ADEM is both a research and an investment program. ADEM Innovation Lab strengthens the Dutch knowledge economy with joint expertise and an open and shared research infrastructure. The program aims to materialize innovations in energy technologies in close collaboration with industry. This will bring new, high quality jobs and improved competitiveness in green technologies.

The energy themes in which this is taking place are wind energy, solar energy, electricity storage (among others for electrical transportation), transport and storage of heat, catalytic processes for biofuels, and fuel cells. Moreover, ADEM is a Green Deal, and apart from promoting the transition to renewable energy conversion, the program also stimulates the use of environmentally and biologically benign materials and the reduction of harmful waste products.

We are continuously tuning our program to the industrial needs around us, complementing the TKI sectorial activities and contributing to the societal needs as stipulated in the Energy Agreement (‘Energieakkoord’) of September 6, 2013.

We have shown that ADEM has significant financial support from industrial partners and that there is also a clear demand from the companies for research on specific materials issues. This also means that we have fulfilled a very crucial boundary condition imposed on the ADEM program and we received in 2013 the formal approval of the Ministry of Economic Affairs to continue our program into the next phase.

In June 2013, an ADEM Program Board has been installed to advise the ADEM Steering Committee on the main direction of the program with a view to the needs of the industry, to make the ADEM program optimally demand driven. The members of the Program Board are listed at the end of this report.

In 2013 the ADEM program has been expanded and modernized, with updated Theme programs for the period 2013 through 2017. The ADEM Program Board has carefully evaluated the research and investment project proposals. As a result in total 15 new PhD projects have been approved (research starting in 2014) as well as 2.8 M€ for investments in new facilities, among which are a solid state NMR (500-600 GHz) at Delft University of Technology and a high throughput ion implanter at ECN. The full list of research projects to be started and acquisitions to be done is listed at the end of this annual report.

We have set up a web based platform that facilitates and promotes the mutual usage of our advanced experimental infrastructure (ADEM Shared Innovation Lab) and we have launched a web based library (ADEM Publication Portal) for all scientific output (publications, presentation slides, posters, etc.) of ADEM research. We hope to make the Facility Sharing site completely functional in the first half of 2014 as well as to present a large number of high quality publications on the Publication Portal.

We have refreshed the team of Theme Coordinators to include Stephen Picken, resuming his role as theme coordinator of Fuel Cells after having been replaced by Eduardo Mendes, and Rinze Benedictus as theme coordinator for Wind, succeeding Adriaan Beukers, who has retired. A major part of the Theme Batteries (electrical storage) has been transferred from Eindhoven University of Technology to Delft University of Technology and is now in a position to make a strong start under the theme coordinatorship of Erik Kelder.
The 2nd ADEM Conference in April 2013 in Ermelo was organized around the objective to create value from (fundamental) research, with keynote speakers such as Angus Kingon, specialist in the organization of entrepreneurship, and Sybrand van der Zwaag, on the ADEM-overarching subject of self-healing materials. At this conference, the ADEM PhD committee was installed, to help with ideas for stimulating the joint utilization of ADEM facilities and for improving the visibility of the program as a whole.

A highlight of 2013 is of course the graduation of the very first ADEM PhD researcher, Vera Popovich, who graduated on Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar Cells at Delft University of Technology (December 16, 2013). Her graduation marks the start of the upcoming long sequence of promising degrees in the field of materials research for energy conversion, transport and storage.

In 2014, the ADEM program will reach full force, with a peak level of filled PhD positions and with an investment program rapidly reaching complete fulfillment. The present annual report shows the scientific progress of our talented researchers and highlights their collaboration with industries, towards industrial innovations for a sustainable energy economy. We recommend that you also keep an eye on www.adem-innovationlab.nl where we present the latest news and show our recent progress.

Prof. dr. Ruud Schropp, ECN, ADEM Scientific Director
June 5, 2014
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Transport, Transfer and Storage of Heat

Within the broad theme of Heat, it was decided to group the ADEM activities around materials for compact heat storage and compact heat engines. Limiting the focus to two system components, which have resembling processes and deploy similar techniques (synthesis of sorption materials, molecular analysis and TGA-DSC measurements) strongly enhances the coherence within the theme.

ADEM Projects
In this theme, materials are examined both in an experimental and numerical manner. At TU Delft, for example, experiments have been conducted and Monte Carlo and Molecular Dynamics simulations have been carried out on the absorption and diffusion of both water and methanol in porous Metal-Organic Frameworks. At University Twente, heat transfer experiments are conducted on surfaces that are covered with Carbon Nano Fibres. Finally, at ECN and at TU Eindhoven, experiments and simulations are conducted on Thermo-Chemical Heat Storage Materials. Particular attention is paid to changes in the material structure resulting from hydration and dehydration reactions.

The ongoing research is actively communicated at conferences and workshops. Moreover, research leaders are participating in NanoNextNL (TU Delft), IEA-SHC Task 42 and KIC InnoEnergy (TU Eindhoven) and a successful proposal for additional research on heat storage with sugar-alcohols has been submitted by TU Eindhoven in the EU FP7 program.

Industrial Involvement
Collaboration with industry exists in related research projects for thermo-acoustic and thermo-chemical heat pumps in paper industry at ECN (supported by SmurfitKappa/IBK/Bronswerk), improvement of regenerators in Stirling engines at University Twente (supported by Nefit) and applications for heat storage at ESSENT/TATA Steel at TU Eindhoven.

Theme Coordinators
Prof.dr.ir. Theo van der Meer
University of Twente
Prof.dr.ir. Anton van Steenhoven
TU Eindhoven
Introduction

Thermochemical heat storage enables loss-free storage of heat, with an energy density that is 5-10 times the energy storage density of water. The largest potential for thermochemical heat storage is seen in seasonal storage of solar heat for domestic applications. The development of seasonal heat storage based on this technology would make individual systems possible (instead of a district system). Therefore, a much higher share of solar heating becomes possible, increasing the market for solar collector systems and also creating a large market for thermochemical heat storage systems. Water vapour sorption in salt hydrates is one of the most promising means for thermochemical seasonal heat storage. In summer, the salt hydrate is dehydrated using solar heat provided by solar tube collectors which can reach temperatures until 150°C. In winter the dehydrated salt can be hydrated again to release the stored solar energy and provide temperatures that are sufficiently high for space heating (30°C) and tap water heating (60°C). In operating conditions of the storage system, the hydration process takes place at a low water vapour pressure of 13 mbar, provided by saturation of the ambient air with the water from a local borehole found at the temperature of 10°C during winter figure 1.

Figure 1: Representation of the thermochemical seasonal heat storage system based on the water vapour sorption process in salt hydrates, integrated into an individual house.

In order to develop adequate sorption materials for this application, this project focusses on establishing the effect of the operating conditions of the system (temperature, vapour pressure) and of the structural and material properties on the heat- and vapour transport during the sorption process. Within this line of research, an experimental material characterization has been carried out at different scales of the material (crystal, grain and powder bed) to identify the influence of these system and material properties. First, the study was carried out on model salts Li₂SO₄·H₂O and
CuSO\textsubscript{4}.5H\textsubscript{2}O which present simple and well established water vapour sorption processes, in order to identify a suitable methodology of research and relevant material characterization techniques under the practical conditions of the seasonal heat storage. Next, these experiments have been extended to other salt hydrate materials ((MgSO\textsubscript{4}.7H\textsubscript{2}O, MgCl\textsubscript{2}.6H\textsubscript{2}O, CaCl\textsubscript{2}.2H\textsubscript{2}O), selected at ECN for their more promising performances as thermochemical materials for the seasonal heat storage application in the residential sector.

**Research results from 1 January until 31 December 2013**

In the previous years of this ADEM project, issues related to slow kinetics and material stability were identified for respectively the sulphate and chloride materials, reducing their performance for long-term heat storage. Improvements of the material properties and system conditions are required to develop a suitable salt hydrate material for a packed bed sorption system. Therefore, the effect of adjusting the operating conditions and changing the material properties by means of chemical mixtures was investigated on the micro-scale by thermal analysis. Subsequently, lab-scale reactor tests figure 2 were carried out to estimate their performance for long term heat storage in a packed bed system.

A kinetic study of the dehydration of the sulphate materials (Li, Cu and Mg) showed an abnormal behaviour of the speed of the thermochemical reactions in function of the operating conditions (temperature, water vapour pressure) applied in the system. This effect, the so-called Topley-Smith effect, shows an optimum in the reaction speed that is different for each material, depending of the material structure reorganization during the process. For MgSO\textsubscript{4}.7H\textsubscript{2}O, identified as the most promising sulphate material for the heat storage application, optimal kinetics were identified for a water vapour pressure of 50 mbar. Under these operating conditions, an up-scaled lab scale reactor showed suitable temperature lift for domestic application (\(\Delta T=18^\circ\text{C}\) for \(T_{\text{inlet}}=50^\circ\text{C}\)) during the heat discharge of the material. However, a too low effective energy density (0.148 GJ/m\(^3\)) was still found due to the slow kinetics displayed by this material figure 3.

For the chloride materials, the focus was on MgCl\textsubscript{2}.6H\textsubscript{2}O, which showed a promising performance during the micro-scale characterization and the up-scaling in a lab-scale packed bed reactor. The material presented sufficient heat release (0.83 GJ/m\(^3\)) and temperature lift (\(\Delta T=12^\circ\text{C}\) for \(T_{\text{inlet}}=50^\circ\text{C}\)) after one cycle of reaction under the expected operating conditions for seasonal heat storage. However, endurance tests on the material showed a reduction of the effective storage density of about 40% after already five succeeding thermal cycles. This phenomenon is caused by material instability issues (overhydration, hydrolysis) present in this material under the operating
conditions in the open sorption system. To improve this, the material properties and operating conditions were modified. A micro scale investigation on modified MgCl₂ hydrates (physical and chemical salt mixtures of MgCl₂-CaCl₂) was carried out and an optimization of the packed bed structure (porosity, particle size) and system conditions (air flow velocity) was performed. However, these modifications did not prevent the material instability issues of MgCl₂·6H₂O. Additionally, a collaboration was established end of 2013, with Shuishan Lan, an ADEM PhD student from the Eindhoven University (TU/e), to characterize the kinetics of reaction of the salt hydrate materials identified by thermal analyses according to nucleation and growth models.

**Industrial collaboration until 31 December 2013**

The objective of the present research project is to obtain fundamental knowledge on the water vapour sorption process of the salt hydrate materials, needed to improve the reaction kinetics and the stability of thermochemical materials. The improvement of these two characteristics is essential to develop a thermochemical heat storage with sufficient durability, power density and energy density for commercial applications. No direct financial commitment on the PhD project has taken place until now. However, the fundamental knowledge on vapour transport and reaction kinetics obtained in the present PhD project is also relevant to other applications of thermochemical materials and several parallel projects at ECN applying thermochemical reactions for different purposes (in particular industrial heat pumping) have received substantial commercial financial contributions.

**All output from 2013**

1. Ferchaud C.J., Zondag H.A., de Boer R. (2013), Material research on salt hydrates for seasonal heat storage application in a residential environment. Conference Paper : Proceedings of the International Symposium on Innovative Materials for Processes in Energy Systems (IMPRES2013), September 4-6, 2013, Fukuoka, Japan, (IMPRES2013-073)

2. Ferchaud C.J., Scherpenborg R.A.A., Zondag H.A. and de Boer R. (2013). Thermochemical seasonal solar heat storage in salt hydrates for residential applications - Influence of the water vapour pressure on the desorption kinetics of MgSO₄·7H₂O. Conference Paper : Proceedings ISES Solar World Congress 2013, November 3-7, 2013, Cancun, Mexico.

**Other**

The end date of this ADEM project has been extended to 31 January 2015.
Introduction

Thermo-chemical materials have great potential to be used for compact, low loss and long term storage of solar heat in the built environment. An important class of materials consists of solid or powdery hydro-sorbents like salt-hydrates and zeolites. Their theoretical heat storage capacities can easily be 10 times higher compared to sensitive heat storage in water. However, up till now, the realized efficiencies are low and decreasing as function of time. For the purpose of the development of solid sorption materials, micro- and meso-scale models will be developed for the hydration and dehydration processes taking place in powdery samples. These processes are a combination of heat and vapor transport in the grains constituting the powdery sample, and in the voids between the grains of the powdery sample as shown in Figure 1.

Figure 1: Schematic illustrations of heat and mass transfer processes in grains and the powdery sample.

Research results from 1 January until 31 December 2013

Microscopy experiments:
The dehydration reaction of Li₂SO₄·H₂O monocrystals was investigated by in situ observations in terms of nucleation and nuclei growth processes. The nucleation and nuclei growth processes during the reaction were recorded photographically using a camera system. In order to measure the growth rate in-depth, measurements on encapsulated crystals were also carried out. Both results are shown in Figure 2. It is observed that the growth of nuclei on the surface has a preferential crystalline direction and the propagation of the reaction front in the crystal is visualized with a sharp interface between the hydrated phase and dehydrated phase.
Figure 2: Microscopic observations of surface nucleation (left column) and growth in the bulk of Li₂SO₄·H₂O crystals (right column).

Reaction-diffusion dynamics of Li₂SO₄·H₂O dehydration reaction
A dynamic model was developed for describing the dehydration reaction of Li₂SO₄·H₂O single crystals. It includes the intrinsic chemical reaction and mass diffusion simultaneously at a microscopic level. Both microscopy experiments and TG measurements were carried out to gain insight into the main phenomena that limit the reaction kinetics together with the numerical model. It is demonstrated that our model provides an effective tool to examine the dehydration reaction in a much more fundamental way. From Figure 3, it can be concluded that the dehydration reaction at 150°C is determined by mass diffusion, while at lower temperatures a transition of the mechanism from diffusion-limited to reaction-limited is observed.
Figure 3: Fractional conversion: experimental results in dashed lines and numerical results in solid lines; Total time = 487 min, 299 min and 200 min for T = 120°C, 130°C and 150°C, respectively.

Industrial Collaboration
None

All output from 2013

1. Conference paper: Lan, S., Zondag, H.A., Rindt, C.C.M. (2013). A kinetic model for the surface nucleation and isotropic growth processes on the grain scale. 2nd International Conference on Sustainable Energy Storage, June 19-21, Trinity College, Dublin, Ireland.
2. Conference paper: Lan, S., van Maris, M.P.F.H.L. Zondag, H.A., Rindt, C.C.M. (2014). In situ observation of the dehydration of Li₂SO₄·H₂O monocrystals. Eurotherm Seminar Nº99, May 28-30, Lleida, Spain.
3. Conference paper: Lan, S., Zondag, H.A., Rindt, C.C.M. (2014). Kinetic study of Li₂SO₄·H₂O dehydration using microscopy and modeling. Proceedings of the 15th International Heat Transfer Conference, August 10-15, Kyoto, Japan.
4. Poster presentation: Lan, S., Zondag, H.A., Rindt, C.C.M. (2013). Micro- and meso-scale models for thermo-chemical heat storage using salt hydrates. Burgersday at TUD (29.10.2013).
5. Poster presentation: Lan, S., Zondag, H.A., Rindt, C.C.M. (2014). Micro- and meso-scale models for thermo-chemical heat storage using salt hydrates, Solar Plus Event at TU/e (17.4.2014).
Project: TUD-P08
Designer Sorbents – Structured systems for heat pumps

Name PhD-candidate: M.F. de Lange

Affiliation: TU Delft, Catalysis Engineering (CE), Engineering Thermodynamics (ETh)
Start date: 1 Jan 2011

Project leader(s): Prof. F Kapteijn, Prof. T.J.H. Vlugt, Prof. Gascon, TU Delft

Introduction
Adsorption of water and methanol on porous materials holds relevance in numerous applications such as heat pumps. These devices use high temperature energy (e.g. solar or waste heat) to generate cooling (or air-conditioning) using ad- and desorption of water or methanol. As large quantities of energy are consumed for air-conditioning purposes, this technique has a high potential for significant energy savings. As current specific power (W kg⁻¹) and thermodynamic efficiency of adsorbent driven heat pumps and chillers are low, the market for commercial devices is small. If specific power were to increase considerably, these devices could become more competitive when compared to their conventional electricity-driven counterparts. This would increase commercial potential significantly, as nearly 40% of Dutch energy consumption is related to heat and cold allocation [1]. The aim of this project is to develop new adsorbents for thermally driven heat pumps and chillers to improve thermodynamic efficiency and mass and heat transfer characteristics. In particular, Metal-Organic Frameworks will be investigated for potential use in adsorption heat pumps. These materials offer a wide range of pore sizes that may result in enhanced transport and high adsorption capacity, essential for applications in heat and cold allocation. The search for improved adsorbents is based on experimental work and molecular simulations (Monte Carlo and Molecular Dynamics).

References
[1] Agentschap NL, Warmte in Nederland, 2010, publ. nr. 2NECW1003

Research results from 1 January until 31 December 2013
The adsorption of Nitrogen at 77 K is one of the main and most commonly used tools to characterize porous adsorbents. From these adsorption measurements, predominantly measured using volumetric adsorption equipment, information on total pore volume, pore size distribution (BJH-method) and specific surface area (BET-method) can be derived. Despite the fact that the different theories to derive these quantities have been around for more than half a century, we observed that many researchers erroneously use these methods, creating misleading or even plainly wrong information on the porous sorbents under investigation. We thus conducted a very laborious and detailed study based on error propagation analysis to assess the uncertainties in the actual N₂ adsorption measurements and in subsequently calculated properties. This study yielded an extensive list of guidelines improve measurement accuracy and to avoid obtaining erroneous or statistically insignificant results. The full manuscript (including detailed appendices a staggering 150 pages long) was submitted to Microporous and Mesoporous Materials in January 2014, from which we would like to mention some of the relevant conclusions:

- The relative uncertainty in measured adsorption isotherm and in pore volume is lowest when the $V_{manifold}/V_{cell}$ ratio is between 2 and 3.
- A simple two-point BET method is proposed to determine a priori the upper relative pressure boundary of the BET window (close to saturation), as alternative to the method reported by Rouquerol et al.
For the lower relative pressure limit determination it is suggested to analyse Studentized residuals. Provided the model isotherm is correct, data points become eligible for possible exclusion when $|\text{resis}| > 2-3$.

The magnitude of the 95% confidence interval found for BJH-pore size distributions severely impedes drawing quantitative conclusions.

Several Al-based MOFs of the CAU family have been investigated for application in adsorption driven allocation of heat and cold, as shown in figure 1.

![Figure 1: H$_2$O adsorption isotherms at 298 K of CAU-1 (■), CAU-1-(OH)$_2$ (●), CAU-8 (▲), CAU-10-H (▼), CAU-10-NH$_2$ (◆) and CAU-10-OH (▲).](image)

Among the investigated MOFs, CAU-10-H has shown to have ideal adsorptive properties. For increased performance, CAU-10-H crystals have been grown directly on both γ-alumina and metallic aluminium.

![Figure 2: SEM images of CAU-10-H synthesized on γ-alumina beads without any acid (a), with addition of acetic acid (b) and with addition of hydrochloric acid (c,d).](image)

This growth of CAU-10-H crystals directly on γ-alumina supports was achieved by using aluminium ions from the substrate as metal source for the MOF. Addition of acids improves the growth of these crystals. Especially hydrochloric acid has a beneficial effect on surface coverage and homogeneity of the formed crystal size and shape. The same approach has been successfully applied to coat CAU-10-H directly on metallic aluminium, which is highly desired for the target application. Again HCl has a beneficial effect on crystal growth. The adsorptive properties of CAU-10-H are similar to that of the bulk material and the coating showed to be stable in at least 5 water adsorption-desorption cycles figure 3.
Figure 3: Repeated H₂O adsorption isotherms at 298 K of CAU-10 supported on a metallic aluminium plate. First (■), second (●), third (▲), fourth (▼) and fifth (◆) measurement. Closed symbols depict adsorption, open desorption. Loading presented per total mass of sample (Al substrate + CAU-10-H). These highly interesting results have been submitted to CrystEngComm in early 2014.

Industrial collaboration until 31 December 2013

There is an ongoing discussion of results with heat pumps experts at ECN. Here scientific outcomes are compared to the current state-of-art in industry.

All output from 2013

1. Adsorption of highly polar vapors on mesoporous MIL-100 and -101: Experiments and molecular simulations, M. F. De Lange, J. J. Gutierrez-Sevillano, S. Hamad, J. Gascon, T. J. H. Vlugt, S. Calero, F. Kapteijn, 17th International Zeolite Conference, Moscow, Russia, 7-12 July, poster presentation
2. De Lange, M. F.; Gutierrez-Sevillano, J.-J.; Hamad, S.; Vlugt, T. J. H.; Calero, S.; Gascon, J.; Kapteijn, F. J Phys Chem C 2013, 117, 7613.
3. M. F. De Lange, J. J. Gutierrez-Sevillano, S. Hamad, J. Gascon, T.J.H. Vlugt, S. Calero, F. Kapteijn, Understanding adsorption of highly polar vapors on mesoporous MOFs, 16th and final Workshop of the International Research Training Group "Diffusion in Porous Materials", Delft, 2-4 April, oral presentation
Introduction

The advancement of high performance thermal systems has stimulated interest in methods to improve heat transfer rates. Considerable efforts have been made to increase heat transfer rates by implementing passive convective heat transfer enhancement methods that require no direct consumption of external power. This is mainly achieved by modifying heat exchanging surfaces which either play a role in disrupting the flow field without increasing surface area (effect of surface roughness) or by increasing surface area and in some cases even both. As a result, surface covered with layer of carbon nanofibers (CNFs) results in high surface area, rough surface morphology and extremely high thermal conductivity which makes it ideal candidate for enhancing heat transfer. These properties of CNFs results in a substantial improvement of the exchange of heat between the surface and the surrounding fluid flow. The aim of the project is to study in depth the effect of carbon nano-fibers deposited on heat transfer surfaces in minimizing exergy losses in heat exchangers. For instance, in thermo-acoustic and thermo-chemical heat pumps which have a large influence on their final application.

Research results from 1 January until 31 December 2013

1 CNFs synthesis

Figure 1 SEM image illustration of carbon layer and CNFs layer on a Ni micro wire. (a) CNF bundles rooted with a-C layer, (b) a-C layer with visible nickel nano-particles, (c) visible surface cracks on a C layer leading to CNFs growth and (d) CNFs layer eruption from underneath the a-C layer.
A controlled growing procedure was successfully achieved in growing both CNFs and a-C layers fig. 1-a and 1-b. During the synthesis process, the a-C layer growth commences earlier than the CNFs layer. The first 10min of the synthesis process, the a-C layer is predominantly produced on the surface of the nickel grains. As the amount of carbon deposition increases, the fragmentation of the nickel grains leads to the growth of the CNFs underneath the a-C layer. The internal mechanical stress, which builds up by the growing CNFs underneath the a-C layer, results in surface cracks the a-C surface see fig. 1-c which leads to eruption of the CNFs layer, see fig. 1-d. The a-C layer anchors the CNFs layer produced hence increases its mechanical stability of the samples to forced flow conditions. However, little growth of CNFs can be seen from the nickel nanoparticles floating on the a-C layer, fig. 1-b.

2 Surface characterization

Depending on the synthesis time, three different CNFs samples are synthesized to analyse the influence of different structural morphology on heat transfer performance. In order to relate the influence of the surface to the heat transfer behaviour of each individual sample, it is important to quantify and characterize the surface of the synthesized samples. It has been previously described that the samples produced are made up of both CNFs layer and a-C layer. These samples exhibit different surface characteristics such as average thickness of the layer of CNFs and a-C, surface roughness intensity, surface area and area coverage of the layer of CNFs. Surface characterization and evaluation of three different samples, which are synthesized at 16min, 23min, and 30min (referred as CNF-16, CNF-23 and CNF-30 respectively), which helps in relating their heat transfer performance to the structural arrangement of the nanofibers.

Using confocal microscopy, samples are scanned point by point from a selected depth (optical sectioning) and a 3D topology of the CNFs sample is reconstructed using the data with the inbuilt computer program (VK analyzer), see fig. 2. All measured surface characteristics of the samples increase with increasing deposition time. Though equal interval of synthesis periods (7min difference) is made during the synthesis, measurement results shows that CNF-23 has a surface roughness on average 4.5% higher than CNF-16, while CNF-30 is on average 25.3% rougher than CNF-23. Moreover, surface area ratios were determined by dividing the surface area of the 3D surface plot to the projected area. The difference of ratios of the surface area between CNF-30 and...
CNF-23 is almost 3 times larger compared to difference between CNF-23 and CNF-16. This is attributed to the faster growth of the CNFs layer after erupting from the a-C layer. Even though, a-C layer deposition commences earlier than the CNFs layer, the deposition rate of CNFs layer is much faster than the a-C layer. Result shows that the deposition of the a-C layer is increased by 11.6% and 28% for sample ‘CNF-23’ and ‘CNF-30’ respectively. The ratio of CNFs layer to a-C layer on average is 2.24, 6.58 and 6.98 for sample “CNF-16’, ‘CNF-23’ and ‘CNF-30’ respectively. In addition, the area coverage of the CNFs layer is increased with increasing synthesis period.

### 3 Heat transfer results

![Heat transfer results graph](image)

**Figure 3** Heat transfer enhancement result obtained for sample produced at 650˚C for a duration of 16 min, 23 min and 30 min.

Figure 3 shows heat transfer characteristics and performance of the different sample tests. Heat transfer enhancement of 12% and 18% was achieved for samples produced for 16 min and 23 min respectively. This enhancement is mainly attributed to the surface roughness and surface area increase of the samples with moderate CNFs surface area coverage compared to the bare samples. However, flow penetration through the porous layer of the CNFs layer is difficult to anticipate due to very dense nature of the layer. Even though CNF-30 exhibits both the highest surface roughness and the highest surface area, there is no significant heat transfer enhancement obtained. It is anticipated that the increase of area coverage of the CNFs layer creates a highly porous impermeable layer which trapped air pockets; hence, insulating the heated surface. However, apart from the indirect involvement of the a-C layer in creating a mechanically stable layer of CNFs and hindering the fast growing CNFs which create a rough surface morphology, future work needs to be done on the direct involvement on the a-C layer on heat transfer performance.

**Industrial collaboration until 31 December 2013**

This project has a strong link to the thermo-acoustic project in the laboratory of thermal engineering at the University of Twente which is funded by Nefti/Bosch. A PhD student is investigating a heat engine which makes use of a thermodynamic cycle similar to Stirling, but with less moving parts, therefore having a much higher reliability. Thus, the student focuses on the optimization of the novel engine generator for application within a micro-CHP appliance. The last step in this ADEM project is to apply the CNF’s on a regenerator for the thermo-acoustic engine. We will use the experimental facilities of the thermo-acoustic project.
All output from 2013

1. T.J. Taha and T.H. van der Meer, “Influence of CNFs layer morphology on convective heat transfer behavior”, 8th World Conference on Experimental Heat Transfer, Fluid Mechanics, and Thermodynamics June 16-20, 2013, Lisbon, Portugal

2. T.J. Taha, L. Lefferts and T.H. van der Meer, “Convective heat transfer enhancement using Carbon nanofibers (CNFs): influence of amorphous carbon layer on heat transfer performance”, Proceedings of the ASME 2013 4th Micro/Nanoscale Heat & Mass Transfer International Conference MNHMT2013 December 11-14, 2013, Hong Kong, China

3. T.J. Taha, L. Lefferts and T.H. van der Meer, “Experimental study of convective heat transfer enhancement using extended layer of carbon nanofibers”, ASME Journal of heat transfer, submitted.
Wind Energy

This annual report 2013 of the ADEM theme Wind Energy presents the state of the art of the initiated R&D projects. The last couple of years the Wind Energy Industry has been hit hard due to the crisis and as well as due to global energy policy changes. The prospects for the coming years will be more flourishing according to various market studies. However, the competitiveness of the various companies have increased and subsequently the performance of their turbines. Cost of Energy is a main design driver for wind turbines and its components like blades. It is becoming more and more challenging to improve the design of the blades to obtain a competitive cost of energy. A strategy to meet this challenge is to create a thorough and profound understanding of the behaviour of composite materials in order to create a weight efficient design. The full glass fibre design of the current 70+ m blades by Senvion and LM illustrates what still can be obtained with a full glass blade without the need to switch to carbon.

ADEM projects

The current ADEM projects “Thick laminates” and “Integral Material Models for Composites” meet this strategy very well. The fundamental questions dealt with in these projects, such as thick laminates static allowable and fatigue life prediction, design rules, scaling effect on laminates, 3D-effects in blade thick subcomponents testing, self-heating in fatigue loading or the manufacturing process influence on the final laminate properties, are contributing to the needed profound knowledge.

Another key topic in the wind industry is cycle time reduction. A characteristic of wind turbine rotor blade manufacturing is the high numbers of blades which need to be produced in the relative short production life of the blade, approximately 3 years. One of today’s business strategies is to build in a time-frame of 3 years at least 1.000 sets (3.000 blades) of rotor blades of the same type. In practice this means that there is a need for 6 production lines. The aim is to find a way to de-mould one rotor blade every 12 hours with a stable and controlled process and thus reduce the required investment with 50%. A way to obtain this is through reducing the process time and curing time. This is directly related to the choice of blade materials, i.e. fibres / fabrics, resin, core material and adhesives, which also need to have acceptable mechanical properties. A reduction of the cycle time from 24 to 12 h has a huge impact on the manufacturing costs of the blades.

The need for faster composite processing is a general need for various industries, especially the automotive industry who are - due to the ever more stringent fuel consumption and CO2 emission requirements - highly interested in composites. This incentive resulted in various material suppliers developing faster curing resins and adhesives. Even 5 min curing RTM thermoset resins are being developed for the automotive industry. Unfortunately, due to the distinct nature of the composite rotor blades (large size, low cost level, ..) developments in e.g. automotive are not easily or not at all transferable.

Industrial Involvement and plans

Currently, a consortium is being formed to prepare the ADEM Wind Energy theme for future material development activities. The strategy is to create a substantial participation of wind industry and wind industry related suppliers in the ADEM Wind projects and to focus on the future challenges in blade design.

Theme coordinators:
Dr.ir. Harald Bersee,
Delft University of Technology
Prof.dr. Rinze Benedictus.
Introduction
On account of the increasing presence of thick laminates in the main parts of the present and future wind turbine blades and the increasing use of thick laminates in various industries, a more comprehensive study on thick laminates behaviour, testing, design and properties is required in comparison with standard thin laminates.

The aim of the project is to identify and quantify effects of large laminate thicknesses. Questions such as thick laminates static allowable and fatigue life prediction, design rules, scaling effect on laminates, 3D-effects in blade thick subcomponents testing, self-heating in fatigue loading or the manufacturing process influence on the final laminate properties, are a matter of interest for this work.

The focus of the current work is on:
1. the manufacturing process influence on thick laminates’ mechanical properties
2. the 3D, scaling effects and design parameters influence on thick laminates testing coupons and subcomponents
3. self-heating in thick laminates and its influence on static, dynamic and fatigue mechanical properties
4. the energy loss factor as an energy dissipation indicator

Research results from 1 January until 31 December 2013
The approach followed in the present work is to identify the main factors involved in the thickness effect, and to evaluate each factor’s contribution to the thickness effect independently. The factors considered in the present work are:

Energy loss factor. In order to understand the role of the loss factor in fatigue loading, crack progression, an extended fundamental research into the effect of these parameters is on-going. For this purpose a video tool to automatically determine the crack length in double cantilever beam (DCB) tests was developed.

Self-heating effect during dynamic loading. This was related with the material energy loss factor. During dynamic loading a certain rate of mechanical energy is dissipated into heat, leading to a rise of the material temperature. When the material temperatures approaches the maximum service temperature a fatigue life reduction can be observed.

The manufacturing process influence. Through-thickness lamina properties study is on-going. Different curing cycles were applied in order to observe the effect of the temperature gradient through the thickness (see Figure 4).
The scaling effect and the coupon geometry influence. The scaling effect was studied for compression coupons via FEM with cohesive elements and fracture mechanics, in order to minimize the scaling effect during thick laminates coupon testing. Thick laminates fatigue life prediction in comparison with thin laminates coupons was studied in scaled compression tests up to 20 mm thick. A parametric FEM analysis with cohesive elements was performed in order to engineer scaled compression coupons showing that as the thickness increases, a stress gradient appears through the thickness Figure 5.

Figure 4: Curing gradient temperature thought the thickness for a 60 mm thick laminate

Figure 5: Stress profile and damage index in axial direction for cohesive and non-cohesive models.

Figure 6: Scaled compression coupons of 4, 10 and 20mm thick tested in static and fatigue.

Static tests of scaled compression coupon for 4, 10 and 20 mm were performed Figure 6, showing no thickness effect in the ultimate strength. In addition Poisson ratios in direction 12 and 13 were measured showing comparable values. Stress gradients through-the-thickness as predicted by FEM models were observed in the tests. While the scaled geometries did not show a reduction of the ultimate strength due to the thickness, they showed a decrease in fatigue life S-N curves slopes with the thickness Figure 7. Further scaled coupons with higher thicknesses need to be tested in fatigue to confirm this trend.
Industrial collaboration until 31 December 2013

A video tool to automatically determine the crack length in double cantilever beam (DCB) tests was developed, and is actively used in WMC for both funded and contract research. The methodology to calculate self-heating of laminates under dynamic loading was applied to a rotor blade of a tidal turbine to find the maximum allowable frequency at which tests could be run without a substantial influence of temperature on the tests.

All output from 2013

1. F. Lahuerta, T. Westphal, R. P. L. Nijssen, F. P. van der Meer, and L. J. J. Sluys, “Measuring the delamination length in static and fatigue mode I tests using video image processing,” Compos. Part B Eng., vol. 63, pp. 1–7, Jul. 2014.
2. F. Lahuerta, T. Westphal, R. P. L. Nijssen, F. P. van der Meer, and L. J. Sluys, “Static and fatigue performance of thick laminates test design and experimental compression results,” in ECCM-16TH European conference on composite materials, Seville, 2014, pp. 1–9.
Introduction

The design of an economical large wind turbine requires an efficient rotor. With the increase in wind turbine size this becomes an ever larger challenge. When increasing the rotor diameter, the energy output increases with the square of the diameter, while the blade mass increases with the cube of the diameter. Moreover, at high blade lengths the gravity loads due to the blade mass itself become a dominant factor, and these scale to the fourth power of the rotor diameter. An increase in rotor weight also results in higher loads on all other structural parts of the turbine, and thus increase in cost. Therefore, detailed knowledge of the properties of rotor blade composites is required for optimal material use in the rotor and thus an economical design.

The design of a wind turbine rotor blade is based on strength and fatigue data obtained from experiments. For design, safety and reduction factors are applied to these data to account for effects such as scatter, temperature, aging, laminate quality, manufacturing method, curing etc., while other effects are not specifically accounted for, such as laminate thickness and moisture. For fatigue analysis empirical models based on models for metals are used, which often do not describe composite behaviour well. Furthermore only the variability of the load is accounted for, variability of other influence factors are not considered. This unsatisfactory approach leads to suboptimal designs that are for a large part overly conservative but still experience unexpected failures.

The goal of this project is to develop an integral material model for composites that incorporates the effect of the most significant influences into a model for strength and life prediction. This will ultimately allow for more optimal use of material while improving reliability, allowing for lighter and more cost effective rotors.

Research results from 1 January until 31 December 2013

Next to the cyclic load one of the most important aspects to consider in the fatigue life of composites is the effect of load ratio. This dependence on load ratio is typically presented in a Constant Life Diagram (CLD) which describes the fatigue life for a given mean and cyclic stress. Early in the project different existing formulations for the CLD were evaluated for their potential to describe the Constant Amplitude (CA) behaviour. Next, fatigue life predictions under Variable Amplitude (VA) loading were evaluated against an experimental campaign in which the VA fatigue experiments were performed for three different wind turbine load spectra. It was found that the models that provide the best fit to the CA fatigue dataset also result in the best predictions of fatigue life under VA loading.

Drawback of the best performing CLD models is that they rely on a large number of parameters (>8) and therefore require the large amount of experimental fatigue data to fit the parameters. Given the large effort involved in fatigue testing this limits their use.
One of the research topics in 2013 was the development of new formulations which are able to describe the CA fatigue behaviour of composites with less parameters. Alternative descriptive variables to describe the ratio of mean stress and amplitude stress Figure 8 open up possibilities to develop models with less parameters. Based on this new formulations are developed of which the general applicability will have to be validated against different datasets.

Another topic was the scatter in fatigue life of composites. Based on micromechanical modelling of composites, using the fatigue properties of bare fibres as input, the very high scatter in fatigue life of fibres could be related to the scatter found in composites. As for fatigue life, also the scatter is highly dependent on the load ratio applied. E.g. the scatter in compression fatigue is typically much higher than in tension fatigue experiments. It was found however that if the scatter is evaluated in terms of fatigue strength rather than fatigue life, the dependence on load ratio is drastically reduced.

A key influence factor addressed in this research is the effect of temperature on fatigue life. Experimental data on unidirectional laminates shows limited influence of low temperature (-40°C), but a large reduction at elevated temperature (60°C), Figure 9.

Temperature effects are likely to be more dominant in laminates without fibres in the main loading direction, i.e. laminates with matrix dominated behaviour such as a ±45° lay-up. Experiments have been performed on ±45° laminates in tension fatigue at room temperature, -40°C and 60°C. Preliminary evaluation shows that a reduced performance, as in UD laminates, is found at 60 °C. At -40°C a positive influence with longer fatigue lives was observed. The next step will be to evaluate the behaviour at other R-ratios, intermediate temperatures and to capture the effect of temperature in an integrated model. Experiments with varying temperature are foreseen to validate predictions for fatigue life in real life conditions.

Figure 8. Representations of Constant Amplitude fatigue behaviour

Figure 9. Effect of temperature on fatigue life of UD laminate

Industrial collaboration until 31 December 2013

Suzlon Blade Technology has been involved in discussions on model development.
All output from 2013

1. Westphal, T., Bortolotti, P., Nijssen, R.P.L., 'Carbon glass hybrid materials for wind turbine rotor blades' EWEA 2013 Conference, Vienna, poster and paper
2. Westphal, T., Nijssen, R.P.L., 'Material and Subcomponent Research for Improved Rotor Blade Design, VDI COWEC Conference, Berlin, June 2013, oral presentation
3. Nijssen, R.P.L., Westphal, T. (presenting author), Lahuerta, F., van Delft, D.R.V., Recent Results in Characterisation and Modelling of Composites for Wind Turbine Blades, Composites Week Leuven, September 2013, oral presentation and paper
Solar Cells and Modules
Solar Cells and Modules

Electricity will play a vital role in the energy transition towards a sustainable energy supply. One of the renewable energy alternatives is Photovoltaics (PV), in which sunlight is directly converted into electricity. With at least 38.4 gigawatts (GW) of newly-installed solar photovoltaic (PV) capacity worldwide and a global cumulative installed capacity of 138.9 GW, 2013 was another historic year for solar PV technology. PV technology now covers 3% of the electricity demand and 6% of the peak electricity demand in Europe (Source EPIA “Global Market Outlook for Photovoltaics 2014-2018”, June 2014).

The PV industry has grown rapidly in recent years and succeeded to significantly reduce the prices and cost of PV technologies. This price reduction resulted in so called grid parity in consumer prices of electricity in many parts of the world including in the Netherlands. By further reduction of the cost of PV systems it is expected that the installations of PV systems world wide will continue to increase at the unprecedented rate. Key factors for reduced cost of PV technologies are improving conversion efficiency, reduction of the material consumption, and sustainability.

ADEM projects

Within the Solar Energy theme of the ADEM Program we focus on increasing the efficiency of different types of solar cells and lowering their costs.

Several novel concepts for increasing the efficiency are investigated. At TU Delft the following topics are studied: the creation and manipulation of quantum dots using silicon or PbSe to manipulate the band gap and obtaining efficient carrier multiplication; fabrication of thin layers of luminescent material to convert high energy photons to one or more lower energy photons; the development of nanostructured silicon-based absorber materials for thin-film solar cells in which the light-induced (metastable) changes in the atomic structure of the silicon matrix are prevented or strongly reduced. At University of Twente the use of laser treatment of specific solar energy materials, such transparent conductive SnO2 material is investigated.

Annealing by ultra-short laser pulses can modify optical properties of thin SnO2 films by means of thermal processing resulting in increased optical transmittance of SnO2 thin films with improved scattering properties of its surface.

At TU Delft the first PhD has successfully finished her research work on mechanical properties of crystalline silicon solar cells that determines the handling of thin wafers, production yield and cell reliability.

Plans

Early in 2014 three additional PhD projects in the Solar Theme were approved. A PhD student at TU Eindhoven will investigate 3D volume organisation of polymer-based photovoltaic devices. Another PhD student will work at Twente University on the topic of surface recombination and minimization of contact resistance of crystalline silicon solar cells. The third PhD student at TU Delft will investigate novel fabrication processes for a better control of doping in silicon solar cells using the new ion implanter at ECN.

Industrial involvement

New PhD projects will result in new expertise in solar cell processing and their applications and are carried out in cooperation with FEI, Tempress, and ECN.

Theme Coordinator

Prof. dr. Miro Zeman
Delft University of Technology
Introduction

The purpose of the project is to study the nature and dynamics of excitons and charge carriers in semiconductor nanocrystals with ultrafast time-resolved spectroscopic techniques. These nanocrystals have distinct advantages as a solar energy material: the tunability of the optical properties with their size, straight-forward wet-chemical synthesis and the possibility for solution-processing. Using techniques such as Transient Absorption and Terahertz and Microwave Spectroscopy, we can study the important processes in these solar cell materials, such as charge generation, transport and decay. The femtosecond laser used in these experimental setups is funded by ADEM. A special focus in the project is on the occurrence of carrier multiplication (CM): the generation of two or more electron-hole pairs per absorbed photon. This process can potentially boost the efficiency of solar cells. Knowledge about the fundamental optical and electronic processes in these nanomaterials can give direction to improvement of material performance in solar cells.

Research results from 1 January until 31 December 2013

The focus in 2013 was on two topics: 1) the dynamics of photo-excited charges in PbSe nanorods and 2) the efficiency of carrier multiplication in PbS nanosheets.

The dynamics of photo-excited charges in PbSe nanorods

PbSe nanorods are of interest because of the efficient charge transport along the rod and enhanced carrier multiplication compared to dots. We studied the nature and dynamics of electron-hole pairs in PbSe nanorods with varying length. We found that for a rod length up to 30 nm, electrons and holes are delocalized over the entire rod, and behave independently. They decay via a third order Auger recombination process. Above a rod length of 50 nm, electrons and holes are becoming bound in the form of 1D-excitons and Auger recombination follows second order kinetics Figure 1. The rate of the Auger processes was found to decrease with nanocrystal volume, which is beneficial for the application of these nanorods in photovoltaic systems and other optoelectronic devices such as lasers.

![Figure 1: Cartoon of electron-hole interaction in nanorods of various lengths.](image-url) We also investigated the thermal relaxation rate of charges with an initial excess energy. The
thermal relaxation rate was found not to vary with nanocrystal shape or size. Hence, the enhanced rate of carrier multiplication in nanorods compared to dots cannot be due to a difference in thermal relaxation rate.

The efficiency of carrier multiplication in PbS nanosheets
The mechanism of the carrier multiplication process, and the efficiency in nanocrystals vs. bulk, is still a hotly debated topic with important implications regarding high-efficiency solar cells. Recent studies show an influence of the dimensionality of the nanocrystal on the eventual CM efficiency. We investigated the efficiency of carrier multiplication in two-dimensional PbS nanosheets (figure 2) of 4 to 7 nm thickness using ultrafast optical pump-probe spectroscopy. The efficiency of carrier multiplication in nanosheets is much higher than for quantum dots, nanorods and bulk material. For the thinnest nanosheets the CM efficiency (per unit excess photon energy normalized to the band gap) largely exceeds that of quantum dots and nanorods and is close to the maximum attainable value of 1. We attribute the high CM efficiency to the high density of states in the nanosheet, which supplies many combinations of hot single excitons and multiple exciton states and makes the conversion very efficient. The decay kinetics of the excited electron-hole pairs show second order Auger recombination. This indicates that excited electrons and holes behave as correlated pairs and form excitons in this material. In 2014 we will investigate the photoconductive properties of these nanosheets using THz and microwave conductivity spectroscopy.

Figure 2: Transmission Electron Microscopy image of a PbS nanosheet

Industrial Collaboration
The group of prof. Siebbeles has an ongoing collaboration with Toyota Motor Europe (Zaventem, Belgium) on nanomaterials for photovoltaics. Toyota provides funds for a postdoc at TU Delft and Dr. Sachin Kinge from Toyota has a part-time appointment as guest assistant professor at TU Delft.

All output from 2013
1. Scientific Paper: M. Aerts; F.C.M. Spoor; F.C. Grozema; A.J. Houtepen; J.M. Schins; L.D.A. Siebbeles. “Auger Recombination and Carrier Cooling in PbSe Nanorods: Crossover from cubic to bimolecular decay” Nano Letters 2013, 13, 4380-4386
2. Oral presentations at GRS Clusters, Nanocrystals & Nanostructures (Mt. Holyoke, MA, U.S.): M. Aerts et al. “Auger recombination in PbSe Nanorods: transition from cubic to bimolecular decay” and at the ADEM conference (Ermelo): M. Aerts et al. “Multiple exciton generation and dynamics in PbSe nanocrystals”
3. Poster presentations at Physics@FOM 2013 (Veldhoven) and at GRC Clusters, Nanocrystals & Nanostructures (Mt. Holyoke, MA, U.S.): M. Aerts et al. “Auger recombination in PbSe Nanorods: transition from cubic to bimolecular decay”
Introduction

The c-Si solar cell technology is leading the solar cell market to date. To make c-Si solar cell technology more competitive with conventional energy sources as well as with other solar cell technologies, the cost per watt ratio needs to be driven downward through time either by the increase of the efficiency or by the decrease in production and materials costs. In the recent past, thin film materials have become more and more important to increase efficiency of c-Si solar cells, for example by acting as optical coatings (anti-reflection or reflective coatings) and/or passivation layers. By using combinations of different material in thin film stacks, it is possible to yield a higher trade off in optical and passivation properties, which can increase the efficiency of solar cells with thin film stacks over solar cells employing single-layer thin films.

Techniques such as plasma-enhanced chemical vapor deposition (PECVD) and (plasma-assisted) atomic layer deposition (ALD) find an increasing number of applications in c-Si photovoltaic devices processing. Most common thin film materials used for optical and/or passivation purposes, are silicon dioxide (SiO2), amorphous silicon nitride (SiNx), amorphous silicon (a-Si:H), aluminum oxide (Al2O3). Each of them has specific advantages and disadvantages, depending on the temperature of deposition, the deposition rate, the refractive index and the surface passivation quality of the films. When combined in stacks, advantages of different material systems can be combined while disadvantages of particular single films can be mitigated.

The goal of the current research project is to investigate the performance of thin film stacks of different materials in terms of surface passivation, optical performance and other relevant material and processing properties. The thin films are deposited by PECVD and ALD. Process development, film characterization and investigation of the surface passivation performance are important aspects of the work.

Research results from 1 January until 31 December 2013

Through an internal collaboration, research was carried out to study selective hole contacts for c-Si solar cells that are highly transparent, passivate the c-Si surface and have low contact resistance. Stacks of Al2O3 and ZnO films were investigated for this purpose. The charge transport mechanism through these stacks is tunneling recombination and it was shown that such stacks can achieve a contact resistance of ~1.5 Ω·cm² for an Al2O3 thickness of 1 nm. Furthermore, it was demonstrated that the surface passivation of such stacks can be greatly improved by the insertion of a 3 nm film of hydrogenated amorphous silicon (a-Si:H) between the Al2O3 and the c-Si, achieving an effective surface.
recombination velocity of ~20 cm/s. The stacks with an a-Si:H layer achieved a contact resistance of ~5 Ω·cm².

Furthermore, research on SiO₂/Al₂O₃ stacks deposited by ALD was started up as it was found that such stacks can serve as zero-charge passivation layers for high-efficiency c-Si solar cells.

Industrial collaboration until 31 December 2013

The research on a-Si:H/Al₂O₃/ZnO stacks was carried out in collaboration with Hanwha Q-Cells who are supporting the STW Flash project of ir. Sjoerd Smit. The research on SiO₂/Al₂O₃ takes place in collaboration with Tempress Systems and Levitech.

All output from 2013

*Metal-oxide-based hole-selective tunneling contacts for crystalline silicon solar cells*, S. Smit, D. Garcia-Alonso, S. Bordihn, M.S. Hansen, and W.M.M. Kessels, Sol. Energy Mater. & Sol. Cells A, 120, 376 (2014).
Introduction

Spectral conversion materials

The efficiency of single junction solar cells is limited by thermalization losses caused by absorbed photons with an energy in excess of the band gap of the cell. In addition, external quantum efficiency can be lower than unity especially in the UV and blue part of the solar spectrum in a number of state-of-the-art solar cells. For the latter reason it is worthwhile to convert the solar spectrum to a spectral range for which the external quantum efficiency of the cell is higher. We develop thin film coatings capable of converting the solar spectrum to this desired spectral range. For example, by placing such a luminescent layer on the surface of a CIGS or CdTe cell it is possible to increase the total cell efficiency by 1.2% or 4.6%, respectively.

Luminescent solar concentrator materials

Luminescent Solar Concentrators (LSC's) aim at lowering cost of solar energy generation by concentrating sunlight onto small area strip solar cells using a low-cost luminescent plate. Current state-of-the-art luminescent materials based on organic dyes or quantum-dots do not absorb the complete visible spectrum. This means low solar conversion efficiency but also bright colouration of LSC's, limiting their applicability. In addition, part of the emitted light is re-absorbed by the material itself during the transport to the solar cells, limiting the efficiency of LSC's with useful sizes to below 2%. As a possible solution, we introduce Tm$^{2+}$ doped halide black phosphors that absorb >60% of power from the sun and emit IR light without self-absorption at 1140 nm that can be converted efficiently to electricity by CuInSe$_2$ PV cells. Detailed balance limit calculations show that the best halide materials so far allow for LSC efficiencies of 12%. We develop magnetron sputtering processes as a thin-film deposition technique for coating glass windows based on the phosphor NaCl:Tm$^{2+}$.

Research results from 1 January until 31 December 2013

Thin-film deposition

We apply combinatorial magnetron sputtering as a thin-film deposition technique for depositing spectral conversion materials as thin-films with a range of compositions of Ca$_x$Si$_y$O$_z$:Eu$^{2+}$, for which the molar ratio of sputtered Ca/Si atoms changes largely as a function of position in the film. In addition NaCl:Tm thin-films are sputtered as LSC material using a combinatorial approach, where NaCl films are sputtered with concentration gradient of Tm. Composition gradients are quantified by performing thickness measurements on films deposited from a single source. Thin-films are characterized with SEM-EDX analysis to monitor the molar ratio of the various deposited materials. XRD measurements are used to identify crystalline phases within the films. Optical analysis includes luminescence excitation/emission measurements and UV-Vis-NIR transmission measurements.
Spectral conversion materials
As-deposited films are transparent with a colouring from light-green to yellow to light-red along the gradient and do not show any crystalline phases nor any luminescence. Anneal treatment at 1200°C for 5 hrs in N₂/H₂ (7%) atmosphere results in formation of various areas with strong and abrupt changes in diffuse reflection along the Ca/Si composition gradient (Fig. 1). When placed under a 360 nm UV light source, yellow emission and local green and orange tints are observed within the films.

XRD analysis shows a variation in film content, ranging from undoped β-Ca₂SiO₄ and CaSiO₃ compounds to Eu₂SiO₄. Luminescence measurements show broad band UV absorption followed by visible light emission that varies with position along the gradient (Fig. 2). This luminescence characteristic is typically observed with 4f-5d transitions of Eu²⁺ ions in Eu₂SiO₄ (630nm) and EuSiO₃ (550nm).

Luminescent solar concentrator materials
As-deposited films are white and semi-transparent, though a grey colouring is observed towards higher Tm concentrations in the film. SEM images in Fig. 3 show a variation in surface structure with varying Tm concentration in the film. EDX measurements at the same positions along the Tm gradient are performed to quantify the Tm to Na molar ratio, showing a linear increase in Tm content with position along the Tm gradient. XRD analysis at several positions along the gradient confirmed the formation of a crystalline NaCl phase.

Transmission measurements in the infrared range are performed on the films to study the presence of characteristic 4f-4f absorption lines of Tm²⁺ and Tm³⁺, corresponding to the 2F₇/₂ → 2F₅/₂ transition of Tm²⁺ and the 3H₆ → 3H₅ Transition of Tm³⁺ expected at 1138 nm and 1218 nm, respectively (Fig. 4). A local decrease in transmission is found at 1134 nm, as well as 1218 nm. By subtracting the measured transmission spectrum from a fit (red dashed curve) without the absorption lines, the relative absorption intensity of Tm²⁺ and Tm³⁺ can be calculated. The top-left and bottom right insets give the relative absorption efficiencies of Tm²⁺ and Tm³⁺ respectively. By determining relative absorption intensities of Tm²⁺ and Tm³⁺ at different positions as a function of the deposited Tm
content relative to Na. It can be concluded that at high Tm content part of the Tm is present as a metallic phase.

Luminescence emission spectra are recorded under 420 nm excitation. The sharp emission line observed at 1134 nm corresponds to Tm$^{2+}$ emission. Luminescence excitation spectra, recorded by monitoring 1134 nm emission, reveal six excitation bands in a wavelength range between 270 and 700 nm (Fig. 5).

The work presented here shows that magnetron sputtering is a promising technique for the deposition of Tm$^{2+}$ doped NaCl. Being able to deposit Tm$^{2+}$ doped halide thin-films is a promising step in the development of high efficiency colorless LSC’s.

Fig. 4: IR transmission spectrum of a NaCl:Tm film. The red dashed curve represents a simulated curve that would emerge if there were no Tm$^{3+}$ or Tm$^{2+}$ absorption. The Insets show the relative absorption intensity calculated from the difference in transmission between the simulated curve and the actual curve.

Fig. 5: Luminescence excitation (black curve) and emission (red curve) spectra and the UV-Vis Transmission of the film (green curve).

Industrial collaboration until 31 December 2013

None

All output from 2013

1. Combinatorial DC/RF magnetron sputter deposition and characterisation of Ca$_x$Si$_y$O$_z$ and Eu$_x$Si$_y$O$_z$ luminescent thin-films with a composition gradient, M. de Jong, M.A. Thijs & E. van der Kolk, Submitted to Journal of Applied Physics.

2. Deposition of luminescent NaCl:Tm$^{2+}$ thin-films with a Tm concentration gradient using DC/RF magnetron sputtering, M. de Jong, W. Kesteloo & E. van der Kolk, submitted to Applied Optics.

3. Luminescent thin films for photovoltaic applications, M. de Jong, K. Hooning, E. van der Kolk, visual presentation Delft Energy Initiative PhD Event.
Introduction
The new generation of thin-film silicon-based solar cells is expected to lead to a market breakthrough and new applications. This is based on a favorable price/performance ratio and the possibility to manufacture flexible and large-area modules. Further, the energy pay-back time is expected to be well below one year. The stabilized efficiency of currently produced modules based on amorphous silicon is still rather modest (9-10%) and increasing their efficiency is an important target in the development of the new generation of thin-film silicon solar cells. This new generation of thin-film silicon solar cells is based on the multi-junction solar cell concept. The stability of the materials used as absorber layers under light exposure is of high importance, since at least 50% of the power output is generated in the amorphous junction in state-of-the-art multi-junction solar cells.

The central aim of this PhD project is the development of nanostructured silicon-based absorber materials for thin-film solar cells in which the light-induced (meta-stable) changes in the atomic structure of the silicon matrix are prevented or strongly reduced. This new class of silicon-based materials is characterized by nanostructural engineering of the hydrogenated amorphous silicon matrix, with the important aim of increasing their stability. The tailoring of the atomic ordering in the amorphous matrix leads to a broad range of materials, spanning the range from nanostructured amorphous silicon to nanocrystalline silicon layers when small nanocrystals are incorporated.

The challenge is to develop deposition technology that enables us to gain control over the nanostructural order of the material during the deposition and to prevent the phase transformation from nanostructured silicon into a fully nanocrystalline silicon film. The material properties before and after light soaking will be determined in detail using a complementary set of advanced optical and electrical characterization and positron annihilation methods. The stability of the developed materials will be tested in solar cells.

Research results from 1 January until 31 December 2013
Due to the complex nature of the hydrogenated amorphous silicon (a-Si:H) nanostructure there is a limited understanding of the native and metastable defects and recombination in this material. This has proven to be a major obstacle in finding the origin of the Staebler-Wronski effect (SWE). The limited understanding of the nanostructure and defect states has led to a wide variety of models that try to describe the SWE, none of which have yet succeeded in providing convincing experimental evidence for their correctness. Another shortcoming of defect studies in the past is that they have usually been conducted on intrinsic films without the presence of an external electrical field due to doped layers, like is the case in the absorber layer of an a-Si:H solar cell.
On the road towards SWE reduction the latest insights into the nature and the kinetics of light-induced defect creation in a-Si:H films and solar cells are presented using a unique combination of Doppler broadening positron annihilation spectroscopy (DB-PAS), Fourier Transform Photocurrent Spectroscopy (FTPS), in situ light soaking of solar cells with automated JV characterization, continuous wave electron-paramagnetic resonance (cw-EPR) spectroscopy, and time-domain pulsed EPR spectroscopy.

The beneficial role that H plays in the mitigation of the SWE in a-Si:H solar cells is ascribed to an improved H passivation degree of open volume deficiencies when depositing the absorber layer from a H-diluted silane plasma at a low deposition rate (Figure 1). FTPS showed that the four defect distributions in the band gap have different kinetics of light-induced defect creation (Figure 2).

**Figure 1**: Results of VEPFIT and JV analyses on four series of a-Si:H films on glass showing (a) the S-W plot, (b) the relation between S and the film deposition rate, and (c) the conversion efficiency degradation after light soaking of a-Si:H pin solar cells with corresponding absorber layers. The colored areas in each plot refer to the different dominant types of open volume deficiencies, i.e. divacancies (DV), multivacancies (MV), and nanosized voids (NV). The arrows illustrate increases in the hydrogen-to-silane gas flow rate ratio, $R$, and the rf-power, $P_{rf}$.

**Figure 2**: The increase of the fitted error function amplitudes obtained after correction for their initial baselines values as observed during in situ light soaking of an a-Si:H pin solar cell with (a) white light and (b) blue light (1 kW/m² at 25 °C). For each of the fitted sub gap contributions a power law slope can be fitted to the error function amplitude increase to obtain the time scaling ~ $t$ of which the values are shown. The absorber layer of this solar cell was deposited at $R = 10$.

Furthermore, the recombination due to defects in the top and bulk parts of the absorber layer are different. DB-PAS and EPR studies provided evidence that the defects are linked to open volumes such as dangling bonds (non-clustered defects) and small open volume deficiencies, such as hydrogen-decorated divacancies (clustered defects). In the initial, non-degraded state there is a correlation between the electron spin density and the Doppler $S$ parameter, while such a dependence of spin density on the a-Si:H nanostructure is not present after light soaking. Since the evolution of the solar cell external parameters during light soaking shows a variety of time dependencies due to multiple physical causes Figure 3, a more complex model for the SWE than currently available is required.
Figure 3: Results of in situ light soaking experiments on pin a-Si:H solar cells with five different absorber layer thickness using (a-d) blue LED light (251 W/m² at 25°C) and (e-h) red LED light (254 W/m² at 25°C) for light soaking and JV measurements. Note that the light intensities are chosen such that the $J_{sc}$ value of the solar cell with an absorber layer of 400 nm matches the $J_{sc}$ of that same solar cell measured under standard white light illumination in order to have comparable recombination currents during blue and red light soaking.

Industrial collaboration until 31 December 2013

None

All output from 2013

1. Paper published: J. Melskens, A. H. M. Smets, M. Schouten, S. W. H. Eijt, H. Schut, and M. Zeman, “New Insights in the Nanostructure and Defect States of Hydrogenated Amorphous Silicon Obtained by Annealing,” IEEE Journal of Photovoltaics 3, 1 (2013) 65-71.

2. Paper published: V. Demontis, C. Sanna, J. Melskens, R. Santbergen, A. H. M. Smets, A. Damiano, and M. Zeman, “The role of oxide interlayers in back reflector configurations for amorphous silicon solar cells,” Journal of Applied Physics 113, 6 (2013) 064508.

3. Paper published: J. Melskens, M. Schouten, R. Santbergen, M. Fischer, R. Vasudevan, D.J. van der Vlies, R.J.V. Quax, S.G.M. Heirman, K. Jäger, V. Demontis, M. Zeman, A.H.M. Smets, “In situ manipulation of the sub gap states in hydrogenated amorphous silicon monitored by advanced application of Fourier transform photocurrent spectroscopy,” Solar Energy Materials and Solar Cells (2014, in press). http://dx.doi.org/10.1016/j.solmat.2014.03.022.

4. Presentations at the MRS Spring Meeting 2013 in San Francisco, CA, United States (poster), the ICANS25 conference in Toronto, ON, Canada (oral), and the JNPV 2013 conference in Dourdan, France (oral).

5. Abstracts accepted for the IEEE PVSC 40 conference in 2014 in Denver, CO, United States (oral, student award nomination), and the EU PVSEC 2014 conference in Amsterdam, the Netherlands (poster).

Other

SOPHIA project together with Helmholtz Zentrum Berlin on the topic of electron paramagnetic resonance measurements on a-Si:H was accepted; publication of results in journal in preparation.
Introduction
One of the greatest challenges facing mankind is the global energy crisis, leading to a growing interest in renewable energy. Solar cells are among the most well-known alternative sources of energy. The overall demand to reduce solar energy costs gives a continuous drive to reduce the thickness of silicon wafers. Handling and bowing problems associated with thinner wafers become more and more important, as these can lead to cracking of the cells and thus to high yield losses. Hence, it is very important to find a compromise between electrical properties, strength and costs of the solar cell, which in terms requires a better understanding of microstructure, stress development and mechanical properties of the cell.

This PhD research focuses on aspects related to the microstructure, defects, strength and stress state of crystalline silicon solar wafers and cells, as well as the effect of solar cell processing conditions on these aspects.

Research results from 1 January until 31 December 2013
Experimental work included:
The project “Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar cells” ended on the 7th of January 2013. However, part of 2013 was devoted to PhD thesis writing and correction. The following paragraphs summarize main conclusions and recommendations of the project. Further details can be found in [1].

Microstructure of Aluminium and Silver Electrical Contacts
1. The aluminium layer has a porous composite-like microstructure, consisting of three main components: 1) spherical (3 - 5 µm) hypereutectic Al-Si particles, surrounded by a thin aluminium oxide layer (150-200 nm); 2) a bismuth-silicate glass matrix (3.3 vol.%); 3) pores (14 vol.%).
2. The thickness of the Al-Si eutectic layer depends on the Al particle size, the amount of Al paste and the surface roughness of the textured silicon wafers. Furthermore, all these parameters affect the fracture strength of metallised solar cells.
3. Drying Al paste at a lower temperature (250 °C) gives smaller process induced cavities and thus a denser Al layer structure, improving the strength of solar cells.
4. An alternative mechanism for Ag contact formation was proposed, where under an oxidizing environment Ag dissolves as Ag⁺ ions into the molten glass and there is a redox reaction between diffused Ag and silicon substrate, which creates inverted pyramidal pits on the Si surface. The Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during firing or as Ag crystals in the inverted pyramidal pits during the subsequent cooling process. This model competes with the previously proposed
5. Furthermore, it was found that there are two main processing parameters affecting the uniformity of the Ag/Si interface, namely the peak firing temperature and the silicon surface roughness.

Fracture Strength of Crystalline Wafer Based Solar Cells
1. The ring-on-ring test combined with finite-element (FE) modelling has been developed within this research to provide a new biaxial fracture strength test method for thin solar cell samples. The FE model was validated by digital image correlation. The use of this ring-on-ring test can be recommended for those applications where the surface properties of solar cells are of interest, such as the effects of crystallinity and the impurity concentrations on fracture strength.
2. Damage-layer removal by etching significantly increases the strength of both multicrystalline (mc) and single crystalline silicon wafers.
3. It was found that mc-silicon wafer crystallinity has a significant effect on the mechanical strength, i.e. the more grain boundaries, the weaker the silicon wafer.
4. Samples taken from the bottom of the multicrystalline silicon ingot are up to 30% stronger than those taken from the top. This effect was most significant for samples with many grain boundaries. The decrease in strength for the top ingot location could be related to a high concentration of oxygen and other non-metallic impurities.
5. There is a significant decrease in fracture strength when an anti-reflective coating is applied. The high application temperature of this SiNx coating, 375°C, induces high thermal stresses in the SiNx layer, which are thought to be the cause of the decrease in the stress at fracture.
6. The composition of the aluminium rear side contact paste has an effect on the mechanical strength of a cell through the total thickness of the Al layer, the thickness of the eutectic layer, the porosity and the bismuth glass concentration. The highest strength was observed for the paste with smaller aluminium particle size. Furthermore, both eutectic layer uniformity and microcrack removal contribute to the improvement of mechanical strength of solar cells.
7. A strong correlation was found between the maximum firing temperature of the Al rear contact and the amount of bowing and the fracture strength of solar cells, i.e. the higher the firing temperature, the higher the bowing and the stronger the cell, which is related to the thickness of Al-Si eutectic layer.
8. The silver contact etches the silicon wafer during the firing process creating small etch pits, which negatively affect the strength of the solar cell.
9. Samples where the Si-wafer surface is polished prior to applying a Ag layer show higher strengths because of the stronger Ag-Si contact interface resulting from a good glass wetting of the silicon surface. Non-uniformity of the glass layer and large voids at the Ag/Si interface, observed for textured and as-cut wafer-surface conditions, have a negative effect on the mechanical strength of the solar cells.

Stress Characterization in Silicon Solar Cells
1. A combination of laboratory X-ray and synchrotron diffraction together with Raman spectroscopy is required in order to obtain a realistic picture of the residual stress distribution in Al and Ag metallic contacts and crystalline silicon wafers.
2. It was shown that there is a stress gradient along the thickness direction in both the Ag and Al layers, resulting from complex composite-like microstructures of the contacts.
3. Residual stresses at the grain boundaries of multicrystalline silicon wafers were found to be higher than within the grain. Grain boundaries are therefore considered the most probable sources of mechanical strength degradation of mc-Si wafers.
4. An amorphous Si phase was found in the layer damaged by the wafer-cutting process and it is thought that the presence of this transformed amorphous Si also affects the mechanical stability of as-cut wafers.

Recommendations for Future Research
The current project was mainly focused on fundamental aspects of microstructure and fracture strength in crystalline silicon solar cells and on processing conditions affecting these aspects.
Implementing the knowledge obtained in this PhD research in a thermo-mechanical model should be one of the main goals for future research in this area. Such a model would allow prediction of the stress state resulting from each processing step during the manufacturing of solar cells. In order to realize this objective, it is recommended to further investigate the following aspects:

- **Characterization of the effect of silicon crystal orientation on fracture strength of silicon solar cells**

  By means of electron back-scatter diffraction techniques in combination with ring-on-ring tests it should be possible to evaluate the effect of silicon crystal orientation on fracture strength.

- **A more precise characterization of the effect of metallic inclusions and SiC needle precipitates on fracture strength and stress state of silicon solar cells**

  It is recommended to use intentionally contaminated mc-Si block cast from scrub material, containing known high amounts of metallic inclusions, and compare it in terms of fracture strength and stress state with a reference uncontaminated mc-Si block cast (with 99.99% purity) using identical processing conditions. The use of photoluminescence and etching techniques is advised in order to locate different defect areas.

- **Effect of soldering on the strength of solar cells and the mechanical behaviour of soldered solar cell interconnections**

  The influence of making a soldered joint on the mechanical strength of a solar cell should be quantified by comparing test results from specimens covered by a silver layer with results from specimens that are exposed to a local heat input comparable with soldering. Furthermore, the strength of soldered joints themselves and also of conductive adhesives should be evaluated. Because of the more complex geometry, a FE model is required to determine the relationship between the applied load during mechanical testing and the stresses in the different layers.

**Industrial collaboration until 31 December 2013**

Industrial activity has included collaboration with ECN for sample preparation and modeling of the relationship between the mechanical properties of the cells and the microstructure of the metallization pastes. The results of this collaboration have provided back-ground knowledge to ECN. This has been used by ECN in consultancy projects with industrial partners including cell manufacturers and metallization paste suppliers.

**All output from 2013**

1. V.A. Popovich, “Microstructure and Mechanical Aspects of Multicrystalline Silicon Solar cells”, PhD thesis, TUDelft, 2013.
2. V.A. Popovich, A. Yunus, A.C. Riemslag, M. Janssen, I.J. Bennett, I.M. Richardson, “Characterization of multicrystalline silicon solar wafers fracture strength and influencing factors”, International Journal of Material Science, Vol.3 No.1, March 2013.
3. V.A. Popovich, M.P.F.H.L. van Maris, M. Janssen, I.J. Bennett, I.M. Richardson “Understanding the properties of silicon solar cell aluminum contact layers and its effect on mechanical stability”, Materials Sciences and Applications, Vol. 4 No. 2, February 2013.
Introduction
In 2013 the research was mainly focused on showing and discussing the effects of picosecond (ps) laser irradiation on the optical and electrical properties of industrially optimized thin SnO2 films. These results can be used to further improve the performance of SnO2-based electrodes for solar cells and/or electronic devices.

Research results from 1 January until 31 December 2013
Areas of SnO2 films, with a thickness of 980 nm, on Borofloat®-glass were irradiated by 6.7 ps, λ = 343 nm laser pulses by two sets of laser conditions, referred to as low and high fluence conditions respectively. We observed two main different regimes as results of the laser treatment for the two laser treated samples. While at low fluence the SnO2 layer remained completely in solid state, showing no changes in the surface morphology, the sample treated at high fluence showed that the top layer of 100-200 nm of the SnO2 film was subjected to melting and resolidification. The latter was concluded on the basis of observed Laser-induced Periodic Surface Structures (LIPSSs). Careful analysis revealed a total absence of amorphous material, even in the outermost atomic layers of both laser treated samples. A tuning of the laser parameters (such as fluence, repetition rate and overlap) was necessary to achieve the optimal inter-pulse heat accumulation, which slows down the resolidification process and avoids amorphization. Simultaneously, the heat accumulation was moderate, which ensured a thermally damage-free film and substrate. The latter is an essential condition to exploit ultra-short pulsed lasers for ultra-shallow thermal treatments even above the melting threshold of the material without damaging the structure of the lattice.
Our investigation revealed multiple effects of the laser treatment on the properties of the SnO2 film, where small changes in the observed macroscopical optoelectronic properties can arise from several combined different phenomena, whose contributions cannot be isolated easily. Chemically, desorption of fluorine was measured as well as of oxygen, which induce shifts in the stoichiometric O/Sn ratio after the laser treatment. Carbon contaminant impurities at the top surface was also reduced after the laser treatment. On the other hand, adsorption of hydrogen from surrounding atmosphere was measured. The presence of laser-induced lattice defects, related to different strains observed in the film, was found in the case of the sample treated at high laser fluence. Those defects are likely created during the rapid self-quenching phase of the process. That is, the velocity of the solid/melt interface is sufficiently high to ‘freeze’ those defects in the lattice, which in turn generates strain in the film. Depending on the laser processing conditions, each of these contributions can play an important role or even dominate the final opto-electronic properties of the films.
In the two laser treated samples, different properties were identified in the top 100 to 200 nm layer of the SnO2 films, when compared to the remaining layer of the film on glass. This difference is sharper in the sample treated at high fluence, where fast resolidification from the molten state has occurred, than in the sample treated at low fluence. This observation indicates that changes in the opto-electronic properties can be mainly attributed to the top 100 to 200 nm layer of the film and only secondarily to the rest of the layer, which remains almost unaffected by the laser annealing. Finally, the overall performance of the SnO2 films before and after the laser treatment were...
compared via the figure of merit $\varphi = T_\text{10} / R_{\text{sh}}$. It was found that the $\varphi$ of already industrially optimized SnO$_2$ films was increased up to 59% due to laser processing.

**Industrial collaboration until 31 December 2013**

The research was carried out in cooperation with TNO, which provided SnO$_2$ samples and facilities for performing required measurements to investigate optical and electrical properties.

**All output from 2013**

1. D. Scorticati, A. Illiberi, G. R. B. E. Römer, T. Bor, W. Ogieglo, M. Klein Gunnewiek, A. Lenferink, C. Otto, J. Z. P. Skolski, F. Grob, D. F. de Lange, and A. J. Huis in ’t Veld, Optical and electrical properties of SnO$_2$ thin films after ultra-short pulsed laser annealing, Proceedings of SPIE - The International Society for Optical Engineering. 8826:88260I-1-12 (2013).
Project: TUD-P16
Silicon based nanoparticles for efficient solar-spectrum conversion in all-silicon tandem cells

Name PhD-candidate: Martijn van Sebille
Affiliation: TU Delft, Photovoltaic Materials and Devices
Start date: 6 Aug 2012
Project leader(s): Prof. dr. Miro Zeman and dr. René van Swaaij, TU Delft

Introduction
Photovoltaic cells convert light directly into electrical energy. Unfortunately solar cells only convert a specific part of the sun’s light spectrum into electricity, limiting their efficiency considerably. In addition, of the light that is converted into electricity only a fraction of the energy is utilized. This limitation is determined by the band gap of the absorber material that is used, which is a fixed material property. Research in nanotechnology has shown that by reducing the size of a crystalline Si particle (referred to as quantum dots, or QD’s) to the nanometer range, its band gap can be tuned. This technology could enable the development of multi junction solar cells, which have theoretical maximum conversion efficiencies up to 68% under 1 sun illumination [1].

In the last decade several studies [2, 3] reported the fabrication of c-Si QD’s from silicon rich compounds of a-Si:H with nitrogen, oxide or carbon in periodic multilayers. Due to phase separation during high temperature annealing, QD’s form in the silicon-rich layer [3, 4] where the thickness of the silicon-rich layer can be used to control the QD size [5]. However, it remains challenging to create uniformly sized and distributed QD’s and to prevent the loss of hydrogen invoked by thermal treatments, which ultimately leads to a high defect density in the material and an increased recombination in photovoltaic devices.

Laser annealing of silicon rich compound multilayers might open up possibilities to increase control of the crystallization process of QD’s. First, the combination of short pulse durations and high energy allows for greater control over, and during the annealing process compared to furnace annealing methods. Secondly, the different optical properties of the multilayers and the QD’s allow for selective heating of the material, using different wavelengths [6]. In addition, the high energy density that can be reached in a short amount of time may reduce the risk of hydrogen loss. Therefore, the goal of this project is to understand QD formation in greater detail and apply the technology in functional device.

[1] A.D. Vos. Detailed balance limit of the efficiency of tandem solar cells. Journal of Physics D: Applied Physics, 13:839, 1980.
[2] M. Künle, T. Kaltenbach, P. Löper, A. Hartel, S. Janz, O. Eibl, and K.G. Nickel. Si-rich a-SiC:H thin films: Structural and optical transformations during thermal annealing. Thin Solid Films, Volume 519, page 151-157, 2010.
[3] M.A. Green, E.C. Cho, Y. Cho, E. Pink, T. Trupke, KL Lin, T. Fangsuwannarak, T. Puzzer, G. Conibeer, and R. Corkish. All-silicon tandem cells based on artificial semiconductor synthesised using silicon quantum dots in a dielectric matrix. In Proceedings of the 20th European Photovoltaic Solar Energy Conference and Exhibition, page 3, 2005.
[4] E.C. Cho, M.A. Green, G. Conibeer, D. Song, Y.H. Cho, G. Scardea, S. Huang, S. Park, XJ Hao, Y. Huang, et al. Silicon quantum dots in a dielectric matrix for all-silicon tandem solar cells. Energy, 2:3, 2007.
Research results from 1 January until 31 December 2013

We have developed a method to quickly and objectively measure all QD’s in a TEM image to obtain the QD size distribution, using a convolution of the TEM image with Laplacian of Gaussian filters within a set scale space. The resulting array can be used to localize QD’s and determine their characteristic scale. A verification step using boundary overlay provides a quick check whether QD’s are detected correctly. Furthermore, we found that the input parameters for this method can be obtained by optimizing them for one TEM image and can then be applied correctly to similar TEM images.

Industrial collaboration until 31 December 2013

None

All output from 2013

1. Poster presentation: PhD Poster event EEMCS 2013, TU Delft
   Title: Embedded Quantum Dot Size Distribution Analysis by TEM;
   Authors: M. van Sebille¹, K. Jarolimek¹, L.J.P. van der Maaten², L. Xie³, R.A.C.M.M. van Swaaij¹ and M. Zeman¹
   ¹Photovoltaic Materials and Devices, Delft University of Technology, The Netherlands
   ²Pattern Recognition Laboratory, Delft University of Technology, The Netherlands
   ³Department of Engineering Sciences, Applied Materials Science, Uppsala University, Sweden
Catalysis, Membranes and Separations

The depletion of fossil fuels necessitates the search for efficient and environmentally acceptable ways to generate hydrogen. Besides, biomass is getting more attention as an alternative to decrease the use of fossil fuel in power production and in the chemical industry. Within the Catalysis, Membranes and Separations (CMS) cluster various technologies are under development for the production of H₂ and the capture of CO₂. This implies catalytic conversion technologies, some of which are based on membranes. Main research areas are on the oxyfuel conversion process with integrated CO₂ capture and the reforming of biomass. These technologies involve the development of novel materials, be it catalysts, membranes, sorbents or solvents. The ADEM program keeps our materials science infrastructure and knowledge up to world-class standard and enables us to remain a key player in this important field of research. In the past year the seven projects in this cluster, all started in 2010 or 2011, result in a better understanding in the several processes and materials and interesting results for (future) applications are obtained.

ADEM projects
Several projects are executed within the biomass conversion theme. For fluidized-bed biomass gasification a model is developed at TU/e to determine the optimal conditions for overall auto-thermal operation of the chemical looping combustion process. In another project the catalytic and chemical looping functions of the olivine bed are studied in order to enhance the gasification efficiency and to reduce the formation of heavy tars. It is shown that a Ca-rich segregation layer on the olivine has positive effects on the overall efficiency in H₂ production. Two other projects are running (one at TU/e and one at UT) on the conversion of biomass to hydrogen by steam reforming of flash-pyrolysis oil. Here several CeO₂-supported metallic catalysts are developed and more insight is obtained in the relation between catalyst (micro)structure and catalytic properties.

An integrated autothermal reformer for natural gas conversion into hydrogen with integrated CO₂ capture is being developed at the UT. The reactor consists of two different ceramic membranes, respectively an oxygen and a hydrogen selective membrane. Dense, mixed ionic-electronic conducting, flat ceramic membranes with high oxygen flux (and stable in CO₂ environment) were fabricated using a tape casting/sintering technique. The hydrogen selective membrane showed good hydrothermal stability, which makes these membranes applicable for water-gas shift reactions. At the TUD, the focus is on solvent based CO₂ capture for either pre- or post-combustion or CO₂ from natural gas. The amine process, currently used for CO₂ capture, is expensive and suffers from drawbacks like corrosive behaviour and sensitivity to degradation. The research at TUD is focussed on the development of relatively inexpensive and/or biodegradable physical ionic liquids.

Industrial Involvement.
A demonstration plant will be constructed for the production of steam for electricity and Sustainable Natural Gas (SNG). This plant includes the chemical looping combustion process as developed in this CMS cluster.

Plans
In 2014 some PhD projects come to an end, while new projects will start. The green light to execute the planned program to the full extent includes the opportunity to make essential additional investments in the materials science research infrastructure.

Theme Coordinator
Prof. dr. Louis Winnubst
Prof. dr. ir. Arian Nijmeijer
University of Twente
Project UT-P07
Hydrogen from Biomass via catalytic steam reforming of flash-pyrolysis oil: how to enhance the activation of water?(2)

Name PhD-candidate: Shilpa Agarwal
Affiliation: University of Twente, Department of Science & Technology, Catalytic Processes & Materials (CPM), MESA+ Institute of Nanotechnology
Start date: 1 Jan 2010
Project leader(s): Dr. Barbara Mojet, Prof. Dr. Ir. Leon Lefferts
Other personnel: Prof. Dr. Emiel Hensen, Eindhoven University of Technology

Introduction
The continuous depletion of fossil fuels has necessitated to look for efficient and environmentally acceptable ways to generate Hydrogen (H₂). Steam reforming combined with gasification of coke in the presence of H₂O is conceptually a promising alternative to generate H₂ from bio-oil (see figure 1 for schematic overview of the process). It is reported that H₂O is able to regenerate hydroxyl groups on oxides like ceria, which increases H₂ yield and catalyst lifetime.

Sustainable Bio-oil Steam Gasification

- Bio-mass promises renewable energy and chemicals production

Biomass → Bio-oil → H₂ → Fuel-cells/chemical industries

Figure 1: Schematic overview of bio-oil steam gasification

It has been suggested that the catalytic performance of cerium oxide (ceria) can be greatly enhanced by tuning the dimension and the morphology of the oxide. The goal of this project is to determine structure – performance relationships, specifically the influence of the ceria surface on water dissociation activity and the reactivity of different types of surface hydroxyls towards model coke compounds. For this reason, ceria was tailored into rod, octahedral and cubic morphology, for investigating the effect of defect sites and hydroxyls on the above-mentioned reactions.
Research results from 1 January until 31 December 2013

Steam reforming of bio-oil combined with the gasification of coke deposits in the presence of water is a conceptually promising alternative to generate hydrogen gas. H\textsubscript{2}O can be activated in the gasification stage to form hydroxyl groups (-OH) on oxide-supported (like ceria) metal catalysts, which increases both the H\textsubscript{2} yield and the catalyst’s lifetime. The reactivity for the water dissociation as well as the reactivity of resulting hydroxyl groups can be further improved by altering the shape and size of ceria support. Based on the recent studies, ceria nanoshapes exhibit excellent redox properties and high specific activity/selectivity in comparison to the bulk ceria particles. However, the knowledge related to the surface species actually responsible for enhanced catalytic activity of ceria nanocatalysts so far remain lacking. The work presented in this thesis highlights the fundamental aspects of ceria nanoshapes, with emphasis on the effects of surface planes on overall catalytic performance. The main objectives of this work are to investigate the true exposed facets, as well as to understand the reactivity of hydroxyl species and the role of defects on the ceria nanoshapes.

In the first part of this project, definitive information on the nature of the exposed surfaces in these CeO\textsubscript{2} nanoshapes is provided using aberration-corrected transmission electron microscopy (AC-TEM) and high-angle annular dark field imaging (HAADF). Prior to the present work, discrepancies in literature existed related to the exposed planes on these ceria nanoshapes. For instance, it was the common belief that rods showed enhanced activity due to the exposure of active {110} and {100} planes. These findings were reported prior to the recent advancements in TEM (of AC and HAADF), and thus the results were unclear. Furthermore, our initial FTIR results suggested that ceria rods and octahedra share similarity in terms of exposed planes. This spurred us to re-examine rods with up-to-date TEM equipment. From the AC-TEM results it is apparent that ceria octahedra and rods both expose {111} surfaces, whereas ceria cubes mainly expose {100} surfaces.

Additionally, H\textsubscript{2}-reduced ceria nanoshapes were examined for water gas shift (WGS) reaction to evaluate the structure performance relationship. It is observed that the WGS activity normalized with surface area (m\textsuperscript{2}) was identical for ceria octahedra and rods, whereas ceria cubes were found to be much more active. Further, to understand the interaction of surface species with CO during WGS catalytic reaction, H\textsubscript{2}-reduced ceria nanoshapes were analyzed using FTIR spectroscopy at 350\textdegree}C. Similar to WGS results, the FTIR spectra specifically, the hydroxyl (-OH) vibration bands and their interaction with CO, for rods and octahedra were observed to be the same. On the other hand, cubes with {100} planes exhibited different relative amount of the surface –OH species and their interaction with CO resulted in different spectral features in comparison to rods and octahedra. It is clearly demonstrated in present work that the nature of the exposed surfaces affects the WGS activity as well as interaction of surface sites with CO. Due to the presence of the same {111} exposed planes, ceria rods and octahedra show similar WGS activity, as well as similar interaction of –OH species with CO obtained using FTIR spectroscopy. Interestingly, cubes with more active {100} surface planes have different –OH bands and interactions with CO, resulting in a higher WGS activity per m\textsuperscript{2}.

It is known that the hydroxyl species are the active sites in CeO\textsubscript{2} supported catalytic reactions such as WGS, and steric constraint can lead to different amounts of hydroxyl species on different exposed planes. In the second part of this work, the role of different types of active hydroxyl (–OH) species on the nanoshapes (wires, octahedra and cubes) and their respective reactivity towards CO and extent of regeneration of –OH species with water has been investigated using in situ FTIR spectroscopy at 200\textdegree}C. All three ceria nanoshapes showed similar –OH stretching bands although with different relative intensities. Likewise rods, wires resemble octahedra in the hydroxyl range of FTIR spectra. The bridged hydroxyl species (–OH\textsuperscript{[bridged]}) on ceria wires and cubes were found to be reactive towards CO, whilst only limited interaction with CO was observed for octahedra. In addition, the formation of hydrogen carbonates was observed only in case of octahedra and the relative amount of defects detected follows the trend: Wires > cubes > octahedra. Based on all these observations, it is suggested that both the presence of defects as well as the shape of ceria nanoparticles influences the interaction of specific hydroxyl groups with CO. Finally, subsequent exposure to water vapor at 200\textdegree}C showed a clear shape dependent water activation to –OH species, resulting in removal of different relative amounts of formates and carbonates formed in either ambient or CO.
It is well known in the literature that the presence of intrinsic defects, as well as the ease of formation of defects during the reaction, strongly influences the ceria-catalyzed reactions. To understand the involvement of defects in ceria rods during the formation of specific formate and carbonate surface species at 200 and 350°C is investigated using a combination of in-situ Raman and FTIR spectroscopies. It was observed at 200°C that the majority of formates and carbonates formed in CO do not form vacancies in the ceria lattice, whilst at 350°C formation of both formates and carbonates (mono/bidentate) result in the creation of vacancies. In addition, formation of stable polydentate carbonates was observed at 350°C. These polydentate carbonates were stable in water vapor as well as not forming vacancies in the ceria lattice. It must be noted that based on temperature the Raman signatures of the defect peaks arising in CO were very similar. However, their chemical origin seems to be different since at 350°C the addition of H₂O is needed to remove the vacancies, while at 200°C the majority disappeared already in He flowed immediately after CO flow. In the present work, it is also proposed that apart from the reported defects, such as anion Frenkel pair and oxygen vacancies, other CO-induced defects, e.g., vacancy clusters, interstitial and Schottky disorder might also form in the ceria lattice. Further theoretical studies are highly recommended for specific defect identification and corresponding peak assignment in the Raman spectra.

Finally, in the last part of the thesis, the defect chemistry of reduced ceria nanoshapes during the interaction with CO and H₂O is extensively discussed as a function of exposed plane. The defect chemistries of both rods and octahedra (with (111) plane) as a function of gas environment were similar. Specifically, the CO-induced defects for rods and octahedra were found to be the same, while the defect formation in CO (i.e., the (100) plane) for cubes was fundamentally different. For instance, in cubes the oxygen vacancy (Ovac) defects were formed in CO at the expense of existing anion Frenkel pair defects (Iₓ), whereas in case of other two nanoshapes both defects (Ovac and Iₓ) were formed irrespective of existing I₀ defects. These Raman findings are further supported by FTIR results that confirm that H₂-pretreated rods and octahedra can be further reduced in CO, simultaneously creating bare cerium ions and forming new defects (Ovac and I₀). In contrast to rods and octahedra, H₂-pretreated cubes are not further reducible in CO and hence undergo structural/vacancy rearrangement to further react with CO. These observations confirm that the defect chemistry on ceria nanoshapes is directly dependent on the surface terminations.

From this work it is clear that the ceria cubes show higher catalytic activity (per m²) than rods and octahedra. This is attributed to the different exposed planes, which give rise to different defect-formation mechanisms, different relative amount and reactivity of hydroxyl species.

**Industrial Collaboration**
None

**All output from 2013**

**Publications**

1. Ceria Nanocatalysts: Shape Dependent Reactivity and Formation of OH S. Agarwal, L. Lefferts, & B. L. Mojet *ChemCatChem* 5, 479–489 (2013)
2. ExposedsurfacesonshapecontrolledceriananoparticlesrevealedviaACTEM and water gas shift reactivity S. Agarwal, L. Lefferts, B. L. Mojet, D. A. J. M. Ligthart, E. J. M. Hensen, D. R. G. Mitchell, W. J. Erasmus, B. G. Anderson, E. J. Olivier, J. H. Neeth-  ūng, & A. K. Datye *ChemSusChem* 6, 1898–1906 (2013)
3. Defect chemistry of ceria nanorods S. Agarwal, X. Zhu, E. J. M. Hensen, L. Lefferts, & B. L. Mojet *J. Phys. Chem C* 118, 4131–4142 (2014)
4. Defect chemistry of ceria nanoparticles as a function of exposed planes S. Agarwal, X. Zhu, E. J. M. Hensen, L. Lefferts, & B. L. Mojet *in preparation*
5. Ceria nano-shapes – structural and catalytic properties S. Agarwal, L. Lefferts, A. K. Datye, & B. L. Mojet *Invited review for book chapter, in preparation*
**Oral presentations**
1. Morphological mysteries of ceria catalysts: Water activation 2nd ADEM conference, NL (25-26th April 2013)
2. Morphological mysteries of ceria catalysts NCCC-XIII, NL (5-7th March 2012)
3. Catalytic water activation 1st ADEM conference, NL (26-27th May 2011)

**Poster presentations**
1. Nano-catalysis with cerium oxide: Water activation Mesa+ Day, NL (18th September 2012)
2. Nano-catalysis with cerium oxide: Water activation 15th ICC, DE (1-6th July 2012)
3. A spectroscopic study of cerium oxide nano-catalyst: Water activation 4th Operando congress, USA (29th April-3rd May 2012) → Received poster prize
4. Tailored ceria nanoparticles for highly active OH species-Green future NCCC-XII, NL (28th February-2nd March 2011)
5. How to enhance activation of water on inorganic oxides 6th EFCTS summer school - Catalysis and surface science for renewables & energy, TUR (13-19th September 2010)
6. How to enhance activation of water NCCC-XI, NL (1-3rd March 2010)
7. In-situ ATR-FTIR spectroscopy of structured zeolite H-ZSM-5 catalysts 16th IZA, IT (4-9th July 2010)
Introduction

Biomass has become an appealing alternative to decrease the use of fossil fuel in the power production and chemical industry. In the ECN Milena process, biomass is converted by the coupling of two separated reactors in order to produce substitute natural gas. In the first reactor the biomass is gasified to syngas. Likewise in chemical looping, circulation of bed material is used to transport heat (sand) and oxygen (olivine) from the combustor reactor (bubbling fluidized bed) to the gasifier (riser). In the riser biomass reacts with steam (oxygen) and the produced gas is mainly synthesis gas. Later the gas can be upgraded to produce synthetic natural gas. The gas produced is nitrogen free, avoiding the NOx production and post processing of the gas to separate it from N2.

The reaction can be intensified by the use of olivine which transports oxygen from the combustor to the gasifier reactor. The unconverted biomass fraction (such as tar and char) and the bed material are circulated back to the combustor where the tar and char are burned to heat up the bed material to the gasification temperature (>800°C). In the frame of this ADEM project, the influence of operating conditions in the performance of the two interlinked reactors is investigated in detail.

The main research goals of the project are as follows:
- Gaining fundamental understanding of the chemical looping process and its application to biomass gasification
- Investigate the influence of operating parameters on the hydrodynamics of bubbling fluidized beds, the main parameters are temperature, external solids circulation, gas production.
- Effect of operating conditions on gas and particle residence time distribution
- Develop a phenomenological model to describe, optimize and scale up the Milena process
- Optimize the rate of heat and oxygen transport between the two interlinked reactors

Firstly, an extensive experimental work is done to investigate the influence of the main process variables on the hydrodynamics of Bubbling Fluidized Beds (BFB). In the present work, Particle Image Velocimetry (PIV) coupled with Digital Image Analysis (DIA) is for the first time extended to elevated temperatures. PIV/DIA is the only technique that provides the bubble phase properties and solids circulation patterns of fluidized beds simultaneously with high temporal and spatial resolution. However PIV/DIA is restricted to be applied to pseudo 2D beds.

A phenomenological model, based on the experimental work is developed for process optimization. Finally, the developed model is used to improve the heat transfer between the reactors for chemical looping and to account for additional oxygen transport and revisit the reactor design for biomass processing (MILENA process)
Research results from 1 January until 31 December 2013

The novel technique with a high temperature endoscopic-laser PIV/DIA (ePIV/DIA) has been validated at room temperature. To improve the technique, a new camera system has been implemented. The new system doubles the resolution of the technique, allowing the study of the hydrodynamics of particles as small as 100 µm. The new recording system has been validated with the use of the high temperature endoscope and the high power laser (Figure 1). Experiments with glass beads at high temperature have been carried out in order to demonstrate the technique capabilities. Figure 2 shows the lateral solids profiles at two different position at different temperatures.

Once the system has been validated and tested, the next step is do a design of experiments to investigate the effect of temperature in the hydrodynamics of gas-solids fluidized beds under production relevant conditions.

As for the phenomenological model, a model for the gasifier and combustor has been developed with Aspen Plus. As a first step, reaction kinetics are taken from the literature. With the developed model the optimal conditions for overall autothermal operation of the chemical looping combustion biomass gasification will be determined and the overall process performance will be evaluated.

Industrial collaboration until 31 December 2013

None

All output from 2013

1. “On the effect of solids recirculation rate on the hydrodynamics of chemical looping processes” Poster presentation at 9th European Congress of Chemical Engineering / 2nd European Congress of Applied Biotechnology, The Hague, The Netherlands, April 21-25, 2013
2. “Development of a high temperature endoscopic-laser PIV/DIA technique for the study of hydrodynamics of gas-solids fluidized beds” Oral presentation. Fluidization XIV conference. Noordwijkerhout, The Netherlands, May 26-31, 2013
Introduction

This research aims at the development of a ceramic membrane reactor concept, enabling hydrogen production with CO₂ capture. Integration of the mixed ionic-electronic conducting oxygen separation membrane into the reactor eliminates the need for costly oxygen. Aim of this subproject is to develop a mixed-conducting membrane with high chemical and mechanical stability, maintaining a high enough oxygen flux under oxygen fuel combustion conditions as well as to develop reliable methods for the fabrication of supported dense thin-film membranes.

Research results from 1 January until 31 December 2013

Electrical conductivity relaxation (ECR) measurements were performed on phases STF30, STF50, and STF70 in the range of \( p_{O_2} 1 - 10^{-2} \text{ atm} \), and temperature 700 - 900°C. Results obtained for, e.g., STF50 are shown in Figs. 1, 2 and 3. In collaboration with the Ural Federal University, Yekaterinburg, Russia, coulometric titration and chemical expansion measurements were conducted for each of the compositions. In the latter study, the chemical expansion is correlated with the change in oxygen nonstoichiometry. Data were recorded in the range 700 - 900°C, down to oxygen partial pressures \( 10^{-15} - 10^{-18} \text{ bar} \). The results will be presented in the next report. The data of coulometric titration experiments also enable us to calculate the thermodynamic factor, which parameter is required to compare transport parameters extracted from data of ECR with those from isotope exchange experiments. As an example, in Fig. 4, the surface exchange coefficient from ECR is compared with that obtained from pulse isotope exchange (PIE) experiments.

In close collaboration with FZJ (IEK-1), asymmetric STF membranes were fabricated using a tape casting technique. For STF50, the membranes show oxygen fluxes close to 2 ml/min at a temperature of 900°C. Experiments for STF30 and STF70, and analysis of data are on-going.

Industrial collaboration until 31 December 2013

None

All output from 2013

1. **Poster presentation** Valencia Summer School 2013: Sebastiaan F.P. ten Donkelaar and Henny J.M. Bouwmeester, Electrical conductivity relaxation on the SrTi₅Fe₁₋ₓO₃-system.
2. **Oral presentation** Valencia Summer School 2013: Sebastiaan F.P. ten Donkelaar and Henny J.M. Bouwmeester, Electrical conductivity relaxation on the SrTi₅Fe₁₋ₓO₃-system.
3. **Poster presentation** Mesa+ annual meeting 2013: Sebastiaan F.P. ten Donkelaar and Henny J.M. Bouwmeester, Electrical conductivity relaxation on the SrTi₅Fe₁₋ₓO₃-system.
Fig. 1 - $D_{\text{chem}}$ and $k_{\text{chem}}$ of STF50 as a function of $T$.

Fig. 2 - $D_{\text{chem}}$ of STF50 as a function of $p_{O_2}$.

Fig. 3 - $k_{\text{chem}}$ of STF50 as a function of $p_{O_2}$. 
Fig. 4 - Comparison of $k$ from ECR and PIE for STF50
**Project: UT-P09**

**Hybrid silica membranes for oxy-fuel conversion membrane reactors**

Name PhD-candidate: Marcel ten Hove

Affiliation: Inorganic Membranes, MESA+ Institute for Nanotechnology, University of Twente

Start date: 1 Feb 2011

Project leader(s): Prof. Dr. Ir. A. Nijmeijer
Dr. A.J.A. Winnubst

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**Introduction**

The growing energy demand combined with increasing concerns about greenhouse gas emissions is driving the research towards the development of processes with integrated CO₂ capture. The present research aims at the development of ceramic membranes for use in a reactor concept, enabling hydrogen production with integrated CO₂ capture, commonly referred to as pre-combustion carbon capture.

**Research results from 1 January until 31 December 2013**

**Hydrothermal stability**

The hydrothermal stability of γ-alumina and lanthanum doped γ-alumina was tested using a simple reflux setup. In this setup the membrane was placed above boiling water for 72 h. The pore size of the membranes was determined by permporometry before and after hydrothermal treatment. This simple hydrothermal treatment method was already severe enough to destroy the γ-alumina layer, since no valuable data was obtained from the permporometry measurements. The lanthanum doped γ-alumina had a smaller pore size after hydrothermal treatment, suggesting a densification of the layer.

BTESE membranes coated onto γ-alumina and lanthanum doped γ-alumina were subjected to the same hydrothermal treatment and characterized by means of single gas permeation. The gas permeation of BTESE on γ-alumina showed no signs of degradation after hydrothermal treatment, while BTESE membranes on lanthanum doped γ-alumina show a small decrease in permeance after hydrothermal treatment. The γ-alumina is protected to degradation by the BTESE membrane, which suggests that with this type of membranes the need for a hydrothermally stable intermediate layer is less of an issue. For BTESE membranes coated on lanthanum doped γ-alumina the decrease in permeance is more pronounced in bigger gases, which suggests that the contraction of the intermediate layer results in a densification of the BTESE membrane as well.

**Zirconia doped hybrid silica**

A 9% Zr doped BTESE sol was synthesized to investigate the effect of amount of dopant on the membrane performance. Figure 1 shows the results for 9% and 16% doped Zr-BTESE, as well as normal BTESE. The performance of these membranes can be tuned by changing the dopant concentration. A higher concentration leads to a better separation with lower fluxes, while a lower concentration of dopant leads to higher fluxes, while compromising on separation.
Metal doping

Different metal dopants have been used in BTESE to evaluate the influence of the metal dopant on the performance of these membranes. Figure 2 shows the performance of the different metal dopants used. All membranes were impermeable for SF$_6$, which gives an indication that all membranes are free of defects. Cobalt doping gives rise to a more open structure and is therefore less interesting for H$_2$/CO$_2$ separation. However, due to its high permeance it could be interesting for dehydrogenation reactions.

The niobium doped BTESE membranes have a low permeance and selectivity when compared to zirconia doped BTESE. However, due to the acidic properties of niobium it can still be considered to be used in wet conditions. In the near future these membranes will be tested in wet conditions to see the influence of water on the membrane performance.
Industrial collaboration until 31 December 2013

None

All output from 2013

Presentation: Niobium-doped hybrid organic-inorganic silica membranes: the quest for reproducibility, Marcel ten Hove, Li Li, Hong Qi, Louis Winnubst, Arian Nijmeijer, Winterschool on membranes, Hirschegg (Austria), January 12-18, 2013

Poster: Facile synthesis of zirconia doped hybrid organic inorganic silica membranes, M. ten Hove, A. Nijmeijer and L. Winnubst, Summer school: Inorganic Membranes for Green Chemical Production and Clean Power Generation, Valencia (Spain), September 4-6, 2013
Introduction

To meet the increasing demand for renewable, CO\textsubscript{2}-neutral energy, biomass (in particular waste products) can be used for the production of fuels. Conversion of biomass can be performed using the gasification process as an initial step in the conversion.

In the ECN MILENA Process, biomass is converted by an indirect route, comprising of a system of two coupled reactors, to produce substitute natural gas. In this integrated gasification system, a bed-material is circulated between an oxidation reactor and a gasification reactor. In the latter, biomass reacts with steam and is converted to a gas mixture consisting mainly of methane, synthesis gas and CO\textsubscript{2}. The bed-material, together with the unconverted biomass fractions and tar are fed into the oxidation reactor, to heat up the bed-material. The hot bed-material subsequently enters into the gasification zone to provide the heat, necessary for gasification. In addition to the main product gases, the gasification process always results in tar formation due to incomplete decomposition of the biomass. Tars decrease process efficiency and can cause fouling of downstream equipment. This constitutes a major obstacle in the way to large scale commercialization of the technique.

The aim of this project is to build catalytic and chemical looping functions into the bed-material, to enhance the gasification efficiency and to reduce the formation of heavy tars. The natural mineral olivine ((Mg,Fe)\textsubscript{2}SiO\textsubscript{4}) is a promising material for this, as it has catalytic functionality for the degradation of tar. Moreover, the iron-oxide in olivine can switch valence from Fe\textsuperscript{2+} to Fe\textsuperscript{3+} and is capable of transferring oxygen from the oxidation zone to the gasification zone.

This project will:

a) Investigate and understand the role of iron/olivine in these functions in order to understand the mechanism of chemical looping, by model studies on olivine.
b) apply this insight in the development of an optimal catalyst for chemical looping and tar removal in indirect biomass gasification.

Research results from 1 January until 31 December 2013

It has been shown that, when olivine is used as a reactive bed-material in industrial scale processes, calcium-rich layers are formed around the olivine, due to interaction of bed material with biomass ash. This Ca-rich layer builds-up in time and has positive effects on the overall efficiency of the process; it increases tar conversion and enhances hydrogen production.

In 2013, we investigated the chemical composition of this coating, deposited on olivine during indirect biomass gasification, and the influence of the coating on the reactivity of the bed-material with respect to enhanced hydrogen production via the WGS reaction. To study the chemical composition of the coating, Scanning Electron Microscopy (SEM) in combination with elemental mapping was used. In addition to this, a depth profile of used olivine was studied using the ADEM X-ray Photoelectron Spectrometer, which gave useful information on both the distribution of the different elements as a function of sample depth as well as the chemical state of the different.
compounds that make up the coating. The activity of the coating towards the WGS reaction was tested in a fixed-bed reactor and the results of the used olivine were compared with olivines, which were not used during biomass gasification, and a sample of pure calcite (CaO). Since the coating is deposited on the bed-material by interaction with ash from the biomass, a sample of ash from beech wood was tested for its WGS activity as well. The SEM-EDX analysis of the used olivine shows significant deposition of calcium on the olivine’s surface. This calcium predominantly forms on iron-rich parts of the olivine particle, suggesting that this deposition is favored by the presence of free iron-oxide.

The SEM-EDX analysis of the used olivine shows significant deposition of calcium on the olivine’s surface. This calcium predominantly forms on iron-rich parts of the olivine particle, suggesting that this deposition is favored by the presence of free iron-oxide.

Figure 1. SEM-EDX elemental analysis of a used olivine particle.

To study the chemical composition of the coating, the ADEM XPS has been used in combination with depth profiling. Figure 2 shows an XPS depth profile of a used olivine particle, where the atomic concentrations of the main elements found are plotted as a function of sample depth. The calcium concentration does not change significantly as a function of analyzed sample depth, indicating that the Ca-rich surface layer is uniform and has a thickness of at least 0.5 µm.

Figure 2. Atomic concentration of elements present in a particle of used olivine, as a function of sample depth. Each etch level corresponds to approximately 35 nm sample depth.

The potassium concentration, on the other hand, is not uniformly distributed in the surface layer of the coating; the relative amount of K present decreases exponentially from 7 atom-% at the outer surface of the particles with increasing sample depth. The atomic surface concentrations of silicon and oxygen do not vary much with increasing etching, indicating that Si and O are homogeneously distributed throughout the sample. The iron concentration at the surface (etch level = 0) is significantly higher compared to fresh olivine and the iron concentration in the subsurface layers (etch levels ≥1) does not decrease exponentially, pointing to an 0.5 µm thick homogeneous iron enriched surface layer, which is in agreement with the SEM-EDX analysis.
Unused fresh olivine has a very low WGS activity up to 800°C. Similar to the fresh olivine, the olivine which has been oxidized for 1 h does not show any significant WGS activity, although the oxidized olivine has 5 times more iron at the surface than fresh olivine. Used olivine has significant WGS activity at temperatures above 600°C, which can be attributed to the coating of the material. Because the coating consists mainly of calcium oxide, a sample of pure CaO (calcite) has been tested as well and showed similar WGS activity compared to the used olivine sample. The highest hydrogen production could be observed for the biomass ash sample, which shows that not only CaO accounts for the H₂ production, but other oxides are active as well.

In conclusion, it has been shown that, when olivine is used as a reactive bed-material in industrial scale processes, a Ca-rich coating builds up on the surface of the olivine. This coating has positive effects on the overall efficiency of the process; it increases H₂ content of the product gas. This work contributes with important information on the fundamental properties of the calcium coating and its effect on the WGS reaction rate.

**Industrial collaboration until 31 December 2013**

ECN is currently working, together with its partners waste- and energy company HVC, Ballast Nedam, Taqa Energy, the province of Noord-Holland, the municipality Alkmaar and Gasunie, on the engineering of a 12 MW MILENA gasifier. This plant will be constructed as a demonstration plant, which eventually will produce steam for electricity and Substitute Natural Gas (SNG). This plant uses the technology described in the Introduction of this project and the results of this ADEM project can be used to make the biomass gasification process more efficient and effective.

**All output from 2013**

1. **Scientific papers:**
   Chemical looping capabilities of olivine, used as a catalyst in indirect biomass gasification
   Remco J. Lancee, A. Iulian Dugulan, Peter. C. Thüne, Hubert J. Veringa, J.W. (Hans) Niemantsverdriet, Hans O.A. Fredriksson. Applied Catalysis B: Environmental 145 (2014) 216–222.

2. **Oral Presentations:**
   Olivine as a Biomass Gasification Catalyst: Dynamic Behavior and Coating Formation by Calcium-Rich Layers. Remco Lancee, Hans Fredriksson, Peter Thüne, Hubert Veringa and Hans Niemantsverdriet. Presented at the North American Catalysis Society Meeting, June 2 – 7 2013, Louisville, KY, USA
Introduction

The amine-process currently used for CO$_2$ capture is extremely expensive and suffers many drawbacks as amines are corrosive, degradation sensitive and volatile. Some of these problems can be overcome by using ionic liquids (ILs), which are salts consisting exclusively of ions and have melting points lower than 100°C. ILs bear some interesting properties, such as: low volatility, relatively high chemical/thermal stability, non-flammability, tunable properties and relatively high CO$_2$ solubility.

The aim of my project is to selectively capture CO$_2$ with a suitable ionic liquid from flue-gas streams, either at pre-combustion, post-combustion or natural gas reservoir conditions. A suitable IL should have a high CO$_2$ solubility, selectivity and a low viscosity. Preferentially, the IL should be biodegradable, non-toxic and cheap. The currently known ILs are performing still insufficient regarding these properties, which obstruct the application of ILs at a large scale. Therefore, the aim is to find/design an IL with improved characteristics with respect to the mentioned properties.

Research results from 1 January until 31 December 2013

Solubilities of CO$_2$, CH$_4$, and mixtures of both have been measured in a variety of ILs [1-3]. The aim was to assess the potential of ILs for natural gas sweetening. CO$_2$/CH$_4$ selectivities in the ILs were calculated and the results were compared with the conventional solvents used in the natural industry (e.g., Selexol). In addition to the experimental work also advanced Monte Carlo molecular simulations have been used to predict the solubility of several gases in ILs. These results will be published soon.

Figure 1: Comparison of ideal CO2/CH4 selectivity in ILs with that of traditional solvents
Industrial Collaboration
None

All output from 2013

1. Ramdin, M.; Olasagasti, T. Z.; Vlugt, T. J. H.; de Loos, T. W. High Pressure Solubility of CO\textsubscript{2} in non-fluorinated Phosphonium-based Ionic Liquids. J. Supercrit. Fluids. 2013, 82, 41-49.
2. Ramdin, M.; Amplianitis, A.; Bazhenov, S.; Volkov, A.; Volkov, V.; Vlugt, T.J.H.; de Loos, T.W. Solubility of CO\textsubscript{2} and CH\textsubscript{4} in Ionic Liquids: Ideal CO\textsubscript{2}/CH\textsubscript{4} Selectivity. Ind. Eng. Chem. Res. (2014), http://dx.doi.org/10.1021/ie4042017 (in press).
3. Ramdin, M.; Amplianitis, A.; de Loos, T.W.; Vlugt, T.J.H. Solubility of CO\textsubscript{2}/CH\textsubscript{4} gas mixtures in ionic liquids. Fluid Phase Equilib. (2014), http://dx.doi.org/10.1016/j.fluid.2014.05.007 (in press).
Introduction
Reforming of biomass to hydrogen provides an alternative for the production of hydrogen from fossil fuels. For this process one requires a metal function to activate the C-C, C-H and O-H bonds. Very often a reactive support is required to cope with catalyst deactivation. A well-known example is the use of ceria which limits carbon deposition during reforming. Ceria has redox activity which can gasify the coke deposits in the presence of oxygen or water. The goal of this project is to determine structure-performance relationships: how does the composition and surface structure of the ceria determine the reactivity for water dissociation as well as the reactivity of the resulting OH groups with model compounds representing coke deposits. The influence of metals on C-C, C-H, O-H and C-O bond activation will be investigated.

Research results from 1 January until 31 December 2013
Ceria supported metal catalyst was an important component in three way catalyst. We proposed an alternative reaction mechanism for CO oxidation by a Rh surface oxide layer stabilized on ceria. It involves oxidation of adsorbed CO by an O adatom of a Rh3O4 cluster followed by its reoxidation by O atoms of ceria. The ceria vacancy is healed by reaction of O2 adsorbed at the interface between the partially reduced Rh3O3 cluster and the ceria surface. This mechanism can explain the absence of self-inhibition by CO and the involvement of ceria O atoms in the catalytic cycle, noted for highly active CO oxidation Rh/CeO2 catalysts. It involves the formation of O vacancies in the ceria surface as a consequence of reoxidation of the thin surface metal oxide film partially reduced by CO. The presence of O vacancies is confirmed by in-situ Raman spectroscopy and the correlation between their density and CO oxidation activity is consistent with the proposal that O2 adsorption is the rate controlling step in catalytic CO oxidation.

Figure 1: Bulk truncated structures (side view) of CeO2 (a) (111), (b) (110) and (c) (100) surfaces.

We then explored reaction paths of CO oxidation of isolated Rh atoms supported on three different terminations of CeO2 namely the (111), (110) and (100) terminations Figure 1. The aim of this work was to examine (i) whether isolated Rh atoms supported on ceria should be considered as the active sites for CO oxidation and (ii) how the ceria surface termination influences the CO
oxidation activity of isolated Rh atoms. On Rh/CeO$_2$(111) the reaction only proceeds when two CO molecules are adsorbed on the Rh ion. The presence of a second CO molecule facilitates the desorption of product CO$_2$. Gas phase oxygen molecule adsorbs on the resulting oxygen vacancy site followed by dissociation. The other CO molecule then reacts with one of the O atoms leading to CO$_2$ desorption, completing the reaction cycle. On Rh/CeO$_2$(110), adsorbed CO can easily react with a ceria surface O atom due to the lower Ce-O bond energy on this surface. Migration of surface O atoms facilitates the CO$_2$ desorption process, which is much easier for Rh/CeO$_2$(110) than for Rh/CeO$_2$(111). Molecular oxygen will adsorb on the resulting vacancy. After desorption of the second CO$_2$ product molecule by reaction of adsorbed CO with another surface O atom, the adsorbed oxygen molecule migrates to the vacancy site and dissociates with negligible barrier. The role of molecular oxygen is to heal the oxygen vacancy rather than being involved in a direct reaction with adsorbed CO. The Rh/CeO$_2$(100) model was found to be inactive for CO oxidation, mainly because of the geometric constraints for the adsorbed CO molecule to react with one of the surface O atoms, despite the lowest Ce-O bond energy of the CeO$_2$(100) surface among the ceria surfaces considered. The main reason is the relatively large distance between the C atom of adsorbed CO and the ceria O surface atoms. The particularities of the CO oxidation mechanism for isolated Rh atoms on these ceria surfaces are in agreement with the experimental activity trends.

Au catalyst supported on ceria was found to show high activity under low temperature conditions. We investigated by DFT calculations the size effect of gold for CO oxidation on a CeO$_2$(110) model surface. Various reaction pathways are explored for a single Au atom and a Au nanorod model representing a nanoparticle. On Au/CeO$_2$(110), we propose a new reaction mechanism by which a single Au adatom supported on the CeO$_2$(110) surface catalyzes the oxidation of CO involving O atoms of the ceria surface. An important step is the migration of the O atom towards the Au atom, resulting in a very facile reaction with CO. In this way, CO oxidation takes advantage of the oxygen atoms, which can be removed from the ceria surface. Different from literature findings for Au/CeO$_2$(111), the Au atom at the vacancy site of CeO$_2$(110) can still absorb and activate O$_2$. This difference between the two ceria surfaces has a geometric explanation Figure 2. The more open CeO$_2$(110) surface allows for the coordination of O$_2$ between Au and the vacancy site. This configuration is not possible for CeO$_2$(111) because the Ce cations are located in the second layer. For the Au/CeO$_2$(110), the catalytic cycle is closed by CO adsorption and reaction with one of the O atoms following dissociation of O$_2$. The proposed mechanism is the first to provide a theoretical explanation for the catalytic activity of Au/CeO$_2$ and, more specifically, the involvement of ceria O atoms. For the model involving a Au nanorod supported on CeO$_2$(110), the candidate mechanisms all involve the interface of the Au nanorod representing a gold nanoparticle and the ceria surface. Three different reaction paths were identified. The first one involves a Mars-van Krevelen type
mechanism in which CO adsorbed on the bottom layer of the Au nanorod reacts with a ceria lattice O atom Figure 3. It is argued that CeO$_2$(110) is more reactive for this reaction than CeO$_2$(111) because of the lower oxygen vacancy formation energy. The generated oxygen vacancy is healed by adsorption of O$_2$ from the gas phase and facile dissociation into a lattice O atom and a very reactive O atom, which is easily removed by CO. This reaction path provides another explanation for the experimentally observed participation of ceria surface oxygen atoms in CO oxidation. The other two reaction paths start with O$_2$ adsorption on the interface between Au nanorod and ceria support. The adsorbed oxygen molecule can directly react with adsorbed CO (co-adsorption mechanism), or dissociate first into an O atom and then react with CO (stepwise mechanism). In both cases, the ceria support facilitates O$_2$ adsorption, and for the stepwise mechanism also dissociation of adsorbed O$_2$. It is concluded that all three pathways contribute to the CO oxidation activity of Au nanoparticles supported on CeO$_2$(110). The Mars-van Krevelen mechanism is not possible for the CeO$_2$(111) because of the higher oxygen vacancy formation energy. Besides, the different terminations of the CeO$_2$(111) and CeO$_2$(110) surfaces prevent O$_2$ adsorption on the interface between Au and the ceria support. We show that, even in the case that O$_2$ adsorption can occur on the interface with a defective CeO$_2$(111) surface, closure of the catalytic cycle will result in catalyst deactivation.

Figure 3: CO oxidation mechanism on Au/CeO$_2$(110) surface.

Industrial collaboration until 31 December 2013

None

All output from 2013

Journals
1. W. Y. Song, V. Degirmenci, D. A. J. M. Ligthart, A. P. J. Jansen, E. J. M. Hensen*, “A computational study of the mechanism of CO Oxidation by A ceria supported surface rhodium oxide Layer”. Chemical Communication, 2013, 49, 3851.
2. W. Y. Song, A. P. J. Jansen, E. J. M. Hensen*, “A computational study of the influence of the ceria surface termination on the mechanism of CO oxidation of isolated Rh atoms”. Faraday Discussion, 2013, 162, 281-292.
3. W. Y. Song, E. J. M. Hensen*, “Structure Sensitivity in CO Oxidation by a Single Au Atom Supported on Ceria”. The Journal of Physical Chemistry C, 2013, 117, 7721.
4. W. Y. Song, E. J. M. Hensen*, "A computational DFT study of CO oxidation on a Au nanorod supported on CeO$_2$(110): on the role of the support termination". *Catalysis Science and Technology*, 2013, 3, 3020.

**Conference contributions**

1. W. Y. Song, A. P. J. Jansen, E. J. M. Hensen*, "A computational study of the influence of the ceria surface termination on the mechanism of CO oxidation of isolated Rh atoms", Faraday Discussion 162, April 10-12, 2013, Berlin, Germany. (oral presentation)

2. W. Y. Song, E. J. M. Hensen*, "A novel mechanism for CO oxidation and water gas shift reactions for gold and rhodium on ceria: on the important role of surface O atoms", 23rd North American Catalysis Conference, June 2-7, 2013, Louisville, American. (oral presentation)
Hydrogen Production and Fuel Cells

The ADEM program on Fuel Cells has a diverse set of research topics. This is due to the fact that there are multiple fuel cell technologies, each with their specific scientific and engineering challenges. The overall program that is performed by 5 PhD students, at various institutes & universities, appears to be running quite well. Also, it is clear that we can benefit from each others expertise, facilities and insights. We will set up a discussion meeting to see how we can sort that out. In addition there are a considerable number of PhD & MSc students, at TU Delft and elsewhere, that are involved with fuel-cell related activities that can provide additional synergy and focus.

Some points of attention are of course related to the making of optimal membranes. In this context there appear to be considerable opportunities making use of, on the one hand, self organized polymer structures like ionic conducting LCPs, and on the other hand, development of hybrid organic-inorganic structures. The self-organisation leads to preferential & enhanced ionic mobility, addition of (nano) particles gives rise to increased free volume, addition of solid state proton conducting fillers might improve high temperature performance. At least the materials under consideration are considerably cheaper that the current state of affairs.

Other aspects relate e.g. to catalysis, how to make more efficient use of very expensive platinum? How to improve the design of the catalysis particles and carbon structures in the electrodes. How to improve barrier properties so that ionic conduction is still easy, while preventing gas cross-over?

Industrial involvement
In the past year(s) we have had some discussions & seminars organised at TU Delft relating to basically informing each other on our mutual interests, which seems to attract some attention from industry and academia. Although the size of the individual economic activities on Fuel-Cell related research and development are as yet still limited there appears to be quite a large interest when we consider the whole. For fuel cell technology as a whole it seems that NL has a rather unique expertise available that should provide a sensible contribution in reforming the energy economy.

Plans
Recently also other fuel-cell related technologies are entering the field like HyET from Arnhem working electrochemical hydrogen compression (from atmospheric up to a pressure of 1000 bar in a single membrane system). Similarly we should see that there are indeed opportunities for alkaline PEMs, alternative fuels/storage systems like NH₃ that might also become available via electrochemical processes. This requires turning the perspective or indeed our way of thinking inside out which is a unique challenge.

Theme coordinator
Prof. dr. Stephen J. Picken
Delft University of Technology

Photo: Ivo Boshuizen
Project: TUD-P02
Super ionic composite membranes for PEMFC

Name PhD-candidate: Miguel E. Cordova-Chavez
Affiliation: TU Delft, ChemE, OMI
Start date: 1 Nov 2011
Project leader(s): Stephen J. Picken
Other personnel: Erik Kelder

Introduction
Fuel cells have been used since the 60’s. PEMFCs are ideal to work as an energy source for small devices or cars, but costs, water management, poisoning of electrodes with CO, and low conductivity are issues that still needs attention. It is important to point out the benefits that would be achieved if it’s possible to get the fuel cell to work above 100°C, this can be the solution to most of the working problems in PEMFCs. In this research, the goal is to fabricate new membranes with a low cost and an easy synthesis process combined with inorganic fillers, capable of improving the electrochemical properties of the membrane. This will be achieved through a simple direct mixing of the compounds and promoting the creation of an organize microstructure. Finally it will lead to a more efficient PEM and also able to keep an acceptable conductivity at temperatures above 100°C. The actual commercial use of PEMFC is determined by Nafion® membranes operating up to 80°C. What is proposed in this research is to overcome the basic problems discussed above with new membranes that differs from Nafion® in two basic aspect. First, we propose the used of PEEK for the polymer matrix, which is a low cost polymer, that can be modify to sulfonated PEEK by a simple reaction between PEEK and Sulfuric Acid at low temperature and could be casted by a solvent evaporation process into a membrane. Second, the creation of inorganic/organic hybrid membranes from sPEEK and an inorganic compound which can create bonds with water (absorb or adsorb water) that can be kept in the inorganic phase at temperatures above 100°C in order, to maintain acceptable proton conductivity. Also we are aiming to have an interaction between the inorganic particles and the Sulfonic groups in the polymer to create a path for the protons to go through the membrane in a more effective way and increase its mechanical stability.

Research results from 1 January until 31 December 2013
- The dry SPEEK was dissolved in N,N-dimethylacetamide (DMAc). The solution was stirred and kept at 120°C. The desired amount of inorganic filler (FeSO4 x 7H2O, LiBPO4 and Detonation Nanodiamonds were added). The solution was cast onto a Petri plate and dried in a fume hood for 24-48 hours and then finally dried at 80°C in a vacuum oven for 1 hour.
- Differential Scanning Calorimetry (DSC) was made under an inert atmosphere (pure nitrogen) using the Perkin Elmer DSC7.
- TGA measurements were performed using the Perkin Elmer TGA7 under air.
- The ionic conductivities were investigated by AC electrochemical impedance spectroscopy (EIS). Different cells were used as also different settings (4 point probe, 2 point probe, Through plane and in plane measurements) The impedance of the cell was measured in the frequency range from 1 Hz to 1×106 Hz with an oscillation of 10mV using Autolab® PGSTAT12, A Autolab® PGSTAT302N and a Novocontrol Broadband Dielectric Spectrometer (20 mV, 1MHz to 0.1 Hz)
- X ray diffraction measurement were made to the powders of the inorganic compounds and the membranes prepared using a Bruker D8 Focus X-ray Diffraction equipment (Powder and film).
Figure 1. XRD results comparing the pure Hydrated Salt, the pristine Polymer and the final membrane to confirm the presence of the crystalline structure inside the membrane.

Figure 2. XRD results comparing the pure Lithium Boron Phosphate, the pristine Polymer and the final membrane to confirm the presence of the crystalline structure inside the membrane.
Figure 3. DSC second Heating dynamic after erasing the thermal history of the sample and control cooling for FeSO₄ (right) and LiBPO₄ (left) membranes with different compositions in weight. The figures show the change in the Tg of the composite as a consequence of the interaction of the polymer matrix with the inorganic compound.

Figure 4. TGA results for membranes with different % of FeSO₄ showing the change in the sample of the water content in direct relation with the amount of inorganic compound present in the sample.
Figure 5. TGA results for membranes with different % of LiBPO4 showing the change in the sample of the water content in direct relation with the amount of inorganic compound present in the sample.

Figure 6. Conductivity measures done by a potentiostat measurement of the different membranes in all the composition range. The samples were 100% hydrated and the measurement was done at 20°C. It can be seen that the samples reach an optimal value. Relationships between this result, the changes in the Tg and the water content are still under investigation.
Figure 7. DSC second Heating dynamic after erasing the thermal history of the sample and control cooling for membranes with different compositions in weight of detonation Nanodiamonds. The figures show the change in the Tg of the composite as a consequence of the interaction of the polymer matrix with the inorganic compound.

Figure 8. TGA results for membranes with different % of Detonation Nanodiamonds showing the change in the sample of the water content in direct relation with the amount of inorganic compound present in the sample.
Figure 9. Conductivity measures done by a potentiostat measurement of the different membranes in all the composition range. The samples were 100% hydrated and the measurement was done at 20°C. It can be seen that the samples reach an optimal value. Relationships between this result, the changes in the Tg and the water content are still under investigation.

Industrial collaboration until 31 December 2013

None

All output from 2013

1. International Conference Polymer Batteries and Fuel Cells 2013 - 6th June 2013 in Ulm, Germany; Oral Presentation, Title “Super Ionic Hybrid NanoDiamonds/sPEEK membranes for PEMFCs” authors: M. E. Córdova, A. Sleczka, A. Korobko, E. M. Kelder and S. J. Picken. (this work was also accepted for oral presentation in the European Polymer Congress EPF 2013 in Pisa, Italy but not presented).
2. Bachelor Thesis Project - J. C. Bek – “Inorganic Fillers for SPEEK-based High Temperature PEM Fuel Cells” Final grade 9/10 – Tutoring by Stephen Picken, Erik Kelder and Miguel Cordova
**Introduction**

The formation of special nano-sized structures normally requires the use of expensive equipment and/or techniques, such as cleanroom or ultra-high vacuum. On the contrary to these methodologies, the proposed approach allows the formation of nanostructure by means of the combination of two inexpensive alternatives: sol-gel and an electrospinning techniques. The proposed methodology, in fact, yields a simple and versatile method for creating nano-sized ceramic structures with full control.

Electrospinning is a well-known electrodeposition technique for fabrication of matrixes of polymeric fibers which are currently used in different fields of technology, such as biological cell growth, advanced batteries and water treatment systems. Recently the research was extended to the applicability of the deposition technique into ceramic applications.

In this study, we propose three types of ceramic structures created using a combination of the aforementioned techniques. The proposed methodology allow shaping the nanostructure of the ceramic material, leading to the formation of nanochannels, nanofibers and nanotubes. These architectures show an improvement of the solid oxide fuel cell (SOFC) microstructure. However, such materials show enhanced properties that can also be applied to other fields such as tissue engineering or micro/nano-electronics.

**Research results from 1 January until 31 December 2013**

Electrospinning is a flexible technique that can be tuned in order to obtain different materials. Herewith we summarize the main preparation methods developed during the project.

*Nanochannels*

This technique consists of using the electrospun fibers as templates which are infiltrated with a sol-gel precursor. This results in ceramics with nanochannel-shaped porosity. Moreover, the deposition of catalyst is controlled by the presence of precursor in the fibers. Therefore, we ensure a high porosity with large surface area and placement of the catalyst on its most active site.

*Figure 1* shows an example of the resulting materials.
Figure 1. Template YSZ with nanochannels where nickel is controlled to be deposited on the surface of the channels. Literature is limited regarding sub-micron porous ceramics. Therefore, we developed a simple method to form such materials with control over catalyst deposition which can be used, for instance, as SOFC anode.

**Nanofibers**
A mixture of ceramic precursor and polymer can be electrospun. Ceramic nanofibers were formed after annealing the green matrix. It has been demonstrated that fiber diameter, alignment and surface morphology can be tuned. Moreover, such material shows enhanced flexibility in some cases. In addition, the composition can be varied. For instance, we have made zirconia, zinc oxide, lead zirconium titanate, calcium phosphate and bioglass fibers. Figure 2 shows an example of the prepared fibers.

![Electrospun zirconia nanofibers](Figure 2)

These nanofibers have shown promising results not only in the field of SOFC but also in micro/nanoelectronics and tissue engineering. Therefore, it can be concluded that electrospinning is a simple and versatile technique that allows the fabrication of functional nanofibers for different applications.

**Nanotubes**
The electrospinning setup can be modified in order to spin two concentric fibers, i.e. coaxial electrospinning. If the inner fiber is a polymer immiscible with the outer precursor-polymer mix then ceramic nanotubes can be formed after annealing of the green matrix. The resulting nanostructure, presented in Figure 3. The tunability for nanofibers in terms of alignment and surface morphology was also successfully applied for nanotubes.
Summarizing, we presented a method capable of making different nanostructured materials in a low cost and facile manner for several compositions and applications.

International collaboration until 31 December 2013
Ajayan Research Group, Rice University, Houston, Textas, U.S.
LEPMI, Grenoble, France
Tissue Regeneration, University of Twente, Enschede, The Netherlands

All output from 2013
1. Ceramic Nanostructures: the Electrospinning Advantage G. Cadafalch Gazquez, P. Wieringa, R. Besselink, B.A. Boukamp, L. Moroni, J.E. ten Elshof
2. Presentation at the Conference for Young Scientists in Ceramic, Novi Sad (Serbia) 6-9 November 2013
3. Presentation at ECERs Student Speaking Contest for the Netherlands, Utrecht 4 April 2013
4. Abstract published at KGK
5. Electrospinning: novel technique to controllably tune microstructure of Anode materials for SOFC at submicron scale. G. Cadafalch Gazquez, P. Wieringa, R. Besselink, B.A. Boukamp, L. Moroni, J.E. ten Elshof
6. Presentation at ECERs 2013, Limoge (France) 23-27 June
7. Electrospinning Technology to Enhance SOFC Anode Microstructures G. Cadafalch Gazquez, P. Wieringa, R. Besselink, B.A. Boukamp, L. Moroni, J.E. ten Elshof
8. Poster at Study Group Meeting: Chemistry in Relation to Physics and Materials Sciences, Veldhoven 4-5 March 2013

Other
Best poster prize award at NWO Study group meeting of Spectroscopy & Theory, Liquids and Interfaces and Chemistry & Structure of Materials. 10-11 February 2014
Introduction

Although Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are very promising alternatives to combustion engines in portable applications because of their higher efficiency and lower CO₂ emission, their large-scale introduction into the market is still hindered because cost and durability are not yet meeting the targets set by for instance the U.S. Department of Energy. These issues are strongly related to the platinum (Pt) catalyst required for the Oxygen Reduction Reaction (ORR). The currently employed catalyst consists of Pt nanoparticles (Pt NPs) adsorbed on high specific surface area carbon. Especially in non-ideal operation conditions, e.g. temperature and potential cycling, the electrochemically active surface area (ECSA) of the catalyst decreases, carbon corrosion being the major degradation mechanism that can cause catalyst detachment. Improving carbon support resistance to corrosion is thus a crucial challenge as it is the main cause of performance degradation in low temperature fuel cells. Recent studies have proven that graphitic materials, such as carbon nanotubes (CNTs), are significantly more resistant to carbon corrosion due to the higher stability of the sp²-hybridized carbon. Within our group, we developed a novel carbon material that consists of networked carbon nanostructures, CNNs, and is currently produced by a TU Delft spin-off company Carbon X. CNNs are 3-D hyper-branched carbon graphitic structures organized in a nano-scale pattern, Figure 1. They can be easily produced by Chemical Vapor Deposition (CVD) of ethene over transition metal catalyst synthetized in bicontinuous microemulsions (BMEs). The formation of networked, sponge-like, carbon graphitic structures is due to the carbonization of the surfactant, being the primary carbon source. CNNs show attractive properties for catalysis of fuel cells such as high specific surface area, high electrical conductivity, great oxidation resistance, surface defects increasing the material ability to disperse in solution and to simplify integration into polymer matrices. The versatility and simplicity of the synthesis route promises a less costly production than CNTs.

Figure 1. CNNs imaged by (a) SEM showing branches and junctions, (b) TEM visualizing two junctions I and II, and (c) showing multiple walls with capped ends and a d-spacing of 0.3 nm. Around the branches a thin amorphous layer is visible.

My PhD research aims to implement CNNs use in PEMFC electrodes, by investigating CNNs as a catalyst support for both noble and non-noble metal catalyst. Additionally, since CNNs synthesis is not fully understood yet, part of my research is also dedicated to the understanding of template properties (BMEs) via Molecular Dynamics (MD) Simulations and to the formation mechanism of NPs in BMEs.
Research results from 1 January until 31 December 2013

A computational microscope: coarse grain simulations of dense BMEs systems

NPMEs are exciting systems that are promising as tunable self-assembling templating reaction vessels at the nanoscale. Determination of the nano-structure of NPMEs is, however, not trivial, and there are fundamental questions regarding their design. We were able to reproduce experimental data for an important NPME system, Sodium-AOT/n-heptane/water, using coarse grained simulations involving relatively limited computational costs. The simulation allows visualization and deeper investigation of controversial phenomena such as bicontinuity, Figure 2, and ion mobility. Simulations were performed using the Martini coarse-grained force field.

Figure 2 Final snapshot for the system containing 20 % water, Water – Light blue, n-Heptane – yellow.

This work is carried out in collaboration with Dr. Alex de Vries, Molecular Dynamic Group, University of Groningen.

Bicontinuous Microemulsions for High Yield Wet Synthesis of Ultrafine Platinum Nanoparticles: Effect of Precursors and Kinetics

We demonstrate that for high yield wet synthesis of monodispersed NPs, high surfactant content BMEs offer an advantageous template as particle size is limited by the embedding matrix whereas particle aggregation is largely prohibited by its structure. We synthetized Pt NPs varying the reaction rate, metal precursor and reducing agent type and concentration, and the composition of the microemulsion (ME) in water content and oil type. High yields of up to 0.4 % of metal produced per weight of template were achieved without affecting the particle size, circa 2 nm. We showed that our method is robust in the sense that particle size is hardly dependent on synthesis conditions. This is attributed to the fact that the packing of surfactant on NP surface is the only parameter determining the particle size. It can only be slightly varied with ionic strength, head group hydration, and tail solvency through oil variation. Water content mainly affects ME stability and through that the colloidal stability of the NPs. Finally we highlighted the differences in comparison to NP synthesis in water-in-oil NPMEs and we propose a mechanism of particle formation, Figure 3.

Figure 3 Proposed mechanistic view of NP formation in BMEs: initially the metal ions and the reducing agent dissociate (a) and upon reaction form primary particles that are stabilized by remaining metal ions (b). When metal ions are depleted, the primary particles aggregate into larger secondary particles (c). Surfactant adsorbs on the exposed metal surfaces and particles are embedded in the ME structure, preferentially in the oil channels, thereby stabilizing them against aggregation.

Covalently, Non-Covalently and Non Functionalized Networked Graphitic Structures as robust catalyst support in PEM electrodes

CNNs result a robust catalyst support in PEM fuel cells electrodes. Pt NPs are attached to covalently, non covalently and non functionalized CNNs. The obtained catalyst activity and ECSA are tested by rotating disk electrode. ECSA decrease is tested by accelerated durability tests, cycling the potential between 0.6 and 1.2 V vs RHE. Oxidation resistance is tested by termogravimetric analysis. Pt/CNNs result more active and more durable than commercial catalyst, Figure 4. CNNs have higher oxidation resistance than other carbon supports, resulting in catalyst higher durability under fuel cell operating conditions.
Additionally, a networked structure allows for an even electrical conductivity thus reducing potential gradients in the electrode responsible of Ostwald ripening. Pt deposited over non-covalently functionalized CNNs result the most durable catalyst, due to the even distribution of monodisperse NPs, efficiently bound to the graphitic surface via $\pi-\pi$ interaction with pyrene carboxylic acid.

**Figure 4** Accelerated durability tests

*Fe-N supported over CNNs grown from Cobalt as ORR catalyst for low temperature fuel cells*

Three iron-nitrogen-containing non-noble metal electrocatalysts, supported on networked graphitic structures, here called CNNs, synthetized using a wet-impregnation method. The three CNN samples differed in cobalt content, ranging from 0.1 to 1.7 % in weight. CNN supports were used to prepare Fe-N/CNN electrocatalysts. ORR activity was evaluated by rotating disk electrode measurements. Interestingly, the ORR-performance increased proportionally to cobalt content. Our best catalyst was tested as the cathode material of a polymer electrolyte membrane fuel cell and of a direct methanol fuel cell. The maximum power achieved in single test cells, 121 mW cm$^{-2}$ and 15 mW cm$^{-2}$ respectively, **Figure 5**, was either superior than or in the same order of magnitude of what reported in similar studies. Durability to potential cycling was tested in half-cell studies and an activity loss of 20% was found after 1000 cycles.

**Figure 5** Polarization and power density curves: a) in H$_2$ single cell at 30 °C and at 60 °C, 0.1 NLPM H$_2$, 0.2 NLPM O$_2$; b) in MeOH single cell, 2 M methanol as anode feed, 100 mlO$_2$ min$^{-1}$ and 60 °C.

*This work is carried out in collaboration with Dr. Alessandro Monteverde Videla and Prof. Stefania Specchia, Politecnico di Torino, and Dr. Vincenzo Baglio, CNR ITAE, Messina.*

**Industrial collaboration until 31 December 2013**

The project has been developed in close collaboration with a TU Delft Spin-off Company, Carbon X, currently marketing CNNs.

**All output from 2013**

Presentations at International conferences and Publication in the proceedings:

1. “Networked Graphitic Structures as Durable Catalyst Support for PEM Electrodes”, Fundamentals and Development of Fuel Cells, April 2013, Karlsruhe (Germany)
2. “Covalently, Non Covalently and Non Functionalized Networked Graphitic Structures as Robust Catalysts Support in PEM Electrodes”, 224th ECS Meeting, October 2013, San Francisco (CA).
3. “Networked Graphitic Structures Grown From Dense Emulsions As High Performance Electrode Material” 224th ECS Meeting, October 2013, San Francisco (CA).
4. “Non-noble electrocatalyst supported on Carbon Nano-Networks for ORR”, European Fuel Cells Technology & Applications 2013, Piero Lunghi Conference, December 2013, Rome, Italy

**Other**

Winner of a COST – Short Term Scientific Mission Scholarship, June-July 2013, to visit the National Research Centre, CNR-ITAE, Messina (IT) to carry out in-situ and ex-situ catalyst testing.
Introduction
A detailed understanding of fuel oxidation on SOFC anodes is necessary for working with real life fuels. This will help in selection of suitable anode materials for particular fuel compositions and come up with suggestions for optimizing anode microstructure. In this work anodes of known geometry are prepared and tested. Electrochemical Impedance Spectroscopy (EIS) measurements are carried out on symmetrical cells at various temperatures and fuel compositions. The response can then be deconvoluted to obtain the various parameters giving information about contributions from diffusion, reaction etc which can be used as a basis for optimising the SOFC anode for different fuels. Realistic system parameters obtained from such studies also shall be used for development of thermodynamic concepts for high efficiency energy systems based on ITSOFCs such as ITSOFC- gas turbine systems which can produce electricity at efficiencies as high as 70-80%.

Research results from 1 January until 31 December 2013
Pattern cells with ceria/ nickel – preparation of pattern electrodes of nickel on ceria, ceria on YSZ and Nickel on YSZ, testing them with EIS

Using the tests above, preliminary modeling of reaction mechanism is undertaken to propose a reaction mechanism to adequately describe impedance obtained

Different cells were made of GDC and YSZ at Imperial college London for studying effect of microstructure on the SOFC impedance. Cells were made with varying thicknesses using screen printing. Anode microstructure was analysed by using FIB SEM tomography for the anodes (ongoing work).

Ammonia cracking measurements were performed on the symmetrical cell test station. Off gases were analysed using a Gas Chromatograph to identify amounts of nitrogen and hydrogen.

Industrial collaboration until 31 December 2013
GENSOS (http://www.gensos.nl/) had originally provided the support letter for this particular ADEM project. GENSOS has been active in the development of integrated systems for use of biomass derived syn gas. In a collaborative project a SOFC integrated supercritical gasification system is being developed to be tested at their facility (SOFC test station is commissioned and a gasifier is being commissioned). The results obtained in this ADEM project can be directly used in selecting a suitable SOFC for such a system.
All output from 2013

1. Manuscript “Ceria Electrocatalysis compared to Nickel using pattern electrodes” accepted in International Journal of Electrochemical Science Available Online (Int. J. Electrochem. Sci., 9 (2014) 4048 – 4053).

2. “Nickel Pattern anodes for studying SOFC electrochemistry” Ceramic Engineering and Science Proceedings 34, Issue 4, 2013

3. “Pattern Electrodes for Studying SOFC Electrochemistry” ECS Transactions 57 (1), 2013. 1613-1618
Introduction
This project concerns the development of a cheap and easily up-scalable technology for thin film electrolytes for solid oxide fuel cells (SOFC). The main focus will be on the synthesis and deposition of electrolyte materials, such as yttria-stabilized zirconia (YSZ; ionic conductor) and yttria-doped barium zirconate (BZY; proton conductor), in order to reduce the operating temperature to 500-700 °C. Here, one should think about the use of sol-gel techniques and chemical solution deposition techniques combined with microwave-assisted rapid thermal annealing (RTA). Furthermore, a fundamental understanding of the influence of synthesis & heat treatment parameters on the final properties of the electrolyte material are necessary.

YSZ Thin Films
YSZ thin films (60-100 nm) are prepared via sol-gel processing and subsequent microwave-assisted RTA. The films have to be isotropic and dense in order to be used as an electrolyte material. Since a real (facile) method for the determination of the thin film density was not available, a lot of effort has been put in finding a protocol to do so. Now, the densification behaviour and microstructural changes of the thin films can be measured. Depending of the density/microstructure of the thin film, the synthesis and heat treatment protocols can be adapted until the requirements for electrolyte materials are met. The final properties of the thin films can be determined by means of Impedance Spectroscopy. Increase of surface area by means of e.g. soft-lithographic patterning[1] may enhance the ionic conducting properties of the thin film.

Synthesis of Y-doped Barium Zirconate
BZY is a promising material for proton conducting fuel cells operating at intermediate temperatures, due to its high proton conductivity. However, due to the refractory nature of the material, high processing temperatures (> 1500 °C) are necessary. Leading to the degradation of its properties. Many attempts to overcome this problem are currently being investigated and described in literature. One possibility is the use of a nano-crystalline powder; high densities may be obtained at lower temperatures due to the high sinterability of the nano-sized material. Nano-crystalline BZY powder is synthesized under near-ambient conditions according to an adapted recipe for the synthesis of barium titanate.[2] The synthesis, sintering behaviour, and conducting properties will be fully investigated. The reaction mechanism of the crystalline phase formation will also be investigated for the formation of barium titanate (no dopants) with time-resolved small-angle X-ray scattering (SAXS) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

References:
[1] S.A. Veldhuis, A. George, M. Nijland, and J.E. ten Elshof, Concentration Dependence on the Shape and Size of Sol-gel Derived Yttria-stabilized Zirconia Ceramic Features by Soft Lithographic Patterning, Langmuir, 28 (42), 2012, 15111-15117.
[2] T.M. Stawski, S.A. Veldhuis, O.F. Göbel, J.E. ten Elshof, and D.H.A. Blank, Effects of Reaction Medium on the Phase Synthesis and Particle Size Evolution of BaTiO3, J. Am. Ceram. Soc. 93, 2010, 3443-3448.
Research results from 1 January until 31 December 2013

Densification YSZ Thin Films

Our proposed method for the density determination of sol-gel derived thin films, can be utilized to investigate e.g. the densification of the amorphous and crystalline phase during drying and sintering, respectively. But also the influence of the substrate strain on the densification behaviour see Figure 1.

Figure 11: Densification of a 3YSZ thin film on a SiO$_2$ and Al$_2$O$_3$ substrate after annealing for 1 h at various temperatures.

Synthesis of Y-doped Barium Zirconate

Nano-crystalline (10-20 nm) BZY has been prepared at temperatures < 150 °C via a sol-gel alkoxide-hydroxide precipitation method. Dilatometry measurements show that the nano-sized grains are highly sinteractive, and densities > 95% have been obtained at 1350 °C. Also, thermogravimetric analysis (TGA) showed hydration behaviour (i.e. incorporation of OH-defects, necessary for proton conduction). The main advantage of a sol-gel approach for the synthesis of this material is that incorporation of OH-defects, inherent to the sol-gel reaction and normally a negative effect, might lead to an enhanced performance.

Reaction Mechanism of Barium Titanate Formation

The formation of nano-crystalline barium titanate (BTO) between 23-78 °C in benzyl alcohol has been investigated using Density Functional Theory (DFT) simulations and various experimental characterization techniques. The computational models agreed well with our experimental data. The benzyl alcohol solvent plays an active role in the stabilization of the Ti precursor (i.e. ligand exchange; steric hindrance) and forms a “capping layer” on the as-formed crystallites. This effect in independent of temperature and results in a finite size of the BTO crystallites Figure 2.

Figure 12: (a) Crystallite size distribution of BTO synthesized at temperatures between 23-78 °C; (b) A dense “capping layer” is formed due to a lower surface curvature at larger crystallite size. The finite size is reached.

Ongoing research focuses on the time-resolved evolution/crystallization/growth of the crystallites using SAXS. Knowledge of the reaction mechanism may help to optimize the reaction conditions for the synthesis of BZY.
International collaborations until 31 December 2013
Collaborating with Dr. A. George (Rice University, Houston TX, USA), Dr. T.M. Stawski (University of Leeds, Leeds, UK), and Dr. S. Guillemet-Fritsch (Paul Sabatier University, Toulouse, France)

All output from 2013
Articles:
1. S.A. Veldhuis, P. Brinks, T.M. Stawski, O.F. Göbel, and J.E. ten Elshof, *A Facile Method for the Density Determination of Ceramic Thin Films using X-ray Reflectivity*, J. Sol-Gel Sci. Technol., 2014, DOI: 10.1007/s10971-14-3336-2.
2. S.A. Veldhuis, W.J.C. Vjiselaar, T.M. Stawski, and J.E. ten Elshof, *The Formation of Nano-crystalline Barium Titanate in Benzyl Alcohol at Room Temperature*, 2014, submitted.
Oral Presentation:
3. S.A. Veldhuis, W.J.C. Vjiselaar, T.M. Stawski, and J.E. ten Elshof, *Reaction Mechanism of the Direct Formation of Nano-crystalline Barium Titanate at Room Temperature*, NWO-CW Meeting, Veldhoven, The Netherlands (Invited, February 10-11, 2014).
Poster presentation:
4. S.A. Veldhuis, W.J.C. Vjiselaar, T.M. Stawski, and J.E. ten Elshof, *Reaction Mechanism of the Room Temperature Formation of Nano-crystalline Barium Titanate*, Sol-Gel 2013, Madrid, Spain (August 25-30, 2013).
Batteries

Today, Li-ion batteries provide the highest energy density of all existing systems. However, most car manufacturers agree that the Li-ion technology is still not satisfactory for long distance EV use (TNO Automotive, HTAS). Higher energy density, reduced costs and improved safety are needed (NXP, Philips). This also concerns rechargeables for medical applications (NXP, Philips). We will carry out research to (I) develop new generations Li-ion batteries delivering roughly twice the energy density and to satisfy the safety requirements of today’s systems, and (II) step in new or relatively unexplored directions if we are to significantly increase energy storage beyond Li-ion, like, e.g. solid-state, Lithium-sulfur, or Lithium-air batteries. These post Li-ion cells offer higher energy storage than Li-ion, but none is a technology at the present time, and hence, are worthy of further study in order to establish their capabilities. Without such studies it will be impossible to determine which ones, if any, could become a viable commercial technology.

The proposed projects

Within the ADEM battery theme, six projects have been accepted to be carried out, and one project (A) has been adjusted and send to the ADEM Program Board being:

A (TUD-P11). Impact of nanosizing on Li-ion insertion electrode materials
B (TUD-P13). Stable high capacity battery anodes
C (TUD-P12). Protective coatings for Si nanoparticles as Li-air anode materials made via combination of laser-assisted chemical vapour pyrolysis and electro-spraying
D (TUD-P21). Modeling rechargeable batteries for future Plug-in (Hybrid) Electrical Vehicles
E (TUD-P22). Sensorless temperature measurements leading to advanced Battery Management Systems
F (TUE-P06). Thin film deposition of battery materials on 3D (nano)structures
G (TUD-P20). High energy density electrode materials for conventional and thin film Li-ion batteries

Due to the situation of future battery research at TU Eindhoven, TU Delft has implemented the projects D, E and G in their research programme, whereas F will stay at the TU Eindhoven.
**Industrial involvement**

Valorisation of and industrial involvement in the proposed work are two of the major tasks concerning the use of the results. In that regard, the interdisciplinary research is characterized by four important features (Note that the interested industries are mentioned between brackets):
- fundamental science (NXP)
- modelling (NXP, Philips)
- materials development and fabrication (Euro Support, Tata Steel, Norit, Süd-Chemie, Roth&Rau, Tempress, Oxford Instruments, Sabic)
- system testing and evaluation (Comibol, IMEC, HTAS).

**Planning**

Most projects within the refreshed start of this theme will start somewhere in 2014. Furthermore, the theme coordinator will further explore and exploit the results of the theme by attracting more industrial interest, and keeping the already involved industries updated.

**Theme Coordinator**

Dr. Erik Kelder

Delft University of Technology

Photo: Roy Borghouts
# Financial Report 2013

## Financiële voortgang ADEM programma

**status per:** 31-12-13  
**rapportdatum:** 31-12-13

| ID code | partner onderzoek/investering | Katalyse/membranen | Batterijen | Fuel-cells | Wind | Warmte | Solar | Aproved Budget* | Aproved Changes | Budget at Completion | Acuals & Obligations |
|---------|--------------------------------|--------------------|-----------|------------|------|--------|-------|----------------|-----------------|---------------------|----------------------|
| ECN     |                                |                    |           |            |      |        |       | 8.500.000       |                 |                     | 4.662.315            |
| ECN-I02 | HP/DSC/TG + OmniStar Mass Spectrometer |            |           |            |      |        |       | 280.000         | 47.875           | 327.875             | 327.875              |
| ECN-I04 | Micro-calorimeter              |                    |           |            |      |        |       | 300.000         | 54.286           | 245.714             | 245.714              |
| ECN-I06 | Vaste-stof NMR (300 MHz)       |                    |           |            |      |        |       | 300.000         | 22.000           | 178.000             | 5.997                |
| ECN-I07 | Solar module characterisation  |                    |           |            |      |        |       | 500.000         | 98.460           | 598.460             | 598.460              |
| ECN-I08 | PS laser (Pharos) met *R2R* optie |                |           |            |      |        |       | 450.000         | 83.333           | 533.333             | 530.372              |
| ECN-I09 | HR/VEG-SEM/EDX/EBSD            |                    |           |            |      |        |       | 280.000         | 47.875           | 327.875             | 327.875              |
| ECN-I10 | Scanning Electron Microscope   |                    |           |            |      |        |       | 500.000         | 98.460           | 598.460             | 598.460              |
| ECN-I11 | XRD                            |                    |           |            |      |        |       | 400.000         | 400.000          |                     |                     |
| ECN-I12 | E-beam evaporation system      |                    |           |            |      |        |       | 350.000         | 100.000          | 250.000             | 250.000              |
| ECN-I13 | Quantachrome Autosorb IQ-C     |                    |           |            |      |        |       | 180.000         | 180.000          | 180.000             | 180.000              |
| ECN-I15 | Facility sharing ECN           |                    |           |            |      |        |       | 1.000.000       | 464.520          | 535.480             |                     |
| ECN-I16 | Testfaciliteit windturbinebladen 22.000 KNewton |      |           |            |      |        |       | 2.250.000       | 2.004.705        | 98.325              |                     |
| ECN-I17 | High-throughput experimentation |                    |           |            |      |        |       | 1.000.000       | 581.000          | 1.462.500           |                     |
| ECN-I18 | Pyroprobe GC-MS (Da Vinci Europe) |                 |           |            |      |        |       | 1.300.000       | 31.600           | 31.600              |                     |
| ECN-I19 | Linear VHF plasma source       |                    |           |            |      |        |       | 1.000.000       | 100.000          | 100.000             |                     |
| ECN-I20 | OptoSolar Spectrale Response with light bias |       |           |            |      |        |       | 1.000.000       | 1.581.000        | 1.462.500           |                     |
| ECN-I21 | Infrastructure ADEM Green Deal |                    |           |            |      |        |       | 1.000.000       | 1.581.000        | 1.462.500           |                     |
| ECN-I22 | Hoge Temperatuur HD cell       |                    |           |            |      |        |       | 1.000.000       | 1.581.000        | 1.462.500           |                     |
| ECN-I23 | Nader in te vullen en onvoorzien |                |           |            |      |        |       | 1.633.000       | 1.633            | 1.633               |                     |
| TUD-I01 | 500-600 MHz vaste stof NMR     |                    |           |            |      |        |       | 3.122.000       | 854.143           |                     |                     |
| TUD-I02 | Variabele temperatuur AFM/STM  |                    |           |            |      |        |       | 1.300.000       | 141.726          | 1.158.274           |                     |
| TUD-I03 | Thermodynamisch lab            |                    |           |            |      |        |       | 372.000         | 40.555           | 331.445             |                     |
| TUD-I04 | Spectroscopie voor zonnecellen |                    |           |            |      |        |       | 600.000         | 65.412           | 534.588             | 402.990              |
| TUD-I05 | CVD depositekamer voor siliconfilms |           |           |            |      |        |       | 150.000         | 16.353           | 133.647             | 151.153              |
| TUD-I06 | Diepte-gevoelige positron levensduuropstelling |       |           |            |      |        |       | 300.000         | 32.706           | 267.294             |                     |
| TUD-I07 | Infrastructuur voor ps/fs metingen |              |           |            |      |        |       | 300.000         | 32.706           | 267.294             |                     |
| ID code | partner onderzoek/investering | Katalyse/membranen | Batterijen | Fuel-cells | Wind | Warmte | Solar | Aproved Budget | Aproved Changes | Budget at Completion | Acuals & Obligations |
|---------|-------------------------------|--------------------|------------|------------|------|--------|-------|----------------|-----------------|-----------------------|---------------------|
| TUE-01  | NMR upgrade 200 MHz          |                    |            |            |      |        |       | 2.901.000      | 316.267-         | 2.584.733             | 1.392.573           |
| TUE-02  | XRD –diffractometer          |                    |            |            |      |        |       | 650.000        | 650.000-         | -                     | -                   |
| TUE-03  | XPS (0.5 micron resolution) + glovebox |            |            |            |      |        |       | 600.000        | 13.482-          | 589.482              | 563.200             |
| TUE-04  | Combinatorial sputter depositieopstelling |        |            |            |      |        |       | 650.000        | -                | 650.000              | -                   |
| TUE-05  | Combined Oxford Instruments CVD/ALD |            |            |            |      |        |       | 576.000        | 13.482            | 589.482              | 563.200             |
| TUE-06  | Reële schaal opslagopstelling |                    |            |            |      |        |       | 50.000         | 5.451-            | 44.549               | -                   |
| TUE-07  | Chemical Looping apparatuur  |                    |            |            |      |        |       | 125.000        | 13.482-          | 111.373              | 89.447              |
| TUE-08  | Chemical Looping apparatuur  |                    |            |            |      |        |       | 125.000        | 13.482-          | 111.373              | 76.508              |
| TUE-00X | nader in te vullen / AI Batteries |                |            |            |      |        |       | -              | 380.066          | 380.066               | -                   |
| UT-01   | Carbon nanofibers apparatuur |                    |            |            |      |        |       | 130.000        | 51.000            | 181.000              | -                   |
| UT-02   | High-end thermobalans        |                    |            |            |      |        |       | 125.000        | 81.000-          | 44.000               | -                   |
| UT-04   | Katalysatoren voor duurzame brandstoffpr. |            |            |            |      |        |       | 250.000        | 77.500-          | 172.500              | 33.803              |
| UT-05   | TGA-DSC + MS (kwantitatief)  |                    |            |            |      |        |       | 250.000        | 107.000-        | 143.000              | -                   |
| UT-06   | Oxy-fuel conversie in membraan reactoren |        |            |            |      |        |       | 200.000        | 41.000-          | 159.000              | 95.670              |
| UT-07   | AFM                           |                    |            |            |      |        |       | 200.000        | 70.000-          | 130.000              | -                   |
| UT-08   | Laserbundel-manipulatiesysteem |               |            |            |      |        |       | 200.000        | 21.804-          | 178.196              | -                   |
| UT-09   | XRF                           |                    |            |            |      |        |       | -              | 199.582          | 199.582              | -                   |

| Promovendi | 14.075.000 | 14.075.000 | 7.172.958 |
| ECN        | 1.050.000  | 1.050.000  | 991.666   |
| TU Delft   | 5.250.000  | 5.250.000  | 2.717.120 |
| TU Eindhoven | 4.200.000  | 4.200.000  | 1.553.754 |
| Universiteit Twente | 3.575.000  | 3.575.000  | 1.910.418 |

| Programmabureau | 1.888.000 | 109.980- | 1.778.020 | 644.812 |
| PMO-1 Managementteam | 913.000   | 80.959-  | 832.041  | 384.709 |
| PMO-2 Communicatie | 380.000   | 11.319-  | 368.681  | 142.189 |
| PMO-3 Act. t.b.b. verbetering NL industr. Innovatie | 300.000 | 8.936-  | 291.064  | 60.397 |
| PMO-4 Facility sharing | 175.000   | 5.213-  | 169.787  | 57.517 |
| PMO-5 Kwaliteitsbewaking | 20.000 | 2.959-  | 19.041  | - |
| PMO-6 Onvoorzien | 100.000 | 596-  | 19.404  | - |

| Totale kosten realisatie ADEM programma | 31.841.000 | 1.841.000- | 30.000.000 | 14.856.274 |

| Industriële bijdragen | 721.000 | 721.000 | 500.000 |
| Katalyse/membranen | 211.000 | 211.000 | - |
| Batterijen | 582.000 | 582.000 | - |
| Fuel-cells | 390.000 | 390.000 | - |
| Wind | 290.000 | 290.000 | 84.737 |
| Warmte | 806.000 | 806.000 | 990.636 |

| Totale industriële bijdragen | 3.000.000 | 3.000.000 | 1.575.373 |

*)c.f. ADEM-programma d.d. 05-06-2009
ADEM Program Board

- Herman Kuipers (Shell Global Solutions) – chair
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- Tim van der Hagen (TU Delft)
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- Leo Warmerdam (NXP Semiconductors)
- Ernst Grannemen (Levitech)
- Kees van der Klauw (Philips)
- Albert Hasper (Tempress Systems)

ADEM Theme Coordinators 2013

- Fuel Cells: Steven Picken, Delft University of Technology
- Wind: Rinze Benedictus, Delft University of Technology
- Catalysis, Membranes and Separations: Arian Nijmeijer, University of Twente
- Heat: Anton van Steenhoven, Eindhoven University of Technology
- Solar: Miro Zeman, Delft University of Technology
- Batteries: Erik Kelder, Delft University of Technology

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- Emanuela Negro, Delft University of Technology
- Taha Jibril Taha, University of Twente
- Tim Westphal, Knowledge Centre WMC
| Projectcode | Titel | Aanvangers | Organisatie | Toekenning |
|-------------|-------|------------|-------------|-----------|
| TUD-P11     | TUD-P11/Impact of nanosizing on Li-ion insertion electrodes materials | Dr. Ir. M. Wagemaker, Dr. E.M. Kieries, Prof. Dr. J.M. Mulder | TU Delft | € 350,000 |
| TUD-P13     | TUD-P13/Stable high capacity battery anodes | Dr. Ir. M. Wagemaker, Dr. E.M. Kieries, Prof. Dr. J.M. Mulder | TU Delft | € 350,000 |
| TUD-P12     | TUD-P12/Protective coatings for Silicon nanoparticles as Li-air anode materials made via combination of laser-assisted chemical vapour pyrolysis and electro-spraying | Dr. Ir. M. Wagemaker, Dr. E.M. Kieries | TU Delft | € 350,000 |
| TUD-P21 (voorheen TUE-P08) | TUE-P08/Modeling rechargeable batteries for future Plug-in (Hybrid) Electrical Vehicles | Prof.dr.ir. W.M.M. Kessels, Prof.dr.ir. P.H.L. Notten | TU Eindhoven | € 350,000 |
| TUE-P06     | TUE-P06/Thin film deposition of battery materials on 3D (nano)structures | Prof. dr. ir. J.H. M. Kelder, Dr. E.M. Kieries | TU Delft | € 350,000 |
| TUE-P22 (voorheen TUE-P13) | TUE-P13/Sensorless temperature measurements leading to advanced Battery Management Systems | Prof. Dr. F.M. Mulder | TU Delft | € 350,000 |
| TUE-P23 (voorheen TUE-P07) | TUE-P07/High energy density electrode materials for conventional and thin film Li-ion batteries | | | | |
| TUD-P09     | TUD-P09/Design of stable metal membranes for hydrogen separation from gas mixtures | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger | TU Delft | € 350,000 |
| UT-P06      | UT-P06/Catalysts for sustainable fuels production in hot compressed water: H2 production from aqueous biomas streams | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger | TU Delft | € 350,000 |
| UT-P10      | UT-P10/Determination of the degradation mechanism of hybrid and organically modified silica membrane | Prof. Dr. ir. Andre ten Elshof | TU Eindhoven | € 350,000 |
| TUE-P05     | TUE-P05/HP/ISORP - Sorbent Development on the Basis of Kinetics, and Mass- and Heat- Transport Phenomena in Sorption-Enhanced Processes at Elevated Temperatures | Prof. Dr. ir. Andre ten Elshof, Prof. Dr. H. Hensen, Fausto Galuzzi, Paul Cobden (ECN) | TU Eindhoven | € 350,000 |
| TUE-P04     | TUE-P04/Multi-layer drying processes of thin separation layers on macro-porous substrates | Prof. G. Pol, Prof. Dr. H.P. Hulin, Prof. Dr. ir. D.M.J. Smolders | TU Eindhoven | € 350,000 |
| UT-P04rev   | UT-P04rev/Warmteoverdracht naar micro en nano-gestructurede diepvlekkeren | Prof. Dr. ir. Th. J. van der Meer, Prof. Dr. ir. L. Lefferts | TU Eindhoven | € 300,000 |
| UT-P12      | UT-P12/Solar cell surface engineering | Prof. Dr. ir. Th. J. van der Meer, Prof. Dr. ir. L. Lefferts | TU Eindhoven | € 300,000 |
| TUD-P18 (voorheen TUE-P10) | TUD-P10/Implantation and low-temperature diffusion steps for solar cells and light sensors | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger (Tempress Systems), Prof. Dr. E. Cherba, Prof. Dr. G. de With, Dr. H. Friedrich | TU Delft | € 350,000 |
| TUE-P11     | TUE-P11/Analysis of 3D volume organization of polymer-based photovoltaic devices | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger (Tempress Systems), Prof. Dr. E. Cherba, Prof. Dr. G. de With, Dr. H. Friedrich | TU Delft | € 350,000 |
| TUD-101     | TUD-101/600-600 MHz and NMR 500 MHz on ADEM Facilities | Prof. Dr. R. van den Berg, Prof. Dr. ir. W.G. Siofo | TU Delft | € 1,518,274 |
| ECN-114     | ECN-114/Ion Implanter | Prof. Dr. ir. W.G. Siofo | ECN | € 1,100,000 |
| TUD-107     | Thin-film position annihilation lifetime spectrometer POM-PALS for advanced characterization of defects and nanostructure of thin film solar cell layers | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger (Tempress Systems), Prof. Dr. H. Schut, Prof. Dr. M. Zeman | TU Delft | € 89,000 |
| TUE-106     | Reliëf schaal oplossing | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger (Tempress Systems), Prof. Dr. H. Schut, Prof. Dr. M. Zeman | TU Eindhoven | € 44,500 |
| UT-109      | Herelocatie UT-101 tot UT-108: XRF toplining | Prof. Dr. ir. W.G. Siofo, Dr. A.J. Böttger (Tempress Systems), Prof. Dr. H. Schut, Prof. Dr. M. Zeman | TU Eindhoven | € 199,500 |
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A green Deal in Energy Materials

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