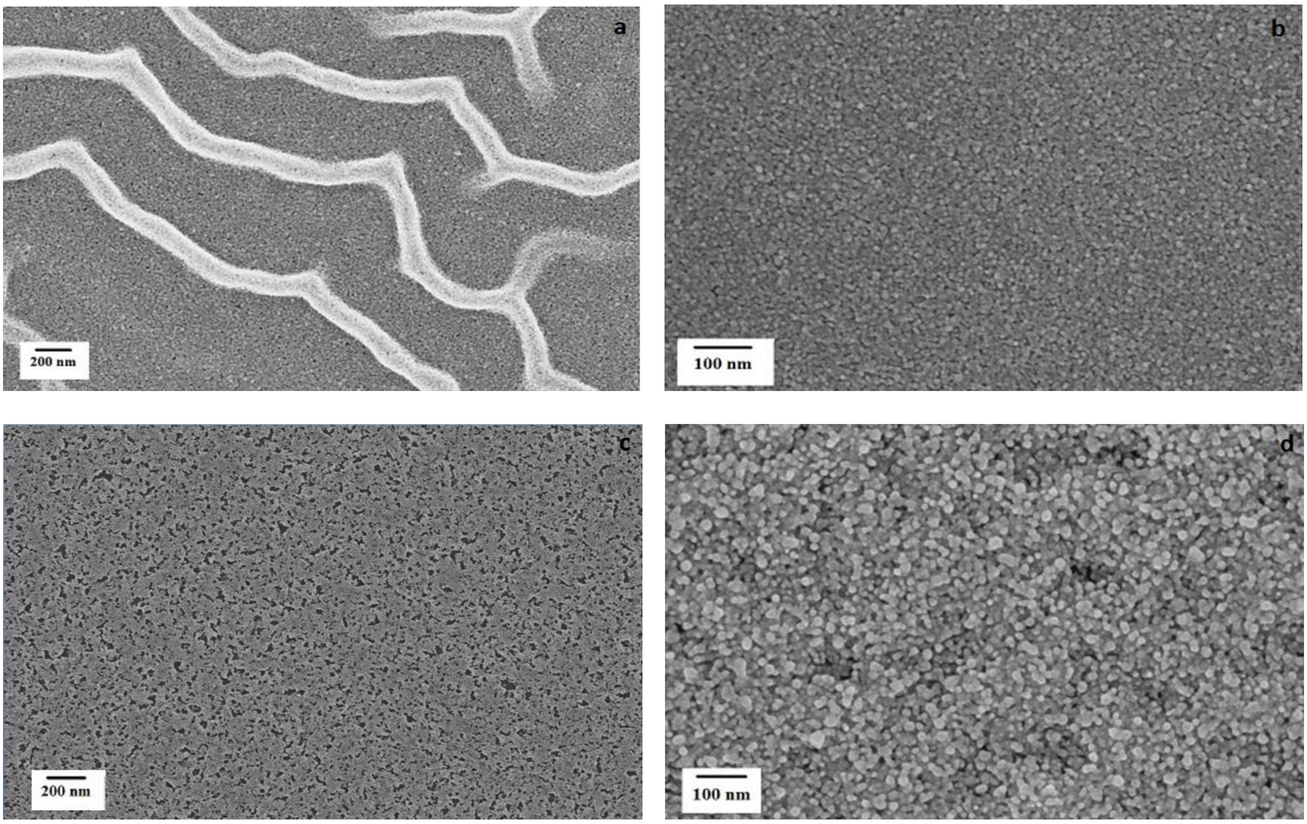

Fig.: Different morphologies of ZnO obtained as thin films with different combinations of solvents(a) DMF and THF mixture solvent at a weight fraction of 39 : 61, (b) pure DMF solvent, (c) DMF and THF mixture with a weight fraction of 10 : 90, (d) DMF and THF mixture with a weight fraction of 30 : 70

The influence of processing additives on the morphology of bulk heterojunction films in organic photovoltaics

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In order to solve the urgent energy problems in the world, various sustainable and renewable energy sources are taken into account in the last decades. As a freely available energy source, solar energy has attracted extensive attentions in different application areas, including solar heating, solar thermal electricity, and solar photovoltaics. In our work, we focus on solar photovoltaics, which convert sunlight into electricity by solar cells. Currently, silicon solar cells are the main product in the solar cell market due to high power conversion efficiency. However, silicon panels have a high price, heavy weight and high cost of energy in production. Therefore, it is desirable to find alternatives to silicon solar cells. Hence, organic solar cells consisting of thin polymer films generate great interest. Compared to standard inorganic solar cells, there are plenty of advantages for these novel systems, such as light weight, easy processibility and low production costs, which make them possible potential alternatives to traditional silicon solar cells.

One key point to bring organic solar cells to the market is to understand how to systematically improve the power conversion efficiency. As is well known, the organic solar cell has donor material and accepter material. The phase separation of the donor and accepter in the film plays an important role in organic solar cells.[1,2] As recorded in literature, interpenetrating phase-separated donor and accepter network in bulk film, called bulk heterojunction (BHJ) film, shows the best efficiency. Thermal annealing or solvent annealing can optimize the morphology of BHJ films. Recently, it has also been observed that by incorporating a few volume percent of alkanedithiols in the solution of BHJs, the power conversion efficiency of photovoltaic cells can be increased a lot. Alkanedithiols selectively dissolve [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM), but the semiconducting polymer poly(3-hexylthiophene) (P3HT) is not soluble. Because of the different selectivity, the morphology of BHJ films can be tuned, which leads to the improvement of the power conversion efficiency of organic solar cells. However, to our knowledge, the fundamental understanding of the morphology inside of BHJ film tuned by alkanedithiols is still unclear.

In this work, in order to modify the morphology, the solvent additive of 1,8-octanedithiol is applied in the blend system rrP3HT/C_{61}-PCBM. Morphology and optical property are compared between the blend system of rrP3HT/C_{61}-PCBM with and without 1,8-octanedithiol. The surface morphology is probed with optical microscopy (Figure1. a1 and b1) and atomic force microscopy (Figure1. a2 and b2). It is found that the P3HT/PCBM film with 1,8-octanedithiol shows phase separation on larger length scales, which is beneficial to charge transport in organic photovoltaics. In addition, the effect on molecular level is investigated by absorption spectra (Figure1. a3 and b3). It is observed that the order of P3HT molecular in the P3HT/PCBM film with 1,8-octanedithiol is improved as compared to the one without 1,8-octanedithiol, which indicates an increased crystallinity of P3HT. Finally, the internal structure is investigated with grazing incidence small angle neutron scattering (GISANS) in time-of flight (TOF) mode, as shown in Figure 1. a4 and b4. An almost identical inner structure size is found in the P3HT/PCBM with 1,8-octanedithiol.

It hence results that when adding 1,8-octanedithiol to the solution of BHJs, more ordered structures of P3HT and more homogenous structures in vertical direction of the P3HT/PCBM film are observed.

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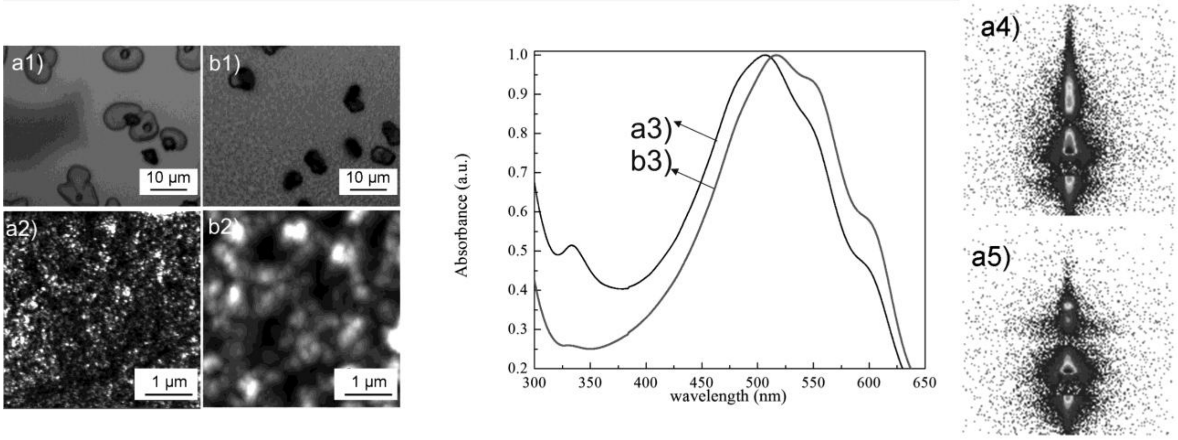

Figure 1: OM image a1), AFM image a2), UV-vis curve a3) and 2D GISANS pattern a4) of P3HT/PCBM without 1,8-octanedithiol, and OM image b1), AFM image b2), UV-vis curve b3) and 2D GISANS pattern b4) of P3HT/PCBM with 1,8-octanedithiol.

Sodium metal halide batteries investigated by neutron methods

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Sodium metal halide batteries offer several advantages for battery applications, such as high energy density, long cycle life and tolerance to short circuits in combination with low cost and easy recyclability of the battery materials. Today, the so called ZEBRA batteries are used in heavy duty transportation and stationary back-up power.

ZEBRA batteries contain plain rock salt and metal (Ni, Fe) as electrode materials and ß''-alumina as separator, which is conductive for Na^+ ions, but an insulator for electrons. The operation temperature of this type of batteries lies between 270-350°C. During charge, NaCl is consumed to form MCl_2 and Na^+ ions, that travel through the ß''-alumina separator and are reduced to sodium metal, while during discharge the reverse process takes place. For M = Fe, an additional intermediate Na_6FeCl_8 phase has been reported to exist [1]. Also, it seems that the reaction progresses from the inner surface of the ß''-alumina separator towards the cathode current collector in the center of the cell [1]. However, not only the size of Zebra batteries but also their steel casing and the elevated operation temperature make it difficult, if not impossible to directly study these processes by conventional methods. In fact, usually a Zebra battery cell has to be cut open to understand what has taken place inside the battery during operation. This is not only destructive and time-consuming - the materials and their morphology can also be altered during cutting and their exposure to air and moisture.

Neutron diffraction, with its unique penetrating power makes it possible to study the electrochemical processes within a battery cell in-situ and non-destructively. We used the diffractometer STRESS-SPEC at FRM II to study the phase distribution in Ni and Fe based ZEBRA batteries by spatially resolved neutron diffraction under operating conditions at 280°C. During cycling, diffraction data was recorded at three different measurement positions within the cell. This allows us to follow the progress of the reaction in the sodium metal halide battery spatially and time resolved and to gain information on the kinetics of the electrochemical reaction.

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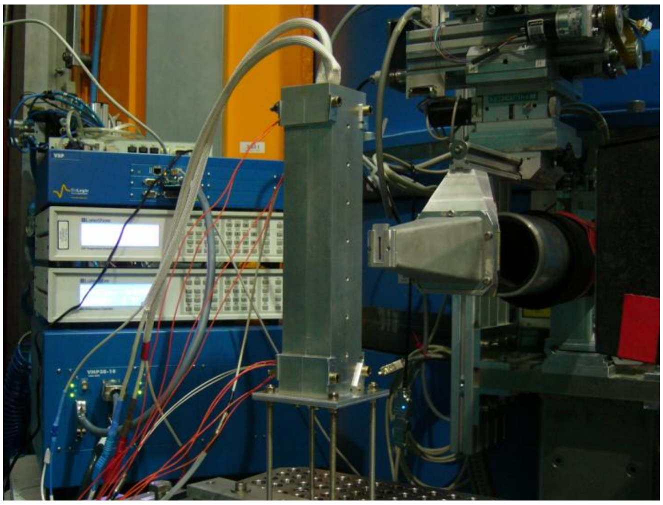

In situ experiment on a Zebra cell at the diffractometer StressSpec at FRM II.

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CPG Center for Power Generation

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