Annual report
2012

Innovation Lab
A green Deal in Energy Materials
In the course of 2012 the PhD students in the ADEM program have been very productive and the already installed new infrastructure has been intensively utilized. Meanwhile, ADEM as an organization has experienced a few major changes.

At the end of the summer, former scientific director Wim Sinke has transferred his directorship to me, while the management office was transferred from Kenneth Heijns to Herman Schoffelen. Fortunately, when Wim Sinke stepped down, the financing scheme had been agreed upon by the Ministry of Economic Affairs and the program was in a fully operational state. ADEM was transformed into a Green Deal already in 2011. We kept the acronym ADEM to express the continuity but renamed the program as “A green Deal in Energy Materials”. In October 2012, we received written commitment from the Ministry of Economic Affairs that ADEM receives the means to continue the complete Program as intended.

The main goals of ADEM are to:
1. accelerate the “greening” of our economy, and at the same time:
2. produce economic benefit from the innovations resulting from materials research and turn them into applications in sustainable energy technology.

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 will take place are Wind energy, Solar cells and modules, Batteries, Transport, transfer and storage of heat, Catalysis, membranes and separations, and Fuel cells.

The industrial commitment to stimulate innovation and economic productivity is guaranteed by contributions to the ADEM program and research infrastructure for an amount of at least 10% of the total program, cash or in kind. At the same time, this is also a prerequisite for the 30 M€ of total funding from the Ministry. In the third quarter of 2013, we aim to demonstrate that the program is on track, showing public-private partnership in the required proportions.

We have remodeled the www.adem-innovationlab.nl website and logo design to reflect the Green Deal status and we started issuing newsletters every 6 weeks. ADEM partners are sharing each other’s expertise as well as the unique modern laboratory tools, for optimal progress in our quest to resolve pressing energy challenges. This progress is made possible by the talented researchers in our ADEM projects, building on the shared infrastructure. This annual report shows their scientific progress and their supporting action towards industrial innovations for a sustainable energy economy.

Prof. dr. Ruud Schropp, Scientific Director
## Preface

### Transport, Transfer and Storage of Heat

- **Project:** Characterization of water vapor sorption process in salt hydrates for seasonal heat storage application
- **Project:** Development of micro- and meso-scale models for heat and vapor transport in storage materials
- **Project:** Designer Sorbents - Structured systems for heat pumps
- **Project:** Heat transfer to micro- and nano-structure surfaces

### Wind Energy

- **Project:** New Materials for Wind Turbine Blades
- **Project:** Thick laminates
- **Project:** Integral material models for composites

### Solar Cells and Modules

- **Project:** Mechanism of energy and charge transport in advanced photovoltaic materials
- **Project:** Advanced passivation schemes for crystalline silicon solar cells
- **Project:** Luminescent thin films for photovoltaic applications
- **Project:** Advanced nanostructured silicon-based films for stable absorber layers
- **Project:** Materials Behaviour of Multicrystalline Silicon Solar Cells
- **Project:** Laser material interactions for PV applications
- **Project:** Silicon based nano-particles for efficient solar-spectrum conversion in all-silicon tandem cells

### Catalysis, Membranes and Separations

- **Project:** CO₂ Capture with Ionic Liquids
- **Project:** Hydrogen from biomass via catalytic steam reforming of flash-pyrolysis oil: how to enhance the activation of water? 1
- **Project:** Hydrogen from Biomass via catalytic steam reforming of flash-pyrolysis oil: how to enhance the activation of water? 2
- **Project:** Fundamentals of Chemical Looping for Biomass Processing
- **Project:** Mixed-conducting ceramic membranes for oxyfuel conversion
- **Project:** Hybrid silica membranes for oxy-fuel conversion membrane reactors
- **Project:** Chemical Looping Processes to Improve the Performance of Indirect Fluid-Bed Gasification Technology

### Hydrogen Production and Fuel Cells

- **Project:** Super ionic composite membranes for PEMFC
- **Project:** Robust Anodes for SOFC
- **Project:** Carbon Nano-Networks for PEM Electrodes
- **Project:** Fuel oxidation on ITSOFC anodes and its influence on system performance
- **Project:** Thin Film Electrolyte Manufacturing Technology for SOFC and SOEC

### Batteries

### Financial Report 2012

### Colophon
Transport, Transfer and Storage of Heat
Transport, Transfer and Storage of Heat

Introduction
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 Thermo-Gravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC) measurements), strongly enhances the coherence within the theme.

Our 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 there 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 heat storage with sugar-alcohols has been submitted by TU Eindhoven in the EU FP7 program.

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 Neft/Bosch) and applications for heat storage at ESSENT/TATA Steel at TU Eindhoven.

Theme coordinator
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 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 vapor 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, with a temperature below 150°C, which is the maximum temperature a solar collector can provide. 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 practical conditions, the hydration process takes place at a low water vapor pressure, about $p(H_2O) = 13$ mbar, which corresponds to the temperature of water in a borehole at 10°C during the winter (figure 1).

Figure 1: Representation of the practical conditions of the (a) dehydration and (b) hydration reactions taking place in the seasonal heat storage system based on the water vapor sorption process in salt hydrates.
In order to develop adequate sorption materials for this application, this project focuses on establishing the effect of structural and material properties on the heat- and vapor transport taking place at different scales in the material (crystal, grain and powder bed) during this process. Within this line of research, some experiments have been carried out on powder samples and monocrystals of two reference materials Li₂SO₄·H₂O and CuSO₄·5H₂O to characterize their simple and well established water vapor sorption process under the practical conditions of the seasonal heat storage. Next, these experiments have been extended to the two thermochemical materials MgSO₄·7H₂O and MgCl₂·6H₂O, selected at ECN as promising thermochemical materials for this application.

Research results until 31 December 2012
The two salt hydrates MgSO₄·7H₂O and MgCl₂·6H₂O, selected prior to this study for their high theoretical energy densities, showed promising performances under operating conditions of seasonal heat storage. MgSO₄·7H₂O can reach a storage density in packed bed around 1 GJ/m³ during the charging phase of the material. However, the slow kinetics of reactions of the material under the operating conditions showed a low heat release during the heat discharge. MgCl₂·6H₂O can store and release heat with fast kinetics of reaction at adequate operating temperatures with a storage density around 0.8 GJ/m³. However, the material presents some issues for a long term chemical stability. Presently, a modification of the material properties of these two salt hydrates and an adjustment of the operating conditions are carried out to improve their long term storage capacity.

Industrial collaboration until 31 December 2012
The objective of the present research project is to obtain fundamental knowledge on the water vapor 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 vapor 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.

Figure 2: In-situ microscopic observations of the dehydration process of (a) a Li₂SO₄·H₂O monocrystal and (b) a CuSO₄·5H₂O monocrystal under a water vapor pressure of 13 mbar.
All output from the beginning until 31 December 2012

- C.J. Ferchaud, H.A. Zondag, C.C.M. Rindt, A.A. van Steenhoven, S. Spoelstra, and M. Bakker, Salt hydrates as TCM for seasonal heat storage, sixth experts meeting of task 42 in the IEA - SHC program, on “Compact Thermal Energy Storage Material Development and System Integration”, 20-22 September 2011, Minneapolis, US.
- C.J. Ferchaud, H.A. Zondag, C.C.M Rindt and M. Bakker, Salt hydrates as TCM for seasonal heat storage, Eurotherm Seminar 93 on Thermal energy storage and transportation: materials, systems and applications, 16-18 November 2011, Bordeaux, France. analyses, Raman spectroscopy and FTIR to clearly understand the phase transitions of these materials during (de)hydration processes.
Introduction
Thermo-chemical heat storage technique has great potential in the application of 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 strongly fluctuating. 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.

Figure 1: Schematic illustrations of heat and mass transfer processes.
Research results until 31 December 2012

- A report about different numerical methods for porous media simulations and different kinetic models is finished. Traditional CFD methods with body-fitted meshes are chosen to be used for the mass and heat transfer in the porous media.
- A kinetic model to describe the surface nucleation and isotropic growth processes on grain scale is developed in Matlab. The advantages of this model are that it is applicable to arbitrary grain geometries in principle, and also valid in non-isothermal and non-isobaric situations. Validation is performed by comparison to an analytical solution using the Mampel model with spherical shaped particles and an experiment is performed on the dehydration of lithium sulfate monohydrate in the cooperation with ECN.
- A conference paper about validations of the kinetic model is written and accepted by the 2nd International Conference on Sustainable Energy Storage.

Industrial collaboration until 31 December 2012

- The experimental work within this project is carried out by C. Ferchaud on the site of the Energy research Centre of the Netherlands (ECN).
- The Energy Technology group is participating in a KIC-project on storage. One of the work packages is defined on a more effective use of solid sorption materials for cooling. This work is carried out in close collaboration with De Beijer RTB, Duiven, developing a solid sorption cooling machine, the Solabccool.

Figure 2: Evolution of dehydration process of a Li₂SO₄·H₂O crystal both from experiment (top) and simulation (bottom).
All output from the beginning until 31 December 2012
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 adsorption 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 with conventional electricity-driven counterparts and 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).

Research results until 31 December 2012
The adsorption of polar vapors water and methanol on mesoporous Metal Organic Frameworks MIL-100(Cr)[2] and MIL-101(Cr)[3], two potential candidates for adsorption driven heat pumps, has been studied in a combined experimental and simulation approach. Results undoubtedly demonstrate that both adsorbate-adsorbent and adsorbate-adsorbate interactions rule the adsorption process. At low loadings, before all coordinatively unsaturated chromium sites are occupied, the MOF structure determines the shape of the isotherm and the molecular model for the polar sorbate is less important. A clear difference is found between fully fluorinated and hydroxylated MIL-101 structures for both methanol and water, demonstrating that partial charges on chromium drive the initial shape of the isotherm. At higher loadings, adsorbate-adsorbate interactions become much more important and the choice of especially the water model is crucial for the agreement between experimental and simulated results. The simplest SPC/E model reproduces experimental results with the best accuracy, in contrast to more advanced models like TIPSPEw, explained by the slightly stronger Coulombic interactions predicted by the former.
For methanol the general TraPPE force field performs well. A composite type IV isotherm for methanol and a composite type V isotherm for water, according to the IUPAC classification have been found. The heats of adsorption are in line with these conclusions. This effect has, to the best of our knowledge, not been observed in adsorption in microporous materials and highlights the complexity behind molecular simulations in periodic meso-structured materials. Lastly, a general adsorption mechanism could be deduced, as shown in Figure 1 for methanol. At low loadings, methanol adsorbs at uncoordinated chromium sites. At slightly higher loadings, molecules start clustering around these chromium sites. If loading is increased further, methanol will “condense” in the porous cavities of the material, starting with the smaller of the two.

References

Industrial collaboration until 31 December 2012
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.

Figure 1: Water (using the SPC/E model) located in (left) medium and (right) large cages as a function of pressure. The top, middle, and bottom structures are for 1 Pa, 15 kPa, and 30 kPa, respectively.
All output from the beginning until 31 December 2012

- De Lange, M.F., Gascon, J., Vlugt, T.J.H., Kapteijn, F., Metal-organic frameworks in heat transfer applications, ADEM conference 26-27 May 2011, oral presentation
- De Lange, M.F., Gascon, J., Vlugt, T.J.H., Kapteijn, F., Metal-organic Frameworks in heat pump applications, 5–7 March 2012, poster presentation
- M. F. De Lange, J.J. Gutierrez-Sevillano, S. Hamad, T.J. H. Vlugt, S. Calero, J. Gascon, and F. Kapteijn, Adsorption of polar vapors on mesoporous MOFs: Combination of experiments and simulations, The XXXVII Iberian Adsorption Meeting (Reunión Ibérica de Adsorción, RIA), 12–14 September, 2012, oral presentation
- M. F. De Lange, J.J. Gutierrez-Sevillano, S. Hamad, T.J. H. Vlugt, S. Calero, J. Gascon, and F. Kapteijn, Adsorption of polar vapors on mesoporous MOFs: Combination of experiments and simulations, 3rd International Conference on Metal-Organic Frameworks and Open Framework Compounds”(MOF 12), 16–19 September, poster 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 plays 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. Development of new materials using CNFs is a technological breakthrough in minimizing the exergy losses in heat exchangers. For instance, in thermo-acoustic and thermo-chemical heat pumps which have a large influence on their final application.

The aim of the project is to study in depth the effect of carbon nano-fibers deposited on heat transfer surface for heat transfer to/from a fluid. Polycrystalline Ni wire (99.9%, Ni270), made by wire drawing mechanism, with a uniform diameter of 50 μm was used in this study to represent a differential strand of common regenerator element such as wire mesh, see figure 1. The surface of the wire was modified by depositing carbon nano structural layer. At first materials are synthesized in a very controlled manner by growing carbon nano-fibers with in situ measurements of the weight increase. Heat transfer to/from the new materials will be determined experimentally. Structural and morphological effect of the CNFs on heat transfer will be studied and optimal configuration will be derived.
**Research results until 31 December 2012**

**CNFs Synthesis and characterization:**
Three different sample synthesis procedure were designed to obtain different CNFs topological structure. It was designed by indicating three different synthesis temperatures (500°C, 600°C and 700°C). However, samples produced undergo similar pretreatment in order to have relatively equal number of nucleation sites where carbon nano structures deposit. The samples synthesized at 500°C, 600°C and 700°C with respect to the synthesis duration will be referred throughout the report as “5-60”, “6-60” and “7-30” respectively.

Figure 1: Heat transfer surface modification of wire mesh regenerator material. (a) wire mesh regenerator material, (b) a differential strand of the wire mesh is used to investigate heat transfer performance, (c) carbon nano-fibers layer synthesized [(b→c)] on the surface of the micro wire using catalytic vapor deposition process and, (d) densely populated porous layer of carbon nano-fibers.
Figure 2: SEM images of surface morphology of CNFs layer produced on 50 μm Nickel wire. (a) densely populated CNFs layer grown at 500°C for 1 hr which is made up of smaller fibers as small as 8 nm diameter entangling larger ones (~100 nm). (b) CNFs layer produced at 600°C for 1 hr with a relatively open CNFs layer, and (c) CNFs layer grown at 700°C for 30 min have rougher morphology and open CNFs structures as well.
Samples with different surface morphology of the CNFs layer was successfully achieved. The CNFs layer thickness on average $55\,\mu m$, $59\,\mu m$ and $19\,\mu m$ for growth temperature of $500^\circ C$, $600^\circ C$ and $700^\circ C$ respectively. However, the range of diameter of the individual fibers is different for the three samples. The average diameter increased with synthesis temperature. SEM image shows that the ‘5-60’ sample is made up of large strand of fibers (~120 nm) entangled with small fibers (as small as 8 nm) which increases the density of the fibers population. Sample ‘6-60’ shows relatively open CNF morphology, compared to the ‘5-60’, with fibers diameter ranging from 30 nm to 120 nm, see Fig. 2-a and 2-b. Sample ‘5-60’ and ‘6-60’ are entirely covered with CNFs layer while ‘7-30’ is partly covered with fibers and partly with amorphous layer of carbon (Fig. 2-c). The layer density of the CNFs layer was compared among the samples with weight of carbon deposit per deposit layer thickness. The amount of carbon deposited on sample ‘5-60’ is ~85% larger than sample ‘6-60’ while the layer thickness of the ‘5-60’ is ~7% less than sample ‘6-60’. This supports the previous argument, deduced from the SEM image in Fig. 2. However, ‘7-30’ results shows an entirely different CNFs layer morphology compared to the ‘5-60’ and ‘6-60’. Sample ‘7-30’ exhibit larger fiber diameter, as thick as 200 nm. The thermal conductivity of the carbon nano structures is dependent on how the graphene is arranged structurally, the diameter and the length of the filaments, the number of structural defects and morphology, and on the presence of impurities. So as to measure the degree of structural order of materials, Raman spectroscopy was applied. Two clear bands are visible for all samples, centered between ~1335 and ~1586 cm$^{-1}$ which indicate the layer is indeed covered with CNFs. The ratio of the relative intensity of the D-band and G-band ($I_D/I_G$) can be utilized to assess the degree of graphitization and the alignment of the graphene planes. As a result, the relative intensity ratio can help in comparing the relative conductivity difference that could exist among the samples made. Results shows that the thermal conductivity of the CNFs layer can be rated as ‘7-30’ > ‘5-60’ ≥ ‘6-60’.

**Heat transfer results:**

Heat transfer measurement were made by controlled dissipation of heat from the micro wire. This measurement method is similar to the common hot wire anemometry calibration technique. The porosity and permeability are important parameters to anticipate the amount of flow penetration to the CNFs layer. Due to the curvature effect of the CNFs covered samples, the porosity and flow permeability increases in the radial direction. This fact creates a region inside CNFs sub-layer, depending on the sample layer morphology, where no flow can penetrate. If the CNFs layer is not permeable to flow, it creates pockets of air which acts as an insulating layer, Hence lower heat transfer. Conversely, if the CNFs layer is permeable to fluid flow, the heat exchanging area increases, therefore higher heat transfer can be achieved. However, it is important to realize that the CNFs layer produced exhibit both the above mentioned surface characteristics.

Lower heat transfer performance was achieved for the ‘5-60’ due to less flow permeability created by the dense CNFs layer morphology. However, heat transfer enhancement was achieved for the ‘6-60’. High heat transfer performance of ‘6-60’ (24%) compared to ‘5-60’ (~26%) is explained by the fact that it has less dense and open structure which acquires better flow permeability, hence higher surface area for heat exchange. The different morphology of the sample ‘7-30’ helped to attain heat transfer enhancement of 34%, attributed to the combined effect of rough and conductive layer of carbon nanofibers which disturbs the flow boundaries across the wire and increase surface area for heat transfer.
**All output from the beginning until 31 December 2012**

Introduction

This annual report 2012 of the ADEM theme Wind Energy presents the state of the art of the four initiated R&D projects. The theme Wind Energy is constantly in motion, due to local developments as well as global energy policy changes.

During the ADEM program definition (2006-2010), which for the theme Wind Energy implied the selection of topics for wind turbine material development, Germany and Spain heavily invested in materials and structures development for the conversion of solar and wind energy into electricity too, with a firm back up of nuclear generated electricity. The Netherlands, however, started to focus on the conversion of fossil coal into electricity and following the USA, the Netherlands is starting to invest in the exploration of shale gas to compensate for the reducing number of easily exploitable oil wells. Shale gas exploration made the USA in a few years time almost self-supporting regarding its energy need, diminishing the dependency of Middle East crude oil import.

And finally the Fukushima disaster in March 2011 caused Germany’s rapid phasing out of the oldest nuclear electricity plants, followed by an accelerated deployment of alternative electricity supply from wind and solar energy plants. Japan’s alternative was as simple as creative: an immediate reduction of electricity consumption and a change to natural gaseous energy carriers in due time.

Our projects

Over the same period of time, the four ‘Wind’ research projects were defined, manned, and deployed with all up’s and down’s and various delays and successes. After four years the new materials program of thermoplastic composites has been finished, the integral material models development is well underway and quite successful; with less specimen test data better fatigue life predictions can be made and plotted in traditional stress level vs. fatigue cycle graphs. The thick laminates project had a slow start and models were made to understand 3D scaling effects, the manufacturing of thick specimen has been conceived and the first measurements to study the effect of self-heating during testing has been started. Last but not the least, the development of the 20,000 kN dynamic test bench, essential for the latter project, has been delayed due to external factors (e.g. EC procurement regulations), the complexity of the system and the implementation of innovative energy reducing features.
New Materials for Wind Turbine Blades
The biggest challenge for tall structures, like wind turbine blades, is the replacement of thermoset composites into recyclable thermoplastics. A cheap solution could be the use of anionic polyamide (APA6), vacuum infused as reactive monomer. To improve both the conversion of the material from monomer to polymer and to improve the mechanical properties at maximum operational temperatures, the processing parameters and the influence of nuclei like nano-clay fillers and carbon nano-tubes has been studied at lab scale. The final project activities are approaching completion.

Integral Material Models for Composites
Improved reliability of fatigue life prediction, by using Constant Life Diagrams, is one of the critical issues in wind turbine blade design. Using the extensive WMC test database of past and recent fatigue test results, made it possible to introduce and verify new ‘Whisper’ fatigue life prediction models with improved accuracy and less parameters (the number of cyclic stress ratios, as well as environmental and specimen variables). The cause of scatter (on bare fibre and specimen level) and the effect of temperatures (thick laminates) are also subject of study. Overall, this R&D project is in the final stage.

Thick Laminates
The increase of wind turbine diameters (from 40 m to 60 m and 80 m), has a direct effect on the loads and thicknesses of the laminates used, especially in the root sections. Subject of this study, the observed reduction of fatigue life with increased laminate thickness. Therefore the possible effects of defects in relation to the manufacturing are investigated and thick test specimen and the influence of the 3D state of stress and self heating during fatigue are tested. This study is partly relying on the Composite Material Models results, however verification mainly relies on the test facility which is under preparation. This part of the project will follow as soon as the facility is operational.

Theme coordinator
Prof. Adriaan Beukers, TU Delft.
Among the thermoplastic resins APA6 was chosen for this study. APA6 is an engineering thermoplastic resin with high modulus and excellent chemical resistance. It offers the possibility of being reactively processed from its monomer resulting in a thermoplastic polymer with high degree of crystallinity and high molecular weight. Due to low viscosity of the monomer APA6 fibre reinforced composites can be processed via liquid moulding which is of particular interest for the manufacturing of big structures like wind turbine blades. In various applications, thermoplastics are not used in their genuine form but mixed with fillers to improve the material properties. Nanofillers exhibit a large surface to volume ratio which leads to a tremendous potential filler–matrix interface. In comparison with conventional fillers, less than 5%wt loading of well dispersed nanofillers can reach the same level of properties enhancement as 30%wt loading of microscale fillers. Carbon nanofillers i.e. carbon nanotubes (CNT) and carbon nanofibre (CNF), are of particular interest due to their intrinsic properties. They are electrically and thermally conductive and have a low density. Therefore electrical and thermal conductivity of the composites are improved apart from general improvement of mechanical properties without increasing the weight. Eventhough the mechanical and electrical properties of CNF are lower compare to CNT. CNF offers slightly better nucleating effect, apart from being cheaper than CNT. Hence moderate enhancement with marginally lower in price of the composite compare to CNT. Moreover CNF knowledge might be able to transfer to the more expensive CNT.

Research results until 31 December 2012
There are many studies related to the enhancement of the properties of CNF-based composites. It is known that the uniform dispersion of CNF is a challenge. Preliminary tests with high intensity ultrasonication showed some good results caused by the high energy cavitation, a momentary implosion of bubbles.

Throughout this report, the samples are denoted as % wt CNF_amplitude_energy. For instance 0.5_50_100 means a nanocomposite sample with 0.5 % wt CNF, sonicated at 50 % amplitude and 100 Ws/mL.

The storage and loss modulus of the nanocomposites and the neat APA6 were examined by the means of 3 point bending DMA. The storage modulus of sonicated APA6 were found to be in the same range as the reference sample. For clarity, only the storage modulus of nanocomposite and the reference sample are shown in the figure. Storage modulus of the nanocomposite was above the reference sample for the whole temperature range tested (-50 to 150 °C). This argument is true for all samples except 1.25_50_100 where the standard
deviation bar overlaps the reference sample. The 1.25_50_100 is a combination of high loading with low ultrasonication energy. Hence agglomeration of nanofiller can be present which may act as stress concentration. Therefore this sample shows biggest standard deviation.

No substantial difference in storage modulus was observed among the 0.5% loading nanocomposites from different ultrasonicated parameters. Only 0.5 % by weight of CNF was used and this might be too low for a reinforcing effect as well as the shorten of CNF due to high intensity ultrasound. There were some reasons that 0.5 % by weight of CNF was chosen in this experiment. The most important reason was that choosing a too high loading value possibly hinders the polymerisation. As the viscosity directly depends on the loading, too high loading might also affect turbulence of the reactive mixture during the sonication. Besides, at lower loading like 0.5 % was a fine resolution which a slight change could be observed.

The lowest SD belongs to the nanocomposites sonicated at 50% amplitude with 250 Ws/ml. This small SD implies well dispersion of CNF. The highest storage modulus among all samples is 1.25_50_250. At room temperature, the storage modulus of 1.25_50_250 was almost 16% higher than the reference sample.

**Industrial collaboration until 31 December 2012**

Suzlon Blade Technology (a division of Suzlon (world’s 3rd largest Turbine manufacturer) responsible for design & manufacturing of wind turbine blades) has formed a consortium to perform research on the Next Generation of Wind Turbine Blades. The consortium consists of Suzlon Blade technology, Ten Cate (preforms, prepregs), PPG (Glass Fibres), Bronk (APA6 resins) and TU-Delft (CNF-APA6 composites). The ADEM sub-project on the development of nanocomposite APA6 is an essential part of this project Next generation Wind turbine blades.

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**Figure 1:** Storage modulus obtained by 3-point bending DMA, against the scanning temperature.

**All output from the beginning until 31 December 2012**

- N. CHAMNANDECHAKUN, A.A.V. GEENEN, and H.E.N. BERSEE. EFFECT OF ULTRASONICATION IN CNF/ANIONIC POLYAMIDE 6 COMPOSITE SYNTHESIS, in International Conference on Interfaces & Interphases in Multicomponent Materials (IIMM), 2010. Sheffield, UK.
**Introduction**

In wind turbines blades, thick laminates can be found in different parts, such as the root or the cap. For a 40 m long blade, thicknesses between 30 to 50 mm are found in the root sections. Moreover, due to the exponential growth of the wind turbines rotor diameters demanded by the on-shore and off-shore industrial sectors, root and cap thicknesses between 50-100 mm will be used in 60 to 80 meters blades.

Current blade designs are based on static and fatigue coupon tests with coupons of 1-5 mm thickness, safety factors prescribed by the certification entities, sub-component (joint) connection tests and a full-scale blade test. Very little work on thicker laminate testing has been published related to property differences between thin and thick laminates both in fatigue or static loading due to the high loads involved in those kind of tests. In the OPTIMAT and INNWIND programmes laminates up to 30 mm thickness were subject of study. Test results showed a reduction in fatigue life up to a factor 10 compared to thin laminates. Questions were raised in view of these results. These questions were mainly related to the testing setup and the behavior of thick laminates on static and fatigue tests, and were primarily related to the self-heating of the specimens (which was not satisfactorily quantified) and the influence of the subsequent (local, distributed) temperature rise on the performance of the specimens.

Furthermore, during these projects no significant experience was gained with manufacturing of thick laminates and the suspected multi-axial internal residual stresses due to curing shrinkage of the resin.

Therefore, on account of the increasing presence of thick laminates in the main parts of the present and future wind turbines blades and the increasing use of composites in the aeronautical industry, a more comprehensive study on thick laminates behavior, testing, design and properties is required in comparison with standard thin laminates.

The aim of the project is to identify and address the main differences and 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 will be on:

- the manufacturing process influence on thick laminates mechanical properties
- the 3D, scaling effects and design parameters influence on thick laminates testing coupons and subcomponent
- self-heating in thick laminates and its influence on static, dynamic and fatigue mechanical properties
- the loss factor

**Research results until 31 December 2012**

The self-heating of thick laminates during fatigue loading was studied in order to understand it and avoid excessive temperatures during the fatigue testing of thick laminates. Based on the hypothesis in which the heat generated during dynamic loading is related with the strain energy and the cyclic loss factor, a finite element (FEM) model was developed to determine the temperatures during the dynamic loading and experimental data including infrared images were recorded to validate the model.

Traction and compression coupons have been designed in order to obtain the maximum static and fatigue properties in thickness scaled tests. The study was based on an extended FEM study in which 3D scale effects, grip effects, coupon self-heating, scale effects and the most suitable manufacturing process for the coupons were taken into account.

Based on the tension and compression coupons designs, an extended test matrix was started in order to study the scale effect in static and dynamic loading which involves around half a ton of composite material to test. The following test set was carried out:

- End loading static and fatigue compression tests from 4 mm to 20 mm thick UD laminate (100 kN to 1000 kN test frames, around 20 million cycles)
- Static and fatigue compression tests from 4 mm to 10 mm thick UD and for 30 mm 90° laminates (100 kN to 1000 kN test frames, around 10 million cycles)

In order to understand the role of the loss factor in fatigue loading and 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. Additionally around 10 million cycles of fatigue testing was carried out in order to characterize the crack growth onset, the delamination growth and the loss factor in Mode I DCB tests.

**Figure 1:** Double cantilever beam Mode I test monitored with the developed video tool
All output from the beginning until 31 December 2012

- F Lahuerta, T Westphal, RPL Nijssen. “Self-heating forecasting for thick laminates testing coupons in fatigue” The Science of Making Torque from Wind, Torque 2012 Oldenburg, poster

Figure 2: 30 mm coupons monitored by the infrared camera in fatigue loading

Figure 3: Gimax interlaminar fracture toughness versus cycles to delamination growth onset ASTM D6115
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 behavior 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 until 31 December 2012
For fatigue loading of composites the ratio of mean stress to the stress amplitude, more commonly expressed as the ratio of the minimum to the maximum of the cyclic stress (R) has a large influence on fatigue life. The dependence of fatigue life on mean stress and stress amplitude is represented in a Constant Life Diagram (CLD), for which several formulations exist, for examples see Figure 1. There are large differences between these formulations; the difference in predicted constant amplitude (CA) fatigue life can be several orders of magnitude depending on the stress ratio.
In the first phase of this project, the CLD-formulation was extensively investigated, leading to the following activities and results. In 2011 several CLD formulations were compared for their ability to match the extensive constant amplitude fatigue dataset of the OptiDAT-Upwind database [1]. In 2012 fatigue datasets for glass epoxy laminates under variable amplitude (VA) loading were finalized using the experimental facilities at WMC. Three standardized wind turbine load spectra were used including a recently developed spectrum representative for modern MW size wind turbines, which has a considerably different cycle content than the older spectra (Figure 2). Based on these data CLD formulations were compared in terms of their prediction accuracy for fatigue life under variable amplitude loading [2].

Figure 1: CLD formulations, Goodman diagram (left) and the Multislope model (right)

Figure 2: Cycle distribution for the Wisper spectrum (left) and the NewWisper spectrum (right)
It was found that good predictions were achieved with CLD formulations that are well matched to a detailed constant amplitude fatigue dataset, see Figure 3. A drawback of these models is the amount of input data required. Currently, new formulations with less parameters are being developed to be able to provide an efficient prediction (high ratio of accuracy over input data).

The OptiDAT test database is dominated by glass-epoxy laminates. This database has been extended with datasets on a carbon and a glass-carbon hybrid laminates [3]. These datasets will be used to validate how the conclusions for glass-epoxy laminates hold up for laminates that include carbon fiber.

A further subject of study is the scatter in fatigue data, looking into its causes and how to account for it. Micromechanical modeling of composites, using the fatigue properties of bare fibers as input (Figure 4), was used to show that the very high scatter in fatigue life of single fibers can be related to the amount of scatter observed in tensile fatigue tests on composite coupons [4].

In composites the fatigue life scatter is dependent on the load ratio and commonly higher scatter is observed in compression fatigue than in tensile fatigue. To enable a probabilistic fatigue life prediction the distribution of fatigue life and its dependence on load ratio distribution needs to be included in a CLD formulation and taken into account in the fitting procedure for the model parameters.
Finally, temperature is known to have a large influence on fatigue life of composites. In the related ADEM project ‘Thick Laminates’ self-heating under fatigue loading is an important topic. Next to this fatigue experiments on thin laminates at different temperatures have been done to quantify the influence of temperature on fatigue life. These data will serve as a basis for including of the effect of temperature in the material model. The decision to include other influence factors such as laminate thickness, laminate quality, aging etc. will be based on their significance for the fatigue life prediction.
Industrial collaboration until 31 December 2012
Suzlon Blade Technology has been involved in discussions on model development.

All output from the beginning until 31 December 2012
Solar Cells and Modules
Solar Cells and Modules

Introduction
The global demand for energy and in particular electrical energy is increasing. There are continuously new electricity production capacities installed to meet the increasing demand. In 2011 Europe installed 73% of new power capacity based on renewable energy sources. In 2012 this trend was consolidated when renewables took 70% share of the new installed capacities. One of the renewable energy alternatives is Photovoltaics (PV), in which sunlight is directly converted into electricity. In 2012 PV power systems with 17 GW installed power made the highest contribution to a newly installed power capacity. Cumulatively there is more than 100 GW power installed all over the word based on PV. In the past the main challenge of solar electricity was its price. However, the PV industry has grown rapidly in recent years and has focused on cost reduction and efficiency increase of solar cells. The average cost of crystalline silicon solar cells, the dominant PV technology, was as low as 0.32€/W in March 2013. This is a remarkable achievement, which means that so called grid parity has been achieved in the Netherlands. This means that the electricity generated by a roof-top installed PV system is cheaper than the electricity from the grid (consumer price is 0.23€/kWh).

Our Projects
Within the Solar Cell theme 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, such as creation and manipulation of quantum dots using silicon or PbSe to manipulate the band gap and obtaining efficient carrier multiplication and fabrication of thin layers of luminescent material to convert high energy photons into one or more lower energy photons. The luminescent film should preferably be integrated in the
anti-reflection coating of the solar cell which typically consists of multi-layered SiOx/SiNx. At TU Delft work is carried out on new generation of thin-film silicon-based solar cells that is expected to lead to a market breakthrough and new applications. The aim of this 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. An important issue in the fabrication of crystalline silicon solar cells is the handling of thin wafers that requires a better understanding of microstructure, stress development and mechanical properties of the solar cell. This research determines the nature and source of the defects controlling the fracture of solar cells and provides information regarding the strength and stresses of solar wafers. This knowledge gained at TU Delft can be used to enhance production yields, improve cell reliability and establish mechanical criteria that lead to a reduction in cell costs. At University of Twente the use of laser treatment of solar energy materials is investigated. An example is the treatment of SnO₂ material that is widely used as a transparent electrode in thin-film solar cells. Annealing by ultra-short laser pulses can modify optical properties of thin SnO₂ films by means of thermal processing without injection of excessive heat. After laser treatment, the optical transmittance of SnO₂ thin films was increased and self-organized nanostructures formed on the surface of the film after irradiation were found to significantly improve the scattering properties of its surface.

Outlook
In 2013 we expect to start three additional projects in the solar cell area that will result in new expertise in solar cell processing and their applications.

Theme Coordinator
Prof. dr. Miro Zeman, Delft University of Technology
Project: Mechanism of energy and charge transport in advanced photovoltaic materials

<table>
<thead>
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<td>Start date:</td>
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Introduction

The breakthrough of solar energy is currently limited by the high costs and/or relatively low efficiency. To increase the efficiency, we would like solar energy materials to absorb more of the infrared part of the solar spectrum, but unfortunately, this also means a lower energy conversion efficiency for the visible/UV part. This drawback could be solved by using materials which show efficient carrier multiplication: the creation of more than one electron-hole pair by absorption of a single high-energy photon. In this project we study semiconductor nanocrystals with promising prospects to enhance the solar cell performance by efficient carrier multiplication.

Semiconductor nanocrystals are crystals in a size range of typically a few to tens of nanometers (figure 1). Nanocrystals in this size range show effects of quantum-confinement, which implies that the properties of excitons and charges are affected by the size and shape of the nanocrystal. In a quantum dot (QD) the confinement in all three dimensions leads to discrete energy states. This leads to the well-known tunability of QD color with size. This easy tunability is an important advantage of using nanocrystals. Just as important is their relatively straight-forward wet-chemical synthesis and the possibility for solution-processing.

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. Using techniques such as Transient Absorption and Terahertz and Microwave Spectroscopy, we can study the important processes in a solar cell material, such as charge generation, transport and decay processes. This knowledge can give direction to improvement of material performance in solar cells.

Figure 1: TEM pictures of PbSe nanocrystals, quantum dots (left) and nanorods (right), synthesized in our lab.
Research results until 31 December 2012

Upon excitation of a semiconductor nanocrystal with light an electron-hole pair is created. This exciton has excess energy if the excitation energy exceeds the band gap. The excess energy can be used to create an extra electron-hole pair by carrier multiplication, which is in competition with thermal relaxation. Carrier multiplication is a well-studied process in PbSe quantum dots in colloidal dispersion. However, two or more electron-hole pairs in a single quantum dot decay rapidly within 100 picoseconds by Auger Recombination. To avoid this, we have brought the nanocrystals in strong contact with each other in a thin film. In this way charges that are initially produced in a single quantum dot can escape from each other by hopping to other quantum dots, and can eventually contribute to the current in a solar cell.

We showed that in a thin film of strongly-coupled PbSe quantum dots multiple free and mobile charges can be produced by absorption of a single photon. Using time-resolved microwave conductivity measurements we could detect these mobile charges on a nanosecond timescale. The Quantum Yield (= the number of charges generated by a single absorbed photon) increases with photon energy to reach a value of 350% for UV light (see figure 2). The additional charges generated by carrier multiplication can lead to a 24% increased solar conversion efficiency. This research was carried out in cooperation with Toyota Motor Company Europe.

Figure 2: The quantum yield increases with photon energy due to carrier multiplication. The band gap is equal to $E_g = 0.63 \text{ eV}$
We have extended our studies on the dynamics of (multiple) photo-excited charges to PbSe nanorods (fig. 1, right). 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 (figure 3) and Auger recombination follows second order kinetics. 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.

Figure 3: Cartoon of electron-hole interaction in nanorods of various lengths.

All output from the beginning until 31 December 2012
- Oral presentation at EXCON2012 (Groningen): M. Aerts et al. “Generation and interaction of multiple mobile electron-hole pairs in PbSe quantum dot arrays and nanorods”
- Poster presentation at CHAINS 2011 (Maarssen) and Physics@FOM 2012 (Veldhoven): M. Aerts et al. “Free charges produced by carrier multiplication in strongly coupled PbSe quantum dot films”
- Poster presentation at QD2012 (Santa Fe, USA): M. Aerts et al. “Efficient formation of multiple mobile electron-hole pairs in PbSe quantum dot arrays and nanorods”
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 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 (SiO$_2$), amorphous silicon nitride (SiN$_x$), amorphous silicon (a-Si:H), aluminum oxide (Al$_2$O$_3$). 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.
The following passivation materials and stacks (as well as their associated deposition techniques) have been identified as being of high interest:

1. Passivation by SiO$_x$/Si$_x$N$_y$ stacks prepared by ETP-CVD. This technique was developed at the TU/e and was commercialized by Roth & Rau B.V. (previously OTB Solar) in their industrial deposition platform DEPx.
2. Passivation by ETP-PECVD a-Si:H. This is of interest for applications requiring high deposition rates and/or high deposition temperatures.
3. Passivation by ICP-CVD SiN$_x$. These films can serve as a bench mark for other passivation studies whereas also the performance of stacks with SiN$_x$ bi-layers (with different values of x) can be investigated.
4. Passivation by ICP-CVD a-Si:H as well as by stacks of ICP-CVD a-Si:H and ETP-CVD ZnO. a-Si:H and a-Si:H/ZnO stacks are of interest for heterojunction c-Si solar cells.
5. Passivation by a-Si:H/Al$_2$O$_3$/ZnO stacks. These stacks are again of interest for heterojunction c-Si solar cells as recently established from results on Al$_2$O$_3$/ZnO stacks (work of Sjoerd Smit). The Al$_2$O$_3$ is prepared by plasma-assisted ALD and the ZnO by ETP-CVD or ALD.

Research results until 31 December 2012
- Developed a process to deposit SiNx thin films by ICP-CVD for passivation of c-Si. Si-rich SiN$_x$ resulted in a lifetime of 1 ms and N-rich SiN$_x$ resulted in a lifetime of 300 $\mu$s both at an injection level of $10^{15}$ cm$^{-3}$. These results are comparable to the results obtained by other PECVD techniques.
- Developed a process to deposit a-Si:H thin films by ICP-CVD for passivation of c-Si. The films were characterized extensively in terms of passivation quality, deposition rate, refractive index, hydrogen content, etc. As-deposited a-Si:H (<10 nm) resulted in a lifetime of 4.6 ms, while post-annealed films (deposited under different conditions) resulted in a lifetime of 8.6 ms (in both cases at an injection level of $10^{15}$ cm$^{-3}$).
- Developed test structures of a-Si:H/Al$_2$O$_3$(1nm)/ZnO(50 nm) with the a-Si:H thickness ranging between 1.5 nm and 6 nm. These stacks are of interest for heterojunction c-Si solar cells. The a-Si:H was deposited by ICP-CVD under the conditions established earlier in this project. The Al$_2$O$_3$ was deposited by plasma-ALD and the ZnO was deposited by thermal ALD and ETP-CVD. A surface recombination velocity of 20 cm/s and a series resistance of 5.6 $\Omega$ cm$^2$ were achieved for a-Si:H films with a thickness of 3 nm.
- Developed SiN$_x$/SiN$_y$ ($x<y$) passivation stacks deposited by ICP-CVD which are of interest for fine-tuning the antireflection coating performance for high levels of surface passivation. These passivation stacks resulted in a lifetime of 3.6 ms at an injection level of $10^{15}$ cm$^{-3}$. This passivation quality is significantly better than for single SiNx films used in industry to date.

Industrial collaboration until 31 December 2012
- Roth & Rau B.V.: SiO$_2$/a-SiN$_x$:H stacks were deposited by ETP-CVD for passivation purposes. ZnO films were deposited by ETP-CVD for the application in a-Si:H/ZnO stacks (Kashish Sharma)
- Hanwha Q Cells: Tunnel current measurements on a-Si:H/Al$_2$O$_3$/ZnO test structures (Stefan Bordihn).
Figure 1: The left axis shows the effective surface recombination velocity of the a-Si:H/Al2O3/ZnO stacks as a function of the a-Si:H thickness. The passivation has been determined on symmetrically passivated p-type silicon wafers. The right axis shows the total series resistance of the tunneling samples determined by fitting the JV characteristic with a double diode model.

All output from the beginning until 31 December 2012
- SiliconPV 2012 conference oral presentation in Leuven. “Surface passivation of Si by high-rate deposited SiO2/a-SiNx:H stacks”.
Introduction
We intend to overcome solar cell efficiency limits by fabricating thin layers of luminescent material to be placed on top of solar cells that convert high energy photons to one or more lower energy photons for which the solar cell has a higher IQE\[1\]. The luminescent film should preferably be integrated in the anti-reflection coating of the solar cell to avoid additional manufacturing process steps. As such coatings typically consist of multi-layered SiO_x/SiN_x[2], our focus is on the fabrication of C_{a,x}S_{i,y}N_{z,op} type thin-films. When doped with Eu^{2+} ions, these materials absorb UV light followed by broad band visible to NIR light emission[3-6].

Research results until 31 December 2012
Deposition and analysis of the many possible C_{a,x}S_{i,y}N_{z,op} materials is a time consuming process. As an alternative, we apply a thin film deposition technique that we call combinatorial gradient co-sputtering. For this the ADEM financed magnetron sputtering system is used, which is shown in figure 1. With this technique a single film of C_{a,x}S_{i,y}N_{z,op}:Eu is deposited from Ca, Si and Eu sputtering targets. By tilting the sputter guns with respect to the substrate, strong composition gradients are obtained in a single deposition.

We have obtained promising results with our deposition technique. We have been able to deposit films for which the composition and the luminescence properties change strongly as a function of position on the substrate. Three of such films are shown in figure 2, illuminated by UV-light at 360 nm.

Preliminary characterization indicates that the films consist of different Eu^{2+} doped C_{a,x}S_{i,y}O_{z} films. Currently we are trying the deposition of luminescent nitride or oxynitride films. So far we found that films completely oxidize, during the post deposition heat treatment. We intend to improve this anneal treatment in order to fabricate not only oxide, but also nitride and oxynitride luminescent films.

A second research goal is the deposition of thin-film luminescent solar concentrators (LSC). LSC’s aim at lowering cost of solar energy fabrication by concentrating sunlight onto small area strip solar cells using a cheap luminescent plate. Sunlight is absorbed by a luminescent material and re-emitted in all directions. A considerable fraction of the light is trapped in the plate by total internal reflection that acts as a waveguide and guided to the perimeter where solar cells convert it into electric power.
This concept device was introduced by Weber and Lambe in 1976 [7]. A commercial breakthrough has never been achieved, because the existing luminescent materials absorb a too small fraction of the solar spectrum and in addition they suffer from losses due to re-absorption of emitted light. We have developed a material that absorbs twice the amount of sunlight compared to previously used materials in LSC’s, with an emission band that does not overlap with the absorption band. This material is currently under review for patenting and is here referred to as “Material E”.

The challenge in this part of my Ph.D. research is the deposition and characterisation of thin films of this material. The first experimental result is shown in figures 3 and 4. We observe a weak excitation in the thin film (figure 3b and blue line in figure 4) that shows similarities with the excitation spectrum of the powder phosphor (figure 3a and brown line in figure 4).

Figure 1: ADEM financed magnetron sputtering system of the FAME section used to make thin film luminescent materials.

Figure 2: Luminescent CxSi14Oz : Eu2+ thin films under UV illumination (λexc = 360nm)

Figure 3a: “Material E” as a powder phosphor

Figure 3b: “Material E” as a thin film

Figure 4: excitation spectra of “Material E” as a powder phosphor (brown graph), and thin film (blue graph)
References


All output from the beginning until 31 December 2012

- Silicon nitride based spectral conversion materials for photovoltaic applications, Physics @ FOM 2012 (poster presentation).
- Silicon nitride based spectral conversion materials for photovoltaic applications, PVSEC 2012 (poster presentation)
- Silicon nitride based spectral conversion materials for photovoltaic applications, IKSS 2012 (poster presentation)
- Progress in luminescent $\text{Ca}_2\cdot\text{Si}_y\cdot\text{N}_z\cdot\text{Eu}^{2+}$ thin film deposition, SOLAR 2012 (oral presentation).
- Stroom opwekken met je raam, Press interview www.kennislink.nl, 06-12-2012

Other

- 2012 Delft Energy Initiative Fund awarded to MSc student Koen Hooning for investing in development of new LSC’s.
- First Price 2012 Dutch Clean Tech Challenge Award with MSc student Koen Hooning and Willem Kesterloo.
- First Price 2012 International Clean Tech Challenge Award with MSc student Koen Hooning and Willem Kesterloo.
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 until 31 December 2012

Due to the complexity of the nanostructure of hydrogenated amorphous silicon (a-Si:H) there is no consensus on the nature of defects in a-Si:H. There are models that solely consider coordination defects such as dangling bonds and there is an alternative view that vacancies have neutral and charged defect states. The limited understanding of the nanostructure and defect states has led to a wide variety of models that try to describe the Staebler-Wronski effect (SWE). However, none of these models have yet succeeded in providing convincing experimental evidence for their correctness. On the road towards SWE reduction the latest insights in the a-Si:H nanostructure and the SWE are presented using Doppler broadening positron annihilation spectroscopy (DB-PAS), Fourier transform infrared spectroscopy (FTIR), and Fourier transform photocurrent spectroscopy (FTPS) with in situ light soaking mode.

A wide variety of a-Si:H samples that have a very different nanostructure has been investigated. The size of the dominant open volume deficiency in a-Si:H can be probed with DB-PAS using the S/Sc-Si parameter, so dense and porous films can be clearly distinguished. Through FTIR analysis on the same a-Si:H samples it is possible to make a similar distinction between samples in terms of nanostructure when the Si-H stretching modes are considered. The dominant type of open volume deficiency in dense a-Si:H seems to be the divacancy. Although DB-PAS and FTIR spectroscopy are very different material characterisation techniques, it can thus be said that they are powerful complementary methods in the analysis of the Si:H nanostructure.

Temperature annealing (from 25 °C up to 500 °C) has been used as a tool to study the nanostructure by monitoring the changes in the distribution of vacancies. By using DB-PAS, FTIR spectroscopy, and FTPS on the same dense a-Si:H film, strong evidence has been found for the occurrence of vacancy agglomeration in a-Si:H during temperature annealing. This shows that vacancies are important in a realistic description of the a-Si:H nanostructure. Moreover, for the first time ever, empirical evidence has been found for the existence of at least four defect states in the band gap of a-Si:H using a photoconductivity measurement. Therefore, it needs to be concluded that the dangling bond has become a less likely candidate to solely model the defect states in a-Si:H, since the dangling bond can only have three possible charged states (1+/0/1–). Instead, it is suggested to associate the dominant defect states in a-Si:H with not fully hydrogenated volume deficiencies, since they can have more than three possible charged states.

The as-deposited state of various a-Si:H materials is studied. The effects of different variations in the plasma deposition conditions, such as the hydrogen-to-silane gas flow rate ratio (R), the deposition pressure and rf power, are shown to result in different dominant types of volume deficiencies. Further, it is shown that increased values of R lead to smaller sizes of the dominant volume deficiencies in the material accompanied with a higher hydrogen (H) passivation degree in vacancies. As a-Si:H deposited at higher values for R appears to be more stable against light soaking, the enhanced H passivation degree of vacancies is suggested to play a crucial role in SWE reduction. The vacancy agglomeration that is observed during annealing up to 400 °C takes place slower for R>0 a-Si:H materials. This indicates that a reduced vacancy mobility appears to be desirable when trying to reduce the SWE. Finally, FTIR spectroscopy and FTPS show that Si-H bonds are being broken above 300 °C while electronic defects are being formed, which further confirms that H passivation of vacancies is linked with electronic defect passivation.
During light soaking the four observed defect distributions are shown to increase in density, first in a 'fast' regime and then in a 'slow' regime where saturation of the defect density eventually sets in. The four light induced defect distributions increase exponentially with time $\sim t^\beta$ in the fast regime, where the scaling exponent $\beta$ varies with R, ambient temperature and light intensity. This indicates that simplified models describing the SWE in terms of a defect density increase proportional to $\sim t^{1/3}$ or $\sim t^{1/2}$ do not reflect the real complex nature of the SWE.

**Figure 1:** Nanostructural variety in different a-Si:H samples achieved by varying the hydrogen-to-silane gas flow rate ratio, the deposition pressure, and the rf-power as characterized by DB-PAS (left). Different dominant open volume deficiencies can be distinguished: divacancies (DV), multivacancies (MV) and nanosized voids (NV). The rf-power variation investigated by FTIR (right) also shows the transition from dense to porous material, meaning DB-PAS and FTIR are powerful complementary tools in determining the dominant open volume deficiency in a-Si:H.

**Figure 2:** DB-PAS measured during in situ annealing of a-Si:H films deposited at different hydrogen-to-silane gas flow rate ratios. The increase in $S/S_{c,Si}$ illustrates vacancy agglomeration that takes place more slowly for higher hydrogen dilution values of the silane gas.
Figure 3: FTPS measurements on a-Si:H devices connected to EQE data to obtain the normalized photocurrent spectra over a large range of photon energies, including the evolution during in situ light soaking (left). Using Gaussian fitting on the derivative of the sub gap current spectra it appears that at least four defect distributions (X/A/B/C) are present in the a-Si:H band gap (right).

All output from the beginning until 31 December 2012
- Presentations at the ICANS24 conference in 2011 in Nara, Japan (oral), the IEEE PV SC 38 conference in 2012 in Austin, TX, United States (invited oral), and the ICPA-16 conference in 2012 in Bristol, United Kingdom (poster)

Other
SOPHIA project proposal submitted in 2012 to start a collaboration with the Helmholtz Zentrum Berlin on the topic of electron paramagnetic resonance measurements on a-Si:H.
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 biggest drawback for a widespread application of solar cells, however, is their price. The major costs (45%) in producing multicrystalline (mc) solar cell panels come from wafer production. One possibility for cost reduction is to reduce the silicon content, thus using thinner wafers. This thickness reduction leads to a high breakage of silicon solar cells. Therefore, nowadays, the research focus shifts towards the mechanical integrity of solar cells and factors influencing it. To reduce yield losses during cell and module manufacture, it is necessary to have a better understanding of microstructure, stress development and mechanical properties of the solar cell. This research determines the nature and source of the defects controlling the fracture of solar cells and provides information regarding the strength and stresses of solar wafers. The relationship between initial material conditions, damage formation mechanisms during production and residual mechanical lifetime is examined within this project. The resulting data can be used to enhance production yields, improve cell reliability and establish mechanical criteria that lead to a reduction in cell costs.

Research until 31 December 2012

Experimental work included:
Residual and Applied Stress Characterization in Silicon Solar Cells
The X-ray diffraction technique, in combination with bow measurements and bending tests, proved to be a powerful non-destructive qualitative and quantitative experimental technique that provides information about fracture behaviour and stress states of silicon solar cells. The results showed a connection between silicon microstructure, processing conditions, defects and mechanical stress.
The residual stresses and stresses resulting from bending in silicon solar cells were investigated using conventional and synchrotron X-ray diffraction measurements, bowing measurements and bending tests. The study showed that:

- It is necessary to combine conventional XRD, synchrotron diffraction and bow measurements in order to obtain a complete picture of the stress distribution in Al and Ag metallic contacts.
- The thickness of the eutectic layer as well as the composition of the aluminium rear-side contact layer can be considered as important parameters controlling mechanical stability of silicon solar cells.
- There is a strong correlation between maximum firing temperature, amount of bowing and residual stress level of solar cells, i.e. the higher the firing temperature the higher the residual stresses and the amount of bowing (Table 1 and 2).

### Table 1: Effect of firing temperature on residual stresses in Ag layer (X-ray penetration depth ~ 2 μm)

<table>
<thead>
<tr>
<th>Firing Temperature (°C)</th>
<th>Biaxial stress σ₁=σ₂ in Ag [311], (MPa)</th>
<th>Amount of bowing (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>51.8±0.5</td>
<td>1.95</td>
</tr>
<tr>
<td>850</td>
<td>68.9±0.8</td>
<td>2.88</td>
</tr>
<tr>
<td>950</td>
<td>48.6±1.0</td>
<td>1.82</td>
</tr>
</tbody>
</table>

### Table 2: Effect of firing temperature (and thus eutectic layer thicknesses) on residual stresses in porous Al layer (X-ray penetration depth ~ 20 μm)

<table>
<thead>
<tr>
<th>Firing Temperature (°C)</th>
<th>Biaxial stress σ₁=σ₂ in porous Al[420], (MPa)</th>
<th>Amount of bowing (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>0.8±1.0</td>
<td>0.48</td>
</tr>
<tr>
<td>850</td>
<td>5.5±1.3</td>
<td>1.40</td>
</tr>
<tr>
<td>950</td>
<td>4.5±3.0</td>
<td>1.80</td>
</tr>
</tbody>
</table>

- It is possible to measure applied bending stresses by X-ray diffraction using an in-situ bending clamp specially designed for thin solar cell specimens (Figure 1).

**Figure 1**: In-situ 4-point bending device for XRD: Bending device inside the diffractometer
- Applied stresses measured using XRD and calculated using expressions for 4-point bending are comparable in magnitude, thus composite beam theory can be considered as appropriate for bending stress calculations in silicon solar cell samples (Table 3).

<table>
<thead>
<tr>
<th>Stress Type</th>
<th>XRD stress, MPa (loading over a few hours)</th>
<th>4-point bending stress at 3 N, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual stress at 0 N load, MPa</td>
<td>60 ± 1.4</td>
<td>-</td>
</tr>
<tr>
<td>Residual stress + stress resulting from applying 3 N bending load (close to failure), MPa</td>
<td>87 ± 2.3</td>
<td>-</td>
</tr>
<tr>
<td>Stress resulting from applying 3 N bending load, MPa</td>
<td>27</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 3: Comparison of stress measured with XRD and calculated on the basis of 4-point bending

- Holding samples at a load of 2 - 3 N results in a stress relaxation effect, possibly due to creep or cracking of the Ag layer.
- Synchrotron diffraction analysis showed that there is a stress gradient in both Ag and Al layers (Figure 2 and 3).

Figure 2: a) Diffraction spectrum of the reference Ag layer and as-fired silver layer, showing peak splitting for Ag {111} in the layer; b) Corresponding d spacing and stresses for 2 {111} peaks of Ag.
Furthermore, it was found that conventional and synchrotron X-ray diffraction methods are not appropriate for stress measurement in the coarse-grained silicon substrates studied in this thesis. Thus, residual and bending stresses in the silicon substrate were investigated using Raman spectrometry, bowing and 4-point bending tests. The Raman study showed that:

- Residual stresses at the grain boundaries are 37 - 40 MPa higher than within the grain;
- Grain boundaries are the most probable sources of mechanical strength degradation of mc-Si wafers;
- The saw-damaged layer contains tensile stresses of ~500 MPa;
- An amorphous Si phase was found only in smooth grooves of the as-cut wafer.
- The presence of transformed amorphous Si could also affect mechanical stability of the as-cut wafers.
- It was found that it is possible to measure bending stress in silicon wafers and solar cells by Raman spectroscopy using an in-situ bending clamp specially designed for thin solar cell specimens.
- An Al inclusion at the grain boundary of mc-silicon creates a local compressive stress field of ~450 MPa (as compared to bulk Si), due to CTE mismatch between the inclusion and the silicon matrix.

![Table and graph](image)

**Table:**

<table>
<thead>
<tr>
<th></th>
<th>2θ, °</th>
<th>d spacing, Å</th>
<th>Stress, (\sigma_1=\sigma_2) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al reference powder</td>
<td>7.9122</td>
<td>2.0237094</td>
<td>--</td>
</tr>
<tr>
<td>fired Al - peak 1</td>
<td>7.9117</td>
<td>2.0238370</td>
<td>4</td>
</tr>
<tr>
<td>fired Al - peak 2</td>
<td>7.8841</td>
<td>2.0309364</td>
<td>192</td>
</tr>
</tbody>
</table>
Industry activities until 31 December 2012
There has been collaboration with ECN for sample preparation and modelling of the relationship between the mechanical properties of the cells and the microstructure of the metallization pastes. The results of this collaboration have provided background knowledge to ECN. This has been used by ECN in consultancy projects with industrial partners including cell manufacturers and metallization paste suppliers.

Output until 31 December 2012
Introduction
An alternative use of ultra-short laser sources, as a future prospect, can be found in thermal processing, e.g. extremely selective annealing, laser doping, etc. The benefit of using ultra-short laser pulses for thermal processing relies on the possibility to be highly selective in depth of the laser induced transformations. This can be exploited for processing thin films or very shallow regions on the top surface of materials. To fully exploit this alternative use of ultra-short laser sources requires a detailed understanding of the heat related phenomena in a fluence range below the ablation threshold.

Research until 31 December 2012
Annealing by ultra-short laser pulses can modify optical properties of thin SnO₂ films by means of thermal processing without injection of excessive heat. After laser treatment, the optical transmittance of SnO₂ thin films was increased and self-organized nanostructures formed on the surface of the film after irradiation were found to significantly improve the haze.

Figure: 1: SEM pictures of the two samples. Left: as deposited SnO₂ surface. Right: SnO₂ surface after laser irradiation.
On the other hand, processing materials with ultra-short pulses may introduce defects and stresses in the lattice, resulting in effects, such as changes in electrical properties. As we reported, after picosecond laser irradiation, SnO₂ layers were showing improved optical properties but also increased sheet resistance.

Several causes, at the atomic scale, can generate a decrease of conductivity, such as: modification of the density of oxygen vacancies, changes in average grain dimensions, amorphization due to fast quenching, introduction of quenched-in defects during fast thermal processing, stress/strain induced by the defects in the lattice. In the case of fast annealed SnO₂, the most detrimental effect on the electrical properties was found to be the generation of quenched-in defects, which cause stresses in the lattice and increase carrier recombination.

Knowledge at atomic level of the occurred phenomena is required to give a satisfactory explanation of the observed modifications in the thin SnO₂ film after irradiation. From a fundamental point of view, a careful description of the laser-induced modifications in the processed material contributes to the understanding of the effects of radiation on materials during laser micro- and sub-micro- machining via ultra-short pulses.

Future research will focus on the fast recrystallization phenomena occurring during short- and ultra-short-pulsed laser irradiation during fast thermal material processing (i.e. annealing and laser doping) in order to understand better the origin of defects and have a better control on their formation.

The research was carried out in cooperation with TNO, which provided SnO₂ samples and facilities for performing required measurements to investigate optical and electrical properties. Analysis of the material structure (TEM, HRSEM, AFM, XPS, XRD) was carried out at the University of Twente using facilities from MESA+ institute and was funded by the Laser Engineering Technology group of the University of Twente. The laser laboratory is a facility provided by the Chair of Applied Laser Technology at the University of Twente.

**Output until 31 December 2012**

- D. Scorticati et al., Thin film surface processing by ultrashort laser pulses (USLP), Proc. SPIE 8438, Photonics for Solar Energy Systems IV, B4380T (June 1, 2012); doi:10.1117/12.922270
Introduction
Photovoltaic cells convert light directly into electrical energy. Unfortunately solar cells are only capable of converting a specific part of the sun's light spectrum into electricity, limiting their efficiency considerably. 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 carbide (SiC) 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.
Excimer laser annealing experiments were performed on amorphous silicon carbide layers with varying carbon concentrations and laser fluences. Silicon quantum dots were formed by the annealing procedure of SiC layers. Quantum dot growth in silicon rich and carbon rich single and multilayers were studied using Raman spectrometry. We showed that the threshold laser energy for crystallization is 80 mJ/cm², see Figure 1. We also show that using a high methane fraction during layer deposition drastically inhibits quantum dot growth. By using this phenomenon we are able to effectively create a growth barrier in multilayer structures. However, during laser annealing of SiC layers, extra defects are created within the SiC material, significantly reducing the electrical properties of the material. Current experiments aim to limit these effects caused by laser annealing; enabling the possibility for laser annealed silicon quantum dot solar cells in a SiC matrix.

![Figure 1: Crystalline fraction (a) and the peak position of the c-Si transverse optical mode (b) for silicon rich (CH₄/(CH₄+SiH₄)=67 %) and carbon rich (CH₄/(CH₄+SiH₄)=96 %) SiC single layers annealed at varying excimer laser fluences.](image-url)

Research results until 31 December 2012

Excimer laser annealing experiments were performed on amorphous silicon carbide layers with varying carbon concentrations and laser fluences. Silicon quantum dots were formed by the annealing procedure of SiC layers. Quantum dot growth in silicon rich and carbon rich single and multilayers were studied using Raman spectrometry. We showed that the threshold laser energy for crystallization is 80 mJ/cm², see Figure 1. We also show that using a high methane fraction during layer deposition drastically inhibits quantum dot growth. By using this phenomenon we are able to effectively create a growth barrier in multilayer structures. However, during laser annealing of SiC layers, extra defects are created within the SiC material, significantly reducing the electrical properties of the material. Current experiments aim to limit these effects caused by laser annealing; enabling the possibility for laser annealed silicon quantum dot solar cells in a SiC matrix.
References


Catalysis, Membranes and Separations

Introduction
World energy use is exponentially increasing. As a result, the CO₂ concentration in the atmosphere is increasing rapidly as well. Within the Catalysis, Membranes and Separations (CMS) cluster, various technologies are under development that can mitigate the CO₂ effects of an ever growing world economy.

Nationally as well as internationally there is a lot of attention for carbon capture. The US Department of Energy has very large programs on the development of carbon capture technologies as has Japan (NEDO) and the EU (within the FP-7 framework). In Norway a large demonstration site for carbon capture has been opened in Mongstad with a cost of about 800 million Euro. In the Netherlands the CATO-II program is dedicated to sustainable carbon capture, transport and storage. The ADEM program is key in keeping our materials science infrastructure up to world class standards to enable us to remain a key player in this very important field of research. Within the carbon capture arena, there are three main technology lines. Pre-combustion carbon capture focuses on separating the CO₂ before combustion, by converting the fuel (either fossil or biomass based) to hydrogen and CO₂. The CO₂ can then be stored and the hydrogen can be used as fuel. Post-combustion carbon capture separates the CO₂ from flue gas and the oxyfuel line of technologies is focused on burning the fuel with pure oxygen in order to have a flue gas consisting of easy separable water and CO₂. All these technologies involve the development of novel materials, be it novel catalysts, membranes, sorbents or solvents.
Our projects

Within the CMS program, we mainly focus on pre-combustion capture, either from natural gas or biomass. Within the biomass conversion theme, two projects are focusing on fluidized bed biomass gasification based on olivine as a catalytically active bed material (both at the TU/e) and two more projects on hydrogen production by steam reforming of flash-pyrolysis oil with novel Rh/CeO$_2$ based catalysts to enhance the activation water in the steam reforming process (one at the UT and one at the TU/e). In these projects a lot of progress has been made on catalyst development as well as fundamental studies on understanding and tuning fluidized bed behaviour.

An integrated autothermal reformer for natural gas conversion into hydrogen with built in carbon capture is being developed at the UT. The reactor consists of two different ceramic membranes, an oxygen conductive membrane and a hydrogen selective membrane. Considerable progress has been made on the development of these membranes and in particular on CO$_2$ stability of the oxygen conductive membrane and on hydrogen selectivity of the hydrothermal stable hydrogen selective membrane. At the TUD, the focus is on solvent based CO$_2$ capture for either pre- or post-combustion or CO$_2$ from natural gas. The research has focused on the development of relatively inexpensive and/or biodegradable physical ionic liquids.

Outlook

2013 will be a very exciting year as the green light is expected to execute the planned program to the full extent. This means that essential additional investments can be made in the materials science research infrastructure and that five more projects can be started.

Theme Coordinator

Prof. dr. ir. Arian Nijmeijer, University of Twente
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. Ionic liquids 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 the project is to selectively capture CO$_2$ with a suitable ionic liquid from flue-gas streams, either at pre-combustion or post-combustion conditions. A suitable ionic liquid should have a high CO$_2$ solubility, selectivity and a low viscosity. Furthermore, the cost (energy) of CO$_2$ regeneration (which is determined by the reaction enthalpy) should be low. Preferentially, the ionic liquid should be biodegradable, non-toxic and cheap. The big challenge is to find an ionic liquid with the mentioned requirements.

Figure 1: High pressure phase behavior of CO$_2$ in the ionic liquid trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate

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Research results until 31 December 2012

Up to now, the research mainly concerned about CO₂ solubilities in relatively inexpensive and/or biodegradable (physical) ionic liquids [1-4]. The results obtained so far show that the solubility of CO₂ in ILs is still too low at post-combustion conditions, but ILs could be applied at the pre-combustion or natural gas sweetening process. One way to increase the CO₂ solubility at post-combustion conditions is to functionalize the IL with an amine-group, which then will react chemically with CO₂. Therefore, in the second part, the research will deal with the synthesis, characterization and CO₂ measurements of chemically functionalized ionic liquids.

All output from the beginning until 31 December 2012


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.

As a starting point, we studied the possible structure and oxidation state of Rh clusters supported on CeO$_2$(111) surface under CO oxidation conditions. This would provide information regarding the nature of the active sites. It was found that under reducing conditions, the Rh cluster will form three-dimensional cluster, while under oxidizing conditions, the two-dimensional oxide film becomes more stable (Figure 1).

The thermodynamic evaluation proves that under typical CO oxidation conditions, the Rh-oxide film is the dominant species, which is speculated to be the active site. The following-up mechanism study based on the identified candidate structure: Rh$_x$O$_y$/CeO$_2$(111) proposed a feasible reaction path (Figure 2). The reaction starts with adsorbed CO oxidized by O from Rh-oxide film. Then the Rh-oxide film was re-oxidized by a facial oxygen spillover process. The O$_2$ adsorbs at the interface between Rh-oxide and ceria surface vacancy, followed by a fast dissociation process. The reaction cycle is closed. In the reaction path, CO oxidation takes place on the Rh-oxide film. O$_2$ adsorption and dissociation takes place on the interfacial sites. This explains the absence of CO poisoning effect for ceria supported Rh-oxide catalyst.
Figure 1

Reducing conditions

\[ \text{Rh} \quad \text{Rh}_2 \quad \text{Rh}_3 \quad \text{Rh}_4 \]

Oxidizing conditions

\[ \text{RhO}_3 \quad \text{Rh}_2\text{O}_6 \quad \text{Rh}_3\text{O}_6 \quad \text{Rh}_4\text{O}_3 \]

Figure 2
Lots of experiments suggest the possibility of complete dispersion of metal supported on ceria because of strong metal-support interaction. Thus it would be logical to ask if the complete dispersion of Rh on ceria could also be active for CO oxidation. Accordingly, we then perform study of single Rh supported on CeO$_2$(111), (110) and (100) surface for CO oxidation. The results show that the single Rh supported on CeO$_2$(111) and (100) is active for the reaction and give a proposal to the experimental observed surface dependence of ceria support. Rh/CeO$_2$(110) was shown to be most reactive because of the much more easy oxygen migration on CeO$_2$(110) surface. No reaction path was found on Rh/CeO$_2$(100) because of the geometrical factor. The results provide an explanation of strong surface dependence of ceria support in CO oxidation as observed experimentally.

We then extended our strategy to Au/CeO$_2$ system, which is extensively studied for various important reactions, e.g. CO oxidation, WGS, and hydrogenation process. However, the active site of Au is under great debate, e.g. whether it is metallic Au cluster of single Au cations. Our previous results shows the most reactive surface is CeO$_2$(110), thus we choose CeO$_2$(110) surface as our model. We build two typical models: single Au and Au nanorod, which could represent typical proposed Au sites: single site Au and metallic Au cluster. For single Au/CeO$_2$(110), surface O bounding to Au can spontaneously migrates to the bridge site of Au and Ce. CO could very easily react with the migrated O. The formed CO$_2$ then desorbs into gas phase, generating one surface oxygen vacancy. O$_2$ then adsorbs at the interface of Au and ceria vacancy site, followed by dissociation. In contrast, for single Au supported on CeO$_2$(111), after CO$_2$ desorption, Au migrates to the generated oxygen vacancy site, inhibiting adsorption of both CO and O$_2$, essentially deactivating the catalyst. Possible reaction paths of CO oxidation on Au nanorod supported on CeO$_2$(110) surface were also indentified. We suggested three CO oxidation mechanisms based this model: (1) adsorbed CO directly reacts with ceria lattice O via Mars-van Krevelen mechanism; (2) CO oxidized by co-adsorbed O$_2$; (3) facile O$_2$ dissociation, followed by CO oxidation. The possibility of Mars-van Krevelen mechanism on Au/CeO$_2$(110) as compared with that of Au/CeO$_2$(111) shows the importance of surface termination in ceria based catalysis. Because of the strong metal-support interaction, O$_2$ adsorption and dissociation were found to be rather easy on the interface between Au and ceria, which makes the co-adsorption and stepwise reaction possible. The proposed mechanism explains the special role played by ceria support and direct participation of surface O in the reaction, as found extensively in various experiments. Combing with the result on single Au/CeO$_2$(110), it can be concluded that the key factor is the surface morphology of ceria support, instead of the Au nucleating.
Publication list

Journal papers

Conference contributions
Introduction
The continuous depletion of fossil fuels has necessitated to look for efficient and environmentally acceptable ways to generate Hydrogen (H$_2$). Steam reforming combined with gasification of coke in the presence of H$_2$O is conceptually a promising alternative to generate H$_2$ from bio-oil (see figure 1 for schematic overview of the process). It is reported that H$_2$O is able to regenerate hydroxyl groups on oxides like ceria, which increases H$_2$ yield and catalyst lifetime.

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.

Figure 1: Schematic overview of bio-oil steam gasification
Results & Discussion

In this project, CeO$_2$ rod § cube morphologies were successfully synthesized using a hydrothermal method. Aberration-corrected TEM (AC-TEM) images (in collaboration with Prof. A.K. Datye, University of New Mexico) of the ceria nano-materials are shown in figure 2. The AC-TEM results show that both ceria octahedra and rods expose (111) surfaces, whilst ceria cubes expose (100) surfaces.

![AC-TEM and HRSEM (insets) images of the CeO$_2$ (a) Octahedra, (b) rods and (c) cubes](image)

To study the relation between the typical –OH groups and their reactivity towards CO/H$_2$O to create hydrogen (figure 3), FTIR spectroscopy (Fourier Transform Infrared Spectroscopy) was performed in-situ for the different ceria samples.

![Schematic overview of FTIR experiments](image)

The different ceria shapes show similar types of –OH species (3800–3000 cm$^{-1}$ range), but with different relative intensity, indicating that the amount of active –OH groups is determined by the ceria shape. In the presence of CO (red spectrum), a decline and shift in –OH peaks is noticed, caused by the interaction of CO with the active –OH species. The reaction between OH and CO also results in a variety of formate and carbonate surface species with vibrations between 3000–2800 cm$^{-1}$ (C=H vibration of formates) and 1800–800 cm$^{-1}$ (C–O vibration of carbonates & formates).
On subsequently treating the CO-ceria samples with H₂O at 200°C, the carbon intermediates start decomposing, thereby reproducing most of the active –OH groups, see Fig. 4 (blue spectra). In addition, the bands in the region 1800-800 cm⁻¹ start decreasing in the presence of H₂O, leaving behind the stable formate and carbonate species.

To summarise, the reactivity of specific –OH groups is explicitly determined by the ceria nano-shape with different carbonate/formate patterns (octahedra ≈ wires < cubes), on exposure to CO. Subsequent reaction with water at 200 °C was also found to be shape-dependent, resulting in different amounts of recovered –OH groups and removed carbonates and formates on the different ceria nano-shapes.

To investigate the catalytic behavior, the nanoshapes were tested in the water gas shift (WGS) reaction in collaboration with ADEM partner Prof. E.J.M. Hensen (TUE). Figure 5 shows the specific CO conversion rates for octahedra and rods are identical, whilst cubes are much more active for temperatures above 200°C. These activity trends are in agreement with our observations from AC-TEM and in-situ FTIR. The similar specific catalytic activities for rods and octahedra can be explained by the dominance of exposed (111) surfaces. However, ceria cubes expose the highly active (100) surfaces, which clearly show enhanced specific WGS activity compared to the stable (111) surfaces.

**Figure 4:** FTIR spectra of ceria (a) octahedron, (b) rods and (c) cubes sample at 200°C in He flow (black spectrum) followed by 33vol% CO flow (red spectrum) and finally regeneration in H2O saturated He flow (Saturator Temperature 5°C, blue). The black dots indicate the formate peaks in the 1800-800 cm⁻¹ region.

**Figure 5:** Rate of CO conversion per m² during water gas shift (WGS) reaction for rods (red), octahedra (black) and cubes (blue) between 200 and 450°C after H₂ pre-treatment at 500°C.
**Conclusions and ongoing works**

These results provide definitive information on the nature of the exposed surfaces in these CeO$_2$ nanostructures and their influence on reactivity for the WGS reaction for producing hydrogen from CO and water. The exact WGS mechanism over ceria nanoshapes and the role of defects are currently being studied by in-situ FTIR and Raman spectroscopy (in collaboration with ADEM partner Prof. E.J.M. Hensen).

**Output**

**Oral presentations**


**Poster presentations**

1. Nano-catalysis with cerium oxide: Water activation, Mesa+ Day (UT), The Netherlands (18th September 2012)
3. A spectroscopic study of cerium oxide nano-catalyst: Water activation, 4th Operando congress, USA (29th April-3rd May 2012) -- Received Poster Award
5. How to enhance activation of water on inorganic oxides, 6th EFCATS summer school, Turkey (13-19th, September 2010)
6. How to enhance activation of water, NCCC-XI, The Netherlands (1-3rd March 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 ADEM project, the influence of operating conditions in the performance of the two interlinked reactors is investigated in detail. The obtained knowledge can be applied to all different industrial applications of gas-solid fluidized beds, ranging from coffee drying to FCC.

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 circulations 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 until 31 December 2012**

Design and development of a high temperature Endoscopic-Laser PIV/DIA (Figure 1). The use of the optical endoscope together with a double pulse laser has been validated at room temperature in a cold flow set up. The standard PIV/DIA is used as benchmark. In the benchmark, illumination is provided by LED lights. Figure 2 displays the solids circulation profiles comparison for 5 different positions along the fluidized bed. The endoscopic PIV/DIA illuminated by the laser overlaps in the confidence interval of the benchmark, demonstrating the reliability of the optical endoscope to run PIV/DIA. Already the initial assessment of phenomenological models for gas-solid reactions in fluidized beds has been carried out, implementation is in progress.

**Figure 1**: High temperature endoscopic-laser PIV/DIA setup.
All output from the beginning until 31 December 2012

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 until 31 December 2012

A series of powders and ceramic specimens were prepared of ABO₃ perovskite-structured strontium ferrate, (co-)doped on either A- or B-site with A = Mg, La, Ce and B = Al, Ti, Nb, respectively. Their stability in CO₂-containing atmosphere was investigated. From these results, a selection was made for further investigation in POM. Oxygen permeation experiments were conducted on ~1 mm thick dense disc membranes of SrTi₀.₅Fe₀.₅O₃₋δ (STF50) and SrTi₀.₃Fe₀.₇O₃₋δ (STF70) as a function of PO₂ (not shown) and temperature. The oxygen flux of STF70 varied between 0.01 and 0.60 ml/cm².min at temperatures 700-950 deg C. In the same temperature range, the oxygen flux of the STF50 varied between 0.01-0.33 ml/cm².min. Electrical conductivity relaxation (ECR) measurements were conducted, as to determine the chemical surface exchange coefficient (kchem) and chemical bulk diffusion coefficient (Dchem). Data was collected as a function of pO₂ and temperature (for selected results, see Appendix 3). From these results the so-called critical thickness was evaluated (referring to the thickness below which oxygen transport through the membrane is predominantly controlled by surface exchange rather than bulk oxygen diffusion). Typical values found for STF70 are 0.05 - 200 μm, whilst for STF50 these are 0.20-350 μm in the range of temperatures 900 to 700 °C, covered by the experiments.
Project: Hybrid silica membranes for oxy-fuel conversion membrane reactors

Name PhD-candidate: Marcel ten Hove

Affiliation: UT, MESA+ Institute for Nanotechnologie, Organic Membranes

Start date: 1 Feb 2011

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

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 until 31 December 2012
Zirconium doped BTESE (Zr-BTESE) membranes were prepared by using zirconyl nitrate as a zirconium source in the sol preparation. Alumina supports with a γ-alumina interlayer were used for dipcoating. After dip-coating the sol onto the support, the membrane was calcined at 400°C in a nitrogen atmosphere. By using a concentration of 0.2M [Si+Zr] in the dipsol a membrane was prepared with a H₂ permeance of 1.7*10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ and a H₂/CO₂ selectivity of 12.

Zr-BTESE membranes were subjected to steam treatment in cooperation with Institute for Energy and Climate Research, Forschungszentrum Jülich. The membranes were exposed to a synthetic WGS composition at atmospheric pressure at different temperatures. Preliminary results show that at 300°C the membranes have a slightly lower flux, but an increased selectivity for H₂/CO₂ of 19.

Another candidate material of interest is niobium doped BTESE (Nb-BTESE). A H₂/CO₂ selectivity of 220 is reported in literature, but reproduction of these results proved to be difficult. Therefore a cooperation with Nanjing University of Technology was engaged to identify the differences in the manufacturing and characterization procedures.
All output from the beginning until 31 December 2012

Introduction

To meet the increasing demand for renewable, CO₂-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 CO₂. 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)₂SiO₄) 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 Fe²⁺ to Fe³⁺ 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 until 31 December 2012

To investigate the role of olivine and the iron in olivine, olivine was extensively characterized by both bulk- and surface sensitive techniques. The conditions that the olivine catalysts are exposed to during gasification of biomass are mimicked for oxidation (air) and reduction (CO, H₂, and H₂O mixtures), both at 750 °C. The resulting changes in the olivine catalysts’ bulk composition were characterized using X-ray diffraction (XRD). Surface chemistry and morphology changes were characterized using X-ray Photoelectron Spectroscopy (XPS) and Thermo Gravimetric Analysis (TGA) was used to quantify the chemical looping capability of olivine.

A large fraction of the Fe in olivine, which is used by ECN, is present as free Fe-phases, which are sensitive to changes in the gas environment. After exposure to oxidizing gases the free Fe phases are: Fe₂O₃ and Fe₃O₄ or MgFe₂O₄. Upon exposure to reducing gases, the iron oxides are converted into Fe⁰ and Fe₃C and formation of graphitic carbon is observed in the X-ray Diffraction Patterns shown below.

Figure 1: Close-ups of the regions where changes are observed in the XRD patterns of olivine, before and after treatment at 750°C, 1h in oxygen (O₂) followed by 1h in various mixtures of H₂, CO and H₂O.

With our ADEM X-ray Photoelectron Spectrometer (XPS), we showed that the elemental composition of the surface of olivine changes dramatically depending on the gas composition it is exposed to. After exposure to oxidizing environments, the amount of Fe at the surface is twice as high as after reduction. Both the change in chemical state of the Fe-phases, the amount of surface Fe and the build-up of surface carbon are fast processes under the applied conditions and significant changes are observed on the time scale of one minute. These observations have important implications for olivine as a tar cracking catalyst, especially when used in dual fluidized bed gasifiers. The fast reduction of the iron oxides upon switching from oxidizing to reducing conditions shows that olivine transports oxygen from the combustor into the gasifier.
Fig. 3 shows the results of the Thermo Gravimetric Analysis (TGA) of an olivine sample under conditions simulating circulation between a gasification zone (reducing conditions) and an oxidation zone (oxidizing conditions) of an indirect gasification reactor. Oxidation (air) and reduction (H₂) times were chosen as 180 s and 60 s, respectively, to represent the conditions in the ECN MILENA process.

The mass change during each cycle is a measure for oxygen transport. Since this change is 1.0 mg in each cycle and the amount of sample is 200 mg, the oxygen transport under these conditions amounts to 0.5 wt.%. Moreover, the material is oxidized and reduced on two distinctly different time scales. The fast process is responsible for 80% of the mass changes and is attributed to surface oxidation/reduction. It was estimated that 18.5% of all the iron present in olivine contributes to the oxygen transport on time scales of one to several minutes.
There are several important consequences of these results for the performance of olivine as a catalyst in biomass gasification:

Olivine is not a stable material during conditions typically applied in biomass gasification. It decomposes during high temperature treatment.

Olivine transports a significant amount of oxygen on times scales, relevant for industrial processes. Changing process conditions influence the iron concentration and oxidation state at the surface. Hence, the oxygen transport capability, as well as the catalytic properties of olivine are heavily dependent on the process conditions, as these conditions determine the composition of olivine, especially in the near surface region.

**Industrial collaboration until 31 December 2012**

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).

During lab scale research, ECN has made significant progress in the reduction of tar concentration in the product gas. Tar can be removed to sufficiently low levels for preventing cooler problems. Moreover, tests with RDF (refuse derived fuel) are scheduled for this year. In 2017, ECN expects that a commercial plant based on the MILENA technology can be constructed with a capacity of 20 – 100 MW.

**All output from the beginning until 31 December 2012**

- **Poster presentations:**
  
  Physical Characterization of Catalytic Bed Materials used in Indirect Biomass Gasification
  Remco Lancee, Hans Fredriksson, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  

- **Oral Presentations:**
  
  Properties of Olivine catalysts for indirect gasification of biomass
  Remco Lancee, Hans Fredriksson, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  
  Presented at: The AIChE Annual Meeting, October 28 – November 2 2012, Pittsburgh, PA, USA

  Properties of Olivine as a catalyst for indirect biomass gasification
  Remco Lancee, Hans Fredriksson, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  
  Presented at: The CATABIO Conference, July 8 – 11 2012, Thessaloniki, Greece

  Surface Properties of (Mg,Fe)2SiO4-catalysts for Indirect Gasification of Biomass
  Hans Fredriksson, Remco Lancee, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  
  Presented at: the North American Catalysis Society Meeting, June 5 – 10 2011, Detroit, MI, USA
Hydrogen Production and Fuel Cells

Introduction

In the pages that follow, a brief description of the recent progress of the research activities of the Fuel Cell Theme of the ADEM program is outlined. The projects carried out in this context deal with the development of new functional materials that are studied in detail in order to enhance the performance of fuel cells. These new materials developed in ADEM deal with a variety of novel physical and chemical concepts encompassing state of the art soft nano-technology such as nano-structured high performance electrodes or new thin film electrolytes. As ADEM is now part of the larger Green Deal program that covers the Dutch ambitions in achieving sustainable initiatives in various fields, such as energy and mobility, generating knowledge and bringing together various players in society, it is appropriate to recall a few examples or remarkable progress in the fuel cell world scene during the last year.

In relation to energy generation and climate, it is worth mentioning that in 2012 the computer manufacturer Apple Inc. constructed “an onsite 10 MW fuel cell installation that uses directed biogas and provides more than 83 million kWh of 24/7 renewable energy”. To date, this is the largest non-utility fuel cell installation operating in the US. Due to their compactness, fuel cell parks, integrated into hybrid sustainable production systems, maybe of great importance to The Netherlands as physical space and landscape are important societal and political issues in the country.
Another remarkable progress at the mobility front of fuel cells technology has been recently announced, with a French company envisaging to participate in the prestigious Le Mans Grand Prix with a fuel cell car. The “Green GT H₂” is powered by a fuel cell stack specially developed by another French company and develops up to 540 HP. It is anticipated that besides the fuel cell technology involved in the fabrication of this unique model, also other technological solutions at the engine, materials and software level have to be envisaged, generating knowledge and know-how profitable to society in the long run.

**Outlook**

The basic knowledge and research competences for carrying out such an inspiring project are also present in the Dutch scientific community. We hope that such kind of activity will take place in this country in the near future, with a more active participation of other players in society.

Theme coordinator  
Dr. hab. Eduardo Mendes  
Associate Professor, Delft University of Technology
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 need 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 differ 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 until 31 December 2012

- Sulfonation of PEEK: (Vitrex 450 PF Mw: 39200) powder (25 g) was slowly added into vigorously mechanically stirred 379 ml of H₂SO₄ (95-98%) (95/5 wt.%) at 55°C for 5h. The solution was cooled down to room temperature and precipitated into ice-cold demineralized water. The polymer was filtered and washed with demineralized water until the pH was neutral.
- 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) was 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 nitrogen atmosphere.
- The ionic conductivities were investigated by AC electrochemical impedance spectroscopy (EIS). 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.

Figure 1: Results for 2nd standard heating on DSC and TGA under nitrogen and at 10°C/min curves for the pristine and the modified PEEK.
Figure 2: TGA from the membranes and SPEEK and 2nd DSC heating under nitrogen and at 10°C/min for the membranes after removing the thermal history at 230°C on the samples

<table>
<thead>
<tr>
<th>Humidity</th>
<th>System</th>
<th>Resistance/Ω</th>
<th>Conductivity/Scm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 % R.H.</td>
<td>Nafion</td>
<td>1.55</td>
<td>6.28x10⁻³</td>
</tr>
<tr>
<td></td>
<td>SPEEK 5h</td>
<td>4.19</td>
<td>5.88x10⁻³</td>
</tr>
<tr>
<td></td>
<td>SPEEK 5h + FeSO₄.x.7H₂O</td>
<td>0.80</td>
<td>8.12x10⁻³</td>
</tr>
<tr>
<td></td>
<td>SPEEK 5h + Li₃xB₃-xPO₄</td>
<td>0.77</td>
<td>1.18x10⁻²</td>
</tr>
</tbody>
</table>

Table 1: Resistance and conductivities values obtained from the impedance measurements

Figure 3: Nyquist plot from galvanostatic impedance spectroscopy for all the membranes test (1 KHz to 1 Hz and 10 mV oscillation, room temperature and 100% RH)

All output from the beginning until 31 December 2012
- Oral Presentation in the ECS PRIME Conference in Hawaii October 2012
The formation of special nano-sized structures normally requires the use of expensive equipment and/or techniques, such as cleanroom or ultra-high vacuum. Contrary to these methodologies, the proposed approach allows the formation of nanostructure by means of the combination of two inexpensive alternatives: sol-gel and 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 matrices of polymeric fibres 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, nanofibres and nanotubes. These architectures show an improvement of the solid oxide fuel cell (SOFC) microstructure.

**Research results until 31 December 2012**

**Nanochannels**

This technique consists of using the electrospun fibres as templates which are infiltrated with Yttrium Stabilized Zirconia (YSZ) sol-gel precursor. This results in YSZ with nanochannel-shaped porosity with diameter of ~220 nm in diameter. Moreover, the deposition of nickel catalyst is controlled by the presence of nickel precursors in the fibres. Therefore, we ensure a high porosity with large surface area and placement of the catalyst on its most active site. As a result, the state-of-the-art technique of using pore formers is improved by increasing the surface area and controlling the catalyst deposition. This makes the present architecture promising for SOFC anodes. **Figure 1** shows the templated nanochannels covered with NiO nanoparticles.

**Nanofibres**

In this case, a mixture of YSZ sol-gel precursor and polymer was electrospun. Ceramic nanofibres were formed after annealing the green matrix. These had an average diameter of ~560 nm with a length up to several μm. Subsequently, the samples were infiltrated with nickel precursor such that the YSZ fibres were covered with NiO nanoparticles as shown on **Figure 2**. Such a configuration is interesting for SOFC anodes.
Nanotubes

The electrospinning setup can be modified in order to spin two concentric fibres, i.e. coaxial electrospinning. If the inner fibre 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, has an average inner diameter of ~230 nm and an average outer diameter of ~530 nm. The porosity and morphology of the fibres can furthermore be tuned by selected heat treatments. This configuration can provide a superior architecture for support of a heterogeneous catalysis due to its large surface area.

Summarizing, we presented a method capable of making different nanostructured materials in a low cost and facile.

Figure 1: Templated YSZ nanochannels covered with NiO nanoparticles

Figure 2: YSZ nanofibers covered with NiO nanoparticles
Figure 3: YSZ nanotubes
Polymer Electrolyte Membrane (PEM) Fuel Cells (FCs) have attracted great interest because of their potential in substituting internal combustion engines in portable applications such as automotive. The main issues preventing the mass-scale commercialization of such promising devices are their cost and their durability that are not meeting the worldwide target requirements. These issues are closely related to PEMFC electrodes and especially their degradation with time and their cost.

Nowadays, PEMFC electrodes consist of porous carbon particles with randomly attached Platinum nanoparticles (Pt NPs) that have been mixed with a proton conductive ionomer, usually Nafion®. Hence, the structure is not well controlled. Pt NPs degrade mainly because of surface migration and sintering, dissolution, and Ostwald ripening. Additionally, the catalyst suffers from low utilization. The carbon support undergoes corrosion that can cause catalyst detachment and increase in wettability, thereby substantially decreasing catalyst performance.

Cost can be effectively decreased by use of smaller amounts of Pt by improving catalyst utilization or by using non-noble metal catalysts. Durability can be improved by using supports composed by graphitic carbon instead than Carbon Black and enhance the stability of catalyst NPs, for example by a more efficient binding to Carbon surface.

Our research is focused on the development of a new PEM electrode structure, which leads to optimal use of the catalyst particles with regard to reaction kinetics and mass transport, and has improved durability compared to conventional electrode. The core of the design is a continuous carbon nanotubes (CNTs) structure grown on Pt or Pt group metals particles. CNTs have already been proven to enhance the durability of PEMFC electrodes, but this approach is novel since the CNTs will form a network in which the catalyst particles are fixed and their migration is no longer possible, consequently inhibiting particles coalescence because of diffusion, Figure 1. The carbon nano-networks (CNNs) structure concept has already been proven by the TU Delft spin-off company Minus 9, which has recently patented its synthesis, Figure 2. They can be obtained by Chemical Vapor Deposition (CVD) catalyzed by transition metal NPs (Fe, Co, Ni, Pt...). The precursor allowing the formation of this special networked structure is the NPs synthesis template, Bicontinuous Microemulsions (BMEs). In fact, as the temperature goes up to 700°C, the surfactant starts to carbonize (250-600°C) by preventing NPs aggregation. The NPs are in such way entrapped in a fixed grid, and their high density allow the growth of interconnected nanotubes.
My PhD research aims to optimize CNNs concept in PEMFC electrodes, by investigating CNNs grown on Pt as catalyst itself for PEM and 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 (i) the understanding of template properties (BMEs) and how they affect CNNs structure; (ii) formation mechanism of NPs in BMEs and relevant parameters to tune NPs size, (iii) mechanism of growth of CNNs and crucial synthesis parameters (surfactant type, NPs concentration, temperature, time, catalyst support) to tune their properties (morphology, porosity, conductivity, thermal resistance).

Research until 31 December 2012

**Novel Approach to High Yield Nanoparticle Synthesis using BMEs**

BMEs are introduced as a highly efficient and versatile template for metal nanoparticle production. This special class of microemulsions is obtained by mixing a high percentage of a suitable surfactant and almost equal amounts of water and oil. Various types of metal NPs, including Pt, nickel, cobalt and core-shell combinations thereof, are produced in these templates having a size range spanning from 2 to 4 nm, with a very narrow size distribution. Particles size was verified by DLS and TEM (Figure 3). Size is tuned by solvent type, metal precursor and reducing agent concentrations. Nanoparticle coalescence is prevented by the microemulsion structure, allowing for a very high level of colloidal stability at high concentrations. In addition, a relatively low cost, in situ technique based both on turbidity and absorption spectroscopy is introduced that allows for on line monitoring of nanoparticle growth yielding detailed information on particle size, concentration, and on growth kinetics (Figure 4).

Figure 1: CNNs Concept

Figure 2: SEM image of CNNs

Figure 3: Pt NPs in BME

Figure 4: Uv-Vis signature of NPs growth
A computational microscope: coarse grain simulations of dense BMEs systems

Dense microemulsions of Sodium–ADT/n-heptane/water were simulated using the Martini coarse-grained force field. From Mean Square Displacement calculation of all species, it was possible to quantify caging effects and ions mobility. Average diffusion coefficients were calculated for all charged species and conductivity was found in quantitative agreement with experimental data. The scattering function was calculated for the hydrophilic species and matched the experimental data obtained from Small Angle X-ray Scattering measurements. Especially, bicontinuity of water and oil was for the first time computationally visualized. Equilibrated coarse grain simulations were reversed to atomistic in order both to compare ion mobility and to catch finer simulation details by saving enormous computational costs. Coarse grained simulations of large and dense microemulsions systems were able to reproduce experimental data with limited computational costs, allowing visualization and deeper investigation of controversial phenomena such as bicontinuity and ions mobility.

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

Figure 5: BMEs Coarse Grain Simulations

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 electrochemically active surface area (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 6. CNNs have higher oxidation resistance than other carbon supports, resulting in catalyst higher durability under fuel cell operating conditions. Additionally, a networked structure allow 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 π−π interaction with pyrene carboxylic acid, Figure 7. The relatively low cost of the synthesis procedure and their good performance make CNNs a potential substitute of actual catalyst support for Fuel Cell applications.
Non-noble electrocatalyst supported on interconnected carbon nanotubes for the reduction oxygen reaction

Three different types of CNNs were synthesized by varying the quantity of Cobalt from 0.1 to 1.7 %, and used as carbon support for non-noble metal catalyst production. Electro catalysts were synthesis by using 2,4,6-tripyridyl-s-triazine as nitrogen source. Iron was incorporated in the framework together with the nitrogen source, for coordinate the molecule and form the active site supported in the carbon nanoparticle. The active site was achieved by conducting the powder under a pyrolysis under nitrogen atmosphere at 850 °C for 3 hr.

Electrochemical tests under rotating disk electrode of three different types of CNNs, were compared with a commercial nanotube. Results show that the use of cobalt in the production of highly active nanotubes is crucial, resulting the best performance the one synthesis with the higher metal content (1.7%). In this case, cobalt acts as growing agent for the carbon production, but does not participate in the reaction because the metal is not available in the surface.

This work is carried out in collaboration with Dr. Alessandro Monteverde Videla and Prof. Stefania Specchia, Politecnico di Torino.

Output until 31 December 2012

Introduction

Electrochemistry of fuel oxidation on low temperature SOFC anodes is not well understood. Clear knowledge of electrochemistry of fuel oxidation when real life fuels are used (natural gas, reformed carbonaceous fuels, syngas from biomass or coal gasifiers etc) is required for selecting anode materials, optimising microstructure, degradation and for system level studies where this knowledge becomes an input. The aim is to gain insight into the mechanism and kinetics of fuel oxidation by accurately performing experiments with known parameters with electrochemical impedance spectroscopy and further de-convoluting the results in order to be able to establish the kinetics for a range of temperatures as well as compositions. It is expected that this information will be used to come up with improved IT-SOFC designs when real life fuels are used. Further system level studies for different fuels are important pointers towards optimization of the system as well as components. Together with the experimental data thermodynamics of the system will be studied in order to come up with refined concepts for highly efficient systems.

Research results until 31 December 2012

Thermodynamic Analysis of Solid Oxide Fuel Cell-Gas Turbine Systems Operating with Various Biofuels:

A thermodynamic analysis of SOFC Gas Turbine systems operating with different biofuels (namely - methane, ethanol, hydrogen, ammonia and methanol) was carried out in order to study the influence of fuel chemistry on the overall system performance and identify subsystems which contribute to exergy losses. This was done using Cycle Tempo. Cycle Tempo is a in-house software developed at TU Delft which can be used for thermodynamic analyses and optimization of power cycles including fuel cells. Cycle-Tempo employs a Gibbs free energy minimization based routine for equilibrium calculations in the fuel cell and combustor. It was found (Table 1) that methane is the most efficient fuel with respect to both energy and exergy efficiency (78 and 75.5 %). The energy as well as exergy efficiency of ethanol is slightly higher than ammonia (76.48 and 70.8 versus 74.7 and 70 %). Hydrogen has lower energy and exergy efficiency (70 and 69 %) but is still similar to that of ethanol or ammonia for exergy but the energy efficiency is much lower than both these fuels. Methanol is more efficient than Hydrogen energetically (73.5%) though the exergy efficiency is lowest (68.5%) among all the fuels in this study.
The causes of exergy losses in subsystems (Figure 1) for various fuels are quite different. The high fuel cell losses are not entirely because of low Nernst potentials. Using global reactions for reforming we can conclude that the imbalance between heats from electrochemical and reforming reactions influences in a large way the flows and hence the split between fuel cell and gas turbine power. The recycle ratios which are set by the inlet temperatures and heat recovery, in turn determine the per pass utilisation across the fuel cell. The high per pass utilisation makes the voltage across the cell higher and hence the fuel cell less efficient.

An important conclusion to draw from this is that at system level, the efficiency of the fuel cell alone does not dictate overall efficiency but it is dependent on other effects mostly attributable to the nature of the fuel. Heat effects play a major part in deciding flow distribution and setting of flows for all equipment. This is important for design at system level where we need to accommodate each fuel uniquely.

Figure 1: Exergy Losses in subsystems for various fuels

Table 1: Energy and Exergy efficiencies for different fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Energy Efficiency</th>
<th>Exergy Efficiency</th>
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</thead>
<tbody>
<tr>
<td>Methane</td>
<td>78.3</td>
<td>75.5</td>
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<tr>
<td>Hydroge</td>
<td>69</td>
<td>70.4</td>
</tr>
<tr>
<td>Ammonia</td>
<td>74.7</td>
<td>70</td>
</tr>
<tr>
<td>Ethanol</td>
<td>75.3</td>
<td>70.8</td>
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<tr>
<td>Methanol</td>
<td>73.1</td>
<td>68.5</td>
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Nickel Pattern anodes for studying SOFC electrochemistry:
The SOFC anode is a complex 3D structure where the gas phase, ionic phase and electronic phases are intermingled. This not only makes it difficult to quantify the triple phase boundary (TPB) length exactly, but also makes individual processes like charge transfer, diffusion, surface diffusion etc, difficult to localise and study. Pattern electrodes offer the advantage of having a well defined TPB length, so that reactions are localised. Impedance spectroscopy on pattern electrodes can provide mechanistic information in addition to identifying rate limiting steps.

In this work nickel is sputtered on YSZ with DC magnetron sputtering using a Nickel target and a metallic mask on YSZ substrate in a specific pattern to give a well-defined TPB length as shown in Figure 2. A TPB length of 0.2027 m/cm² was achieved. This method is much easier and is less expensive than the photolithographic techniques used earlier. Impedance spectroscopy is carried out on symmetrical cells in pure hydrogen with 4.3 % water vapour. Preliminary results (Figure 3) from equivalent circuit fitting of the impedance spectra indicate that the results are comparable to results available in literature and the rate limiting mechanisms can be identified.

Figure 2: Nickel pattern design with dimensions (not to scale)
Industrial collaboration until 31 December 2012
Not exclusively within this project but in general on related projects we co-operate with Royal Hoskoning DHV, Priva

All output from the beginning until 31 December 2012

Figure 3: Impedance spectra with Nickel Pattern anodes
Introduction

The purpose of this project concerns the development of a cheap and easily upscalable technology for thin film electrolytes for solid oxide fuel cells (SOFC) and solid oxide electrolyser cells (SOEC), e.g., yttria-stabilized zirconia (YSZ), and gadolinia doped ceria, on porous steel and optionally dense substrates. Because of these demands the attention will be focused primarily on the development of a wet-chemical route. Here one should think about the use of sol-gel techniques and chemical solution deposition, i.e., techniques with which a wet film with the proper molar ratio of cations can be deposited at room temperature. Techniques such as dip coating, spin coating and misted deposition will be employed to deposit films. Flame assisted spray pyrolysis will be considered as alternative. The advantage of this set of techniques is that they all employ similar kinds of precursor solutions and they are all suited for both planar and non-planar substrates.

An important issue in this project concerns the thermal consolidation of the dried films. Both conventional techniques and microwave-based rapid thermal annealing techniques will be employed. The latter technique has the additional advantage that the thermal consolidation step is very fast, and it is possible to sinter dense films at much lower temperatures than is possible with conventional sintering, and the microstructure can be controlled well.

All above-mentioned techniques have a broad parameter space, which renders the development and optimization time-consuming and labor-intensive. For this reason physical deposition, e.g., pulsed laser deposition, will be used in the optimization process, in order to screen parts of the parameter space quickly. The sintered films will be tested with gas tightness tests to determine the defectivity of the layers. High temperature electrochemical impedance spectroscopy will be employed to characterize the ionic conductivity of the layers.
Research results until 31 December 2012

1. Thin Film Density
1.1 Introduction
Sol-gel chemistry in combination with spin-coating is used to prepare thin YSZ films for SOFC applications. It comprises the hydrolysis and condensation of a stabilized metal alkoxide precursor into an amorphous gel and its crystallization after subsequent heat treatment. It is an often used technique because of its simplicity, low costs and control on the molecular level. However, no methods are currently available to accurately determine the density of sol-gel thin films. Since the use spin-coating allows the production of vast numbers of thin films, a high-throughput method is necessary.

1.2 X-Ray Reflectivity
X-ray reflectivity (XRR) is an X-ray technique that probes the surface of thin films at low angles of incidence. Typical properties such as density, film thickness, and roughness can be determined. This is mostly achieved by modeling the data to well-known models. The density of a thin film is determined by the so-called critical angle, where total external reflection is observed. Perfectly smooth films ($\beta/\delta=0$) act as a mirror, and the determination of the critical angle is easily determined with a step function, see Figure 1. For less smooth or imperfect films the absorption coefficient increases (i.e. as expected for sol-gel derived thin films), and the determination of the critical angle becomes increasingly difficult.

A facile method has been developed to accurately determine the thin film density, without prior knowledge of the investigated system. Simulations of our films with varying densities were made with the commercially available Leptos software package. For every simulated density, the deflection point (where the rapid intensity drop is observed) was determined and calibration curves were obtained. Consequently, our thin films were measured and the density was determined by the position of the deflection point (pseudo-critical angle) on the calibration curve. The method was validated by the density determination of single crystal substrates ($\rho_{rel}=100\%$) and of our films using a combination of Rutherford backscattering spectroscopy (RBS; amount of [Zr+Y] atoms/cm$^2$) and scanning electron microscopy (SEM; thickness), see Figure 2.

Figure 1: Simulated reflectivity curves according to Parratt’s formalism, with a fixed critical angle of $\theta=0.65^\circ$. At increasing layer imperfection, the absorption coefficient $\beta/\delta$ increases and determination of the critical angle of total external reflection becomes increasingly difficult.
1.3 Thin Film Densification
With the abovementioned technique, we are able to study the densification behavior of the YSZ thin films. The influence of e.g. substrate (strain) and temperature on the densification can be measured. Also, the exact sintering conditions to obtain gas-tight YSZ films, necessary for use as a SOFC electrolyte material, can be derived.

2. Low-temperature Synthesis of Proton-Conducting BaZr$_{1-x}$Y$_x$O$_{3-\delta}$

2.1 Introduction
Yttrium-doped barium zirconate (BZY) has received extensive attention in recent years due to its outstanding proton conducting properties. It is therefore a suitable candidate for fuel cells operating at 500-600 ºC. However, due to refractory nature of BZY, the densification of the ceramic is very difficult with solid state sintering, and temperatures >1600 ºC are needed for complete densification; causing degradation of the material’s properties. Therefore, alternative synthesis routes (e.g. wet-chemical syntheses) a explored to obtain nano-crystalline BZY at lower temperatures.

The basic working principle is equal to the SOFC, only the nature of the charge carriers is different. Oxygen vacancies are incorporated into the perovskite lattice by charge compensation of lower valency dopants. Exposure to humid atmosphere then results in the formation of hydroxyl defects.

2.2 Experimental
The synthesis is based on a paper from Stawski et al., and nano-crystalline BZY was obtained at temperatures as low as 78 ºC. Due to the small crystallite sizes obtained, a density of ~95.6% was obtained after sintering for 24 h at 1350 ºC. Full characterization of the as-synthesized material is currently in progress.

Reference
Scientific Papers:

Presentations:
Batteries

In preparation for start in 2013

Theme coordinator

Prof. dr. Peter H.L. Notten
In August 2012, the Green Deal proposal was signed by the Dutch Minister of Economic Affairs and in December the new, final decision was received. In anticipation of this decision, no new investment obligations were entered into, and in 2012 expenditure was limited to investments for which obligations already existed.

In 2012, in the framework of the ADEM program, costs were claimed for the amount of k€ 3,427. The total cost of the entire ADEM program claimed until the end of 2012 is thus k€ 9,037. The claimed costs are divided into costs for research assistants appointed for conducting materials research, costs for realised investments within the ADEM program and costs of the program office. Most of the research assistants have a multi-annual commitment of four years to conduct their research. The amount of k€ 4,172 exclusively entails submitted and paid investments that were approved by the ADEM program office. By the end of the financial year, most of the partners of the ADEM program still need to submit the realised investment costs for 2012. The costs that still need to be submitted for 2012 amount to k€ 1,951. It is expected that the € 15 million available in the first tranche of the ADEM program will be realised within the first four years of the program.

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Total realized ADEM investments ultimo 2012

- Setaram High Pressure (HP) Differential Scanning Calorimetry (DSC) Thermogravimetry (TG) + OmniStar Mass Spectrometer
- Equipment for partial IEC61215 and 61730 solar module characterisation (degradation in module performance after testing)
- ps laser (Pharos) met "R2R" optie + Q-sys 4-axis motion control
- Hitachi SU70 High resolution (HR) Field Emission Gun Scanning Electron Microscope (FEG-SEM) + Oxford Aztech element analysis (EDX) and crystallographic orientation analysis (EBSD)
- Hitachi S3700 Scanning Electron Microscope with large chamber + Oxford Aztech element analysis (EDX) + Hitachi IM4000 Ion Milling
- e-beam evaporation system
- Quantachrome Autosorb iQ-C + temperature programmed desorption
- Pyroprobe GC-MS (Da Vinci Europe)
- FAP LQ400E Linear VHF plasma source for dynamic thin film silicon deposition
- OptoSolar Spectrale Response with light bias
- Infrastructure ADEM Green Deal: Tempress reactor FANCY (4-stack process furnace) and Levitech Levitrack thermal ALD reactor
- Hoge druk Raman opstelling
- Magnetron Sputtering System for optically active coatings
- CVD deposition chamber for silicon thin films
- Tempress Boron deposition oven
- NMR upgrade 200 MHz
- XPS (0.5 micron resolution) + glovebox
- Combined Oxford Instruments CVD/ALD deposition equipment
- Chemical Looping Apparatus
- HPLC for catalysts for sustainable fuel production
- Conversions Inspector for Gas Separations
- Tempress SiN deposition tool
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