ADEM (Advanced Dutch Energy Materials innovation lab) is a joint initiative of ECN and the 3 Dutch Universities of Technology (Delft, Eindhoven and Twente), aimed at stimulating and accelerating innovations in the field of selected energy technologies. The Ministry of Economic Affairs, Agriculture and Innovation has financed ADEM with a 15 M€ first tranche. ADEM started in 2010, see the Annual Report 2010 and www.adem-innovationlab.nl, and ramped up its research activities in 2011. The majority of the PhD-students have been appointed, with the exception of those in the research theme “Batteries”.

In the course of 2011 the Ministry of Economic Affairs, Agriculture and Innovation, ECN, the 3 TU’s and a group of companies in the field of energy technology agreed upon the second phase of ADEM as part of the Green Deal Materials for Energy applications (GDME). Thus it has been secured that the research and investment program ADEM will be fully integrated in the new Dutch innovation policy framework, with clear involvement and commitment of the private sector. On behalf of the Dutch government, Minister Verhagen signed a large number of Green Deals, including GDME, in August 2011. Eight companies committed to invest in ADEM signed the GDME on behalf of the private sector. However, the administrative procedure following the public signing ceremony has not been concluded and therefore the second tranche of 15 M€ is not yet available. As a consequence the investment program of ADEM is partly on hold.

Nevertheless, impressive progress has been made in the research projects that did start in 2010 and 2011 and this part of the ADEM research and investment program is reaching full swing.

An international team of very talented and highly motivated young scientists tells its story in this Annual Report. Enjoy!

On behalf of the ADEM-partners
Wim Sinke, Scientific Director
Introduction

Plenary ADEM conference 2011
Green Deal - Materialen voor Energietoepassingen

Transport, Transfer and Storage of Heat

Project: Characterization of water vapor sorption process in salt hydrates for the 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: Integral material models for composites

Project: Thick laminates on wind industry

Solar Cells and Modules

Project: Solar Spectral Conversion Efficiency Enhancement of Photovoltaic Devices

Project: Advanced nanostructured silicon-based films for stable absorber layers

Project: Silicon based nano-particles for efficient solar-spectrum conversion in all-silicon tandem cells

Project: Materials behavior of multicrystalline silicon solar cells

Project: Mechanism of energy and charge transport in advanced photovoltaic materials

Project: Advanced passivation schemes for crystalline silicon solar cells

Project: Laser material interactions for PV applications

Catalysis, Membranes and Separations

Project: Chemical looping processes to improve the performance of indirect fluid-bed gasification technology

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

Hydrogen Production and Fuel Cells

Project: Carbon Nano-Networks for PEM Electrodes

Project: Fuel oxidation on ITSOFC anodes and its influence on system performance

Project: CO₂ capture with ionic liquids

Project: Robust anode for SOFC

Project: Thin Film Electrolyte Manufacturing Technology for SOFC and SOEC

Batteries
Materials for sustainable energy
The urgent need for a more sustainable energy system has become apparent in everyday life. According to many scientists the first effects of climate change are now clearly visible. High and very volatile energy prices show our strong dependence on supply from just a few parts of the world. Air quality is an important issue in many cities and regions throughout the world. And so on. Development and rapid large-scale deployment of more efficient and sustainable energy technologies, as well as energy savings are essential building blocks for the solution of these problems. Advanced materials, in turn, are enablers for the development of new energy technologies. ADEM, the Advanced Dutch Energy Materials innovation lab, therefore acts at the heart of the potential solutions.

Green Deal
Successful energy innovation requires the close and efficient cooperation between public and private stakeholders. Within ADEM, ECN, the 3 Dutch Universities of Technology therefore work together closely with companies in the broad field of energy technology and the Dutch government. This has been formalized in a "Green Deal Materials for Energy applications" (GDME), which is currently being shaped and operationalised. Since the government has not yet officially signed the GDME, ADEM partners could unfortunately not give full throttle in terms of financial commitments yet. Hopefully green light will be obtained in 2012. World developments take place at breathtaking speed, so The Netherlands needs to accelerate to stay “in business”. In parallel to shaping the Green Deal, ADEM partners build the open innovation lab, which is available for other research groups and organizations, giving ADEM a truly national scope.

ADEM gets company
Materials availability and the development of advanced new materials, employing nanotechnology and other novel approaches, has rapidly become a key area field of interest for industries and policies worldwide. Several important strategy papers and roadmaps have been published in 2011. In Europe, the publication of an EC “Materials Roadmap Enabling Low Carbon Energy Technologies” and the development of the “Energy Materials Industrial Research Initiative” (EMIRI) underlined the importance of materials for the future of our energy system and economy. ADEM was initiated well ahead of this trend, showing the vision of the partners involved.

ADEM organization
ADEM is organized in 6 research themes, each with its own coordinator. The overall coordination is done by the Steering Committee, in which representatives of all 4 research partners have a seat. Day-to-day management is done by the Program Office, in which the Scientific Director and Program Secretary team up. This is also the point of contact for the government, the private sector and other external stakeholders. With ADEM becoming part of a Green Deal, a Program Committee will be established, through which the stakeholders, and especially the participating private partners can advise and help steering the research program into the optimum direction, i.e. high-quality research with maximum utilization.
The first plenary ADEM conference ‘Connect to the future in Energy materials’ was held on May 26th and 27th 2011. Goal of the ‘internal’ event was to further develop the ADEM community, meeting each other in person and sharing information, knowledge and experience. Two days of interaction did the job!

After a motivating and inspiring presentation of ADEM by Scientific Director Wim Sinke, small working groups of PhD candidates, with the support of project leaders, collaborated on sketching wild, marketable product ideas within their theme. Furthermore, the groups were challenged to analyse the weaknesses and the market potential of their product idea and how to capitalize on this. This served as a preparation for the business awareness workshop the next day.

In the evening guest speaker Dr. Ton Bastein (TNO) sketched the consequences of worldwide scarcity of materials in his keynote presentation. Discussions on scarcity and its consequences for clean energy solutions, carried right through dinner. A lively buffet with students concentrated on making the best out of their innovation. Across theme’s and institutions those directly involved with the program found each other.

The next day started early to enable all PhD students to present their research project. Each student addressed both the core of his or her research as well as the industry relevance, practicing their skills to present and defend their work along the way. A complete overview of ADEM-research sparked the interest of all present and created valuable interaction between researchers from different disciplines and institutions. In between the large number of presentations two parallel sessions focused on the link between business and research.
**Business collaboration**

Wim Sinke led a session with project leaders and theme coordinators on industry collaboration. In a lively discussion potential industry partners were discussed as well as the status of cooperation within the projects already started.

**Business awareness**

A down to earth talk by seasoned business developer Heiko Sportel (program manager at M2i) allowed the students an insight into the reality of business development. This inspired the groups of PhD students to present their business analysis of the marketable innovations, in a way that would attract industrial partners. For some a new way of looking at the industry relevance of their research, for all a great exercise in commercial thinking.

After the last PhD presented her project and after the closing remarks, drinks were served and the conference informally evaluated. All agreed it had been an excellent conference, inspiring to learn more about the scientific work within the program, to recognize opportunities for using research facilities across the institutes and to exchange industry, knowledge and innovation contacts.

The participants had indeed connected to the future in Energy materials.
Ondergetekenden:

1. De Minister van Economische Zaken, Landbouw en Innovatie, hierna te noemen: Rijksoverheid;

2. De kennisinstellingen:
   a. Stichting Energieonderzoek Centrum Nederland (ECN)
   b. Technische Universiteit Delft
   c. Technische Universiteit Eindhoven
   d. Universiteit Twente

2. De kennisinstellingen:
   a. Stichting ATO
   b. BioMCN
   c. Levitech
   d. Nefit B.V. / Bosch Thermotechnology
   e. NXP Semiconductors Netherlands N.V.
   f. Suzlon Blade Technology
   g. Tempress Systems B.V.
   h. Knowledge Centre WMC

Hierna tezamen ook genoemd: Partijen;
Partijen hebben gezamenlijk het volgende vastgesteld:

1. Het kabinet beoogt een ‘Green Deal’ met de samenleving, die bijdraagt aan verduurzaming van de maatschappij op korte en langere termijn en die lonend is voor overheid, bedrijfsleven en maatschappij.

2. Partijen zien publiek-private samenwerking als de beste manier om verduurzaming van onze economie te versnellen en hier ook economisch van te profiteren. Creativiteit, ondernemerschap, kennisdeling en innovatie zijn onmisbaar om deze verduurzaming mogelijk te maken.

3. Bij de Green Deal gaat het om concrete initiatieven op het brede gebied van duurzaamheid, waarbij barrières worden weggenomen, innovaties worden ontwikkeld, gefinancierd en toegepast en kansen worden benut. In de praktijk wordt de maatschappij geconfronteerd met belemmeringen die initiatieven voor verdere verduurzaming in de weg staan. In de Green Deal willen partijen concrete afspraken maken om deze belemmeringen weg te nemen, zodat initiatieven die anders moeilijk van de grond komen ruim baan krijgen. Initiatieven kunnen betrekking hebben op bijvoorbeeld decentrale energie, energiebesparing, schaarse grondstoffen, broeikasgassen, biodiversiteit, duurzaam inkopen, etc. Deze initiatieven kunnen vervolgens als voorbeeldfunctie dienen voor andere partijen en daarmee de totale markt in beweging zetten (vliegwieleffect). Doel van de Green Deal is laten zien dat groen en groei hand in hand gaan.

4. Nederland heeft een goede en op enkele onderdelen leidende kennis- en technologiepositie op het gebied van duurzame energietechnologieën. Versterken en uitbouwen van deze positie biedt belangrijke kansen om duurzame “groene banen” te creëren en om de toepassing van duurzame energie te verbreden en te versnellen: groen en groei in de praktijk gebracht.

De Green Deal Materialen voor Energietoepassingen (GDME) tussen genoemde partijen omvat de volgende aspecten en afspraken:


- **Wat?** De GDME beoogt 1) de verduurzaming van onze economie te versnellen en 2) hier ook economisch van te profiteren, door materiaalonderzoek ten behoeve van de ontwikkeling en toepassing van nieuwe en verbeterde duurzame energietechnologieën. Het economische effect betreft zowel groei in banen als groei in innovatief vermogen en concurrentievormgen. Daarbij gaat het in het bijzonder om: windenergie, zonneenergie, elektriciteitsopslag (onder meer i.t. elektrisch rijden), warmteopslag (onder meer i.t. energiebesparing), biobrandstoffen en brandstofcellen. Het programma Advanced Dutch Energy Materials Innovation Lab (ADEM) vormt de kernactiviteit van de GDME.

Waarom?
Materiaalonderzoek vormt de basis van belangrijke innovaties op het gebied van duurzame energietechnologieën en biedt inherent “groen en groei”. Versterking van dat onderzoek en bundeling van krachten tussen kennisontwikkelaars en -toepassers (de kern van deze GDME) zijn essentieel om in de sterk competitieve mondiale context een concurrerende positie te behouden en om technologieën snel en grootschalig te kunnen toepassen. Daarmee levert deze Green Deal onmisbare ingrediënten voor langdurige, hoogwaardige economische activiteiten en voor verduurzaming van de energievoorziening en het energiegebruik. Bij het onderzoek zullen de kennisinstellingen zich vooral richten op funderend onderzoek en opleiden1 van hoogwaardige kenniswerkers en de industrie op toegepast onderzoek.

Hoe?
- Het Energieonderzoek Centrum Nederland (ECN) en de drie Technische Universiteiten (TUD, TU/e en UT) bundelen hun krachten en delen hun kennis op het gebied van materiaalonderzoek ten behoeve van energietoepassingen en hebben daartoe een samenwerkingsovereenkomst gesloten. De krachtenbundeling betreft zowel onderzoekprojecten als onderzoekinfrastructuur.
- Genoemde onderzoekspartijen werken in het kader van deze GDME thematisch en doelgericht samen met bedrijven op het gebied van energietechnologieën, met het doel om de basis te leggen voor de ontwikkeling en marktinintroductie van geavanceerde nieuwe producten. Bedrijven leveren bijdragen aan het onderzoekprogramma en de onderzoekinfrastructuur, om de GDME samenwerking mede vorm te geven en zo maximale spin-off te genereren voor een duurzame economie.

Partijen spreken af:
- Vertegenwoordigers van bedrijven die een bijdrage leveren (de industriepartners), vertegenwoordigers van de ADEM-onderzoekspartijen, alsmede vertegenwoordigers van het Ministerie van EL&I vormen een Programma raad die de interactie tussen overheid, bedrijven en onderzoeks partijen structureert, die mede richting geeft aan het onderzoek (vraagarticulatie en –sturing) en die actief innovatie en utilizatiemogelijkheden verkent. In de Programma raad hebben zitting: zie bijlage. Deze Raad kiest een voorzitter uit haar midden en staat garant voor de realisatie van het ADEMonderzoeksprogramma. Gezien de inhoudelijke verbondenheid van deze GDME met het Materials Innovation Institute M2i zullen partijen een geschikt samenwerkingsmodel ontwerpen en implementeren, teneinde de effectiviteit van het Nederlandse materiaalonderzoek te optimaliseren.

1 Alleen al binnen het ADEM-programma betreft dit het opleiden van 40 promovendi.
Het ADEM-onderzoeksprogramma wordt inhoudelijk volledig geïntegreerd in en vormt de onderzoekskern van deze Green Deal. De Rijksoverheid heeft, in het kader van het ADEM-innovatieprogramma, €30 mln. toegezegd. De tweede tranche van de overheidsbijdrage aan ADEM (15 M€) wordt vrijgemaakt en verstrekt ten behoeve van de uitrol van het ADEM-onderzoeksprogramma, binnen de kaders van deze Green Deal en met tenminste 10% (>1,5 M€) private bijdragen (cash of in-kind). De eerste tranche van de overheidsbijdrage aan ADEM (15 M€) is reeds in een ander subsidiekader aan het ADEM-consortium verstrekt en is geen onderwerp van deze Green Deal. De flexibiliteit in het ADEM-programma in termen van nog te definiëren onderzoeksprojecten en (investeringen in) onderzoeksinfrastructuur wordt volledig benut om invulling te kunnen geven aan de vraagsturing door de industriepartners in de GDME. Partijen zijn bereid nadere voorwaarden af te spreken over de nog niet gecommitteerde gelden teneinde het onderzoek maximaal vraaggestuurd te maken, en bereid bilaterale overeenkomsten af te sluiten over specifieke onderzoeksomwerking en gebruik van resultaten. Daarnaast geven industriepartners en overheid via de Programma raad mede richting aan de onderzoeksprojecten en het verder inrichten van het ADEM Open Innovatielab dat onderzoeksfaciliteiten beschikbaar maakt.

Getekend te ’s-Gravenhage op <datum>
De Minister van Economische Zaken, Landbouw en Innovatie
Drs. M.J.M. Verhagen
Bijlage: Programmaraad

- Ministerie van Economische Zaken, Mr. E.J. de Vries
- ECN, P.A.O.G. Korting
- TU Delft, Prof.dr.ir. T.H.J.J. van der Hagen
- TU Eindhoven, Prof. dr. P.H.L. Notten
- Universiteit Twente, Prof.dr.ir. L. Lefferts
- Stichting ATO, J.M. Bais
- BioMCN, P. Compagne
- Levitech, E. Granneman
- Nefit B.V. / Bosch Thermotechnology, Dr. S. Park
- NXP Semiconductors Netherlands N.V., L. Warmerdam
- Suzlon Blade Technology, Dr.ir. H.E.N. Bersee
- Tempress Systems B.V., Dr. A. Hasper
- Knowledge Centre WMC, D.R.V. van Delft
Transport, Transfer and Storage of Heat
Within the broad theme of heat, it was decided to group the ADEM activities around the sorption materials for heat pumps, improved structuring of heat transfer surfaces and compact heat storage materials. Limiting the focus to two system components that have resembling processes (heat storage and heat pump) and deploy similar techniques (synthesis of sorption materials, molecular analysis and TGA-DSC measurements) strongly enhances the coherence within the theme.

In this research, materials are examined in an experimental as well as in a numerical manner. In 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 (see figure). In Twente, heat transfer experiments are conducted on surfaces that are covered with Carbon Nano Fibres. Finally, at ECN and in Eindhoven, experiments and simulations are conducted on Thermo-chemical storage materials. Particular attention is paid to changes in the material structure resulting from hydration and dehydration reactions.

The ongoing research is actively communicated at conferences and workshops. Moreover, research leaders are participating in IEA-SHC Task 42 and KIC InnoEnergy and successful requests/proposals have been submitted in the framework of the EU FP7 programme.

**Theme coordinator**

**Prof. dr. ir. Anton van Steenhoven**
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(H2O) = 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](image)

In order to develop adequate sorption materials for this application, this project focuses its research to establish the effect of the structural and material properties on the heat- and vapor transport taking place at different scales of 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 Li$_2$SO$_4$.H$_2$O and CuSO$_4$.5H$_2$O 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 MgSO$_4$.7H$_2$O and MgCl$_2$.6H$_2$O, selected at ECN as promising thermochemical materials for this application.

**Research until 31 December 2011**

During this first year of the project, a literature research, in collaboration with PhD students in Eindhoven, was carried out to identify relevant experimental characterization techniques to characterize the water vapor sorption process in salt hydrates. The techniques of thermal analyses (TG-DSC), X-ray diffraction (XRD) and microscopic observations on monocrystals have been selected and adapted under well-controlled experimental conditions (temperature, water vapor pressure) simulating the seasonal heat storage process. Next, the characterization of the dehydration reactions for the four materials mentioned previously has shown that different processes are involved at molecular and grain levels that influence the heat and vapor transport in the materials (figure 2).

**Figure 2**: Representation of the heat and mass transfer processes during dehydration of a powder bed at (a) crystal and (b) grain scales. The dashed red lines indicate the heat flow and the solid blue lines the vapor flow.

The results obtained from the different measurements show that the release of the water molecules and the reorganization of the crystal lattice structure taking place during the dehydration reactions of these materials induce a compaction at the molecular level, which directly influences the grain level by the formation of cracks in the material (figure 3) and a reduction of mechanical strength of the material. However, the results obtained for the four materials studied in this project have shown that the behavior of each material is different and an individual study of their process is required.

**Figure 3**: In-situ microscopic observations of the dehydration process of a Li$_2$SO$_4$.H$_2$O monocrystal under a water vapor pressure of 13 mbar with a heating rate of 0.5°C/min.
The studies carried out on the two most promising TCM materials MgSO4.7H2O and MgCl2.6H2O have shown interesting characteristics in term of heat storage for the seasonal application. MgSO4.7H2O showed an energy density of 2.12 GJ/m3. However this result should be treated with caution. Parallel studies at ECN showed that this material does not provide sufficient temperature lift during hydration under the practical conditions of seasonal heat storage. MgCl2.6H2O, which presents an energy density of 1.83 GJ/m3, is the most interesting material for seasonal heat storage application. However, previous studies for this material showed some problems with instability and decomposition of the material. In this first year of the project, it has been established that a restriction of the operating temperature range between 40 and 130°C in MgCl2.6H2O would overcome these problems.

Industry activities until 31 December 2011
The objective of the present research project is to obtain fundamental knowledge on 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. Several companies developing low-energy buildings (BAM), manufacturing domestic heating systems (Nefit, Redenko, and Remeha), and supplying the required salt hydrates for this application (Nedmag and Xsorb) have been contacted for participation in this ADEM project. These companies have shown an interest in this technology for developing cost-effective heat storage systems for individual houses but no financial commitment has taken place until now. However, a collaboration with a large European manufacturer of HVAC equipment and a new material supplier started related to the materials studied in this project. For confidentiality reasons, the names of these companies cannot be disclosed in the present report.

Output until 31 December 2011: Conferences participations
2. 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.
3. 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.
An important class of solid sorption materials constitutes of the crystalline salt hydrates like magnesium and calcium chloride. One of the bottlenecks in the application of these sorption materials in seasonal heat storage systems is the rate at which the material can be hydrated or dehydrated. This rate is highly determined by the transport properties of vapor and heat in the matrix structure of the material on the one hand and in the pore structure of the material on the other hand. The goal of this research line is to gain more physical insight into the limiting transport properties of vapor and heat, which will be used to set up design guidelines for new solid sorption materials and systems. Within this line of research validated micro- and meso-scale models will be developed for the hydration and dehydration processes taking place in powdery samples of crystalline salt hydrates. These processes are a combination of heat and vapor transport in the crystalline matrix structure of the grains taking into account the presence of fractures/dislocations and cracks, and in the pore structure of the powdery samples (in between the grains). Using the developed models the material properties will be optimized with respect to the transport properties of vapor and heat, determining the power density, and the sorption capacity of vapor, determining the energy density. Special attention will be given to the influence of structure properties of the materials like the porosity of the sample, the grain size, the presence of fractures/dislocations and cracks, on the aforementioned quantities.

Figure 1: Schematic of the heat and mass transfer processes during dehydration of a powdery sample: the dashed red lines indicate the heat flow and the solid blue lines the vapor flow. In the left figure both a crack and fractures/dislocations are schematically shown influencing growth of the dehydration front in the grain and vapor transport out of the grain.
Research from 01 November 2011 until 31 December 2011

The CFD software OpenFOAM is studied on its suitability to model heat and vapor flow in a porous medium consisting of spherical particles. Besides, a literature study is in progress on the hydration and dehydration reactions taking place in salt hydrates. The models developed will be validated with meso-scale experiments on powdery level carried out in a parallel-running ADEM-project at ECN.
The allocation of heat and cold in the Netherlands takes up 38% of the total primary energy consumption (3233 PJ). This is considerably more than the energy demand for electricity production (27%), transportation (17%) and raw materials for the chemical industry (18%) [1]. The process of heating and cooling thus holds a great potential for energy savings and subsequent reduction of CO$_2$-emissions.

Thermally driven chillers and heat pumps, based on the reversible adsorption and desorption of a working fluid on an adsorbent, could help realizing these energy savings. The energy required to drive these adsorption heat pumps could be taken from low temperature heat sources (e.g. ground heat exchangers), industrial waste heat or even solar energy, reducing primary energy requirements. Conventional adsorbents are silica gels and zeolites, often using water as working fluid. Common drawbacks for adsorption driven heat pumps are low thermodynamic efficiencies, discontinuous mode of operation and large volume and weight compared to traditional mechanically driven heat pumps (based on vapor-compression).

This project aims at developing new adsorbents for thermally driven heat pumps to improve both the thermodynamic efficiency and mass and heat transfer characteristics. In particular a new class of materials, Metal-Organic Frameworks (MOFs), are being investigated for potential use in adsorption heat pumps. These frameworks consist of inorganic clusters linked together by organic linkers to form three dimensional porous crystalline structures. MOFs offer a wide range of topologies and pore sizes (from meso to micropores and even combination of both) that may result in both enhanced transport and high adsorption capacity, essential for applications in heat and cold allocation. The search for improved adsorbents is based on a conjunction of both experimental work and molecular simulations (e.g. Monte Carlo, Molecular Dynamics).

Starting point of this project is a screening of different frameworks for potential application in adsorption driven heat pumps. This is based on scientific literature, adsorption isotherm measurements and detailed simulations on a molecular level. For water as working fluid, a few promising frameworks are depicted in figure 1. Clearly, exceptionally high loadings of water can be achieved on these frameworks. MIL-101(Cr) [2], for example, reaches up to 1 gram of water per gram of solid. This is considerably higher than conventional silica gels (~0.2 g H$_2$O per gram [3]) and zeolites (~0.3 g per gram [3]). Furthermore this material, structure depicted in figure 2, has proven to be stable upon contact with water, by no means a trivial feature when regarding MOFs.
However, the majority of water adsorption in MIL-101 (and MIL-100) occurs at relative pressures unsuitably high for the envisaged applications. Therefore, efforts are being conducted to tune the adsorption properties by functionalization. By grafting organic molecules and by adding functional groups to the organic linkers, either before or after material synthesis, it is possible to change the hydrophilicity of the framework and subsequently the (relative) pressure at which water starts to adsorb. Alternative working fluids are also being studied.

Parallel to these endeavors, molecular simulations are performed to investigate adsorption and diffusion phenomena on a molecular scale. A collaboration with the group of prof. Sofia Calero (RASPA) of Pablo de Olavide University, Seville, has been set up, as this group is experienced in molecular simulations involving MIL-101 and other MOFs. These molecular insights will be very helpful in directing functionalization efforts. Future plans include the investigation of diffusion of water and methanol in and the thermal conductivity of these materials and a small scale proof-of-principle.

References
Ever since the discovery of carbon nano-fibers (CNFs), it was anticipated that these nanostructures would have truly remarkable mechanical and heat-transport properties, given to the strength of the carbon-carbon bond within graphene layers in graphite. Nowadays, there is growing evidence, coming from both experimental and theoretical studies, that CNFs do indeed have an outstandingly high Young’s modulus, high thermal stability and thermal conductivity. Due to their high extremely thermal conductivity, carbon nanotubes are being used in heat exchanger surfaces. This 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. These losses have a large influence on their final application.

Research until 31 December 2011

CNFs Synthesis:
Growth of CNFs was achieved on a simplified heat transfer structure using catalytic vapor deposition process. Currently, we have achieved synthesis of CNF on a 50 μm Nickel (Ni270, 99.9%Ni) and Nickel based (80%Ni,20%Cr) wires. Prior to CNF-synthesis, the samples were first oxidized and then reduced in a quartz reactor heated by a horizontal furnace with air and a mixture of H2 in N2 at 700°C for 1 hr and 2 hrs respectively. This pretreatment is essential for creating grains on nickel wire surface, which support the nucleation and growth of CNFs. Followed by reduction pretreatment, the samples were exposed to a reactive gas mixture of C2H4, H2 and N2 at 600°C for 1hr. The samples were subsequently cooled down in N2 to room temperature.

Figure1: SEM image illustrating CNF growth on Ni270 (left) and Nichrome (right) samples.
After the growing process, samples were characterized for their size and amount of carbon deposited. A jungle of CNFs was observed for both substrate materials, see figure 1. The fiber length exceeds 50 microns which creates a larger diameter of the sample. Currently, the rate of deposition as a function of temperature and time of deposition are being investigated. Controlling the deposition rate will help to optimize the length of the CNFs. As for the density of the CNF along the heat exchanging surface, new surface treatment is proposed.

**Heat transfer setup and measurement:**
A constant temperature heat transfer measurement setup was built to measure heat transfer from the wire to the ambient. The setup includes heat flux measurement and temperature calibration. Once the sample is synthesized and characterized, the wire sample is spot welded to a probe.

As cold air flows from a nozzle (with a uniform velocity profile) across the cylindrical wire, the cooling effect reduces the resistance of the heated wire sample. To keep the temperature of the sample wire constant, additional current is supplied. The additional current measurement helps in achieving the amount of heat dissipated due to the flow, which further helps in measuring the convective heat transfer coefficient. Comparisons will be made with bare wire and the enhancement level can be investigated.

Heat transfer measurement was made for sample produced and evaluated. Results show heat transfer enhancement is not achieved due to the large CNF surface deposit. Reducing the length of the CNFs and lowering the density across the surface are some of the parameters considered to research further.

**Output until 31 December 2011**
Materials for Wind Turbine Blades

Since last year all three PhD projects are manned and under steam. Two durability subjects on thermosetting composites are studied at the Wind Turbine Materials and Constructions Test Centre (WMC, Wieringermeer). At the Design and Production of Composite Structures group (Delft University) a PhD is working on thermoplastic composites. She is investigating the processing of low cost APA6, upgraded by carbon nanofibres. And finally, the design and development of a huge 20,000,000 N dynamic testing machine to study the fatigue resistance of very thick wind turbine sections is completed at WMC and in the stage of materialization, see the figure.

The 20MN test frame
The design of this tall fatigue test jig (see figure) is completed at WMC with focus on the major critical structural parts and control units. For the year to come a European procurement process will be started.

Theme coordinator
Prof.ir. Adriaan Beukers
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. Even though 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 until 31 December 2011

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. Different methods to disperse CNF in APA6 were attempted, namely mechanical stirring, high shear mixing and ultrasonication in a sonication bath. These techniques resulted in agglomerations due to insufficient energy. Preliminary tests with high intensity ultrasonication showed some good results caused by the high energy cavitation, a momentary implosion of bubbles. Therefore, this technique was selected for this study. The local temperature near the cavitation can be as high as 5,000°C with 2,000 atm pressure. This process generates high shear stresses that are able to break the CNF agglomerates, and might as well affect the resin. Therefore the feasibility of applying high intensity ultrasonication to the APA6 system was investigated. APA6 is reactively processed from its monomer. Therefore the processing temperature (and
hence polymerisation) is a crucial processing parameter. The process characteristics of the sonicated APA6 and the nanocomposites were investigated. 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. Sonicated Caprolactam is referred as C_xx_xx.

As shown in figure 1, the heating rate depends solely on the amplitude regardless of type of sonicated liquid; monomer, reactive mixture nor reactive mixture with CNF. The temperature at the end of sonication depends on initial temperature, heating rate (amplitude) and sonication duration (energy per unit volume). Even the curing temperature was set at 160 °C, due to exothermic reaction, the temperature in the middle of the reactive mixture reached 200 °C. Kinetic curves for different processing parameters are shown in Figure 2. For low energy ultrasonication, the kinetics of the reactions were similar to the reference sample, 0_0_0. High intensity ultrasound was found to accelerate the ring open polymerisation. The difference in kinetic reaction of the sonicated APA6 was therefore the result of the increase in temperature as well as chemical effect of high intensity ultrasound.

Figure 1: Temperature of the mixture during sonication.

Figure 2: Kinetic curves of the reactions.
Industry activities until 31 December 2011

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.

Output until 31 December 2011

A wind turbine rotor blade is a structure that is heavily loaded in many ways. The fatigue loading has a stochastic nature with a number of cycles that is order of magnitude higher than for instance an aircraft. Large blades suffer severe gravity loading. Furthermore, wind turbines operate in a variety of environmental conditions, including heat, cold and humidity. The load carrying structure consists of various materials including different fibre orientations, laminate thicknesses, sandwiches, and adhesives. With the increase of wind turbine size and the requirement for reliability, the need for accurate design rules increases as well. The knowledge of material behaviour has to keep pace with the increasing demand for accurate design rules. In previous material research projects, such as OPTIMAT BLADES, UpWIND and InnWIND, several European institutes cooperated. Several effects influencing material behaviour were established and resulted in improved design recommendations and an extensive large database of test results.

On this basis a more integral model of the material behaviour can be developed and used for establishing more accurate design rules resulting in a more optimal design of wind turbines. The existing database contains experiments designed to find direct relationships between load and fatigue life, but implicitly also contains a wealth of information on interdependent and confounding effects of temperature, frequency, specimen and laminate definition, laminate thickness, external temperature, material, etc. on life. In this project statistical analysis of this data, combined with physics-based material modeling will be used to extract this information and to develop integral material models to account for the combined effect of different parameters on material performance. On the effect of laminate thickness, the related ADEM project ‘Strength and fatigue of thick laminates, connections and repairs for large offshore wind turbines’ will provide input.

**Research until 31 December 2011**

In an early phase of the project, the existing database was reviewed and optimized for automated statistical evaluation by a customized (Python-based) script. For the analysis of fatigue data statistical methods were reviewed and tested. The least squares method is commonly used for regression of fatigue data, however this method is limited in flexibility and robustness. A maximum likelihood estimation based regression method has been developed for fatigue data, which addresses these limitations. This method provides direct improvements, most importantly in the field of proper handling of run-out data in the regression and flexibility of using different distribution functions.
The existing dataset is not statistically balanced with respect to all parameters investigated. Therefore, experimental research is ongoing. For validation of life prediction methods for variable amplitude fatigue behavior, additional experiments were performed using wind turbine specific load spectra. For the first time, a set of fatigue data was generated for the NEW WISPER2 spectrum and the UPWIND/INNWIND reference material. This new spectrum was developed in the UPWIND project and is representative for current multi-MW size wind turbines. Other experimental work addressed a.o. the interlaminar shear fatigue properties, including development of a dedicated interlaminar shear fatigue fixture for faster testing, behavior of biaxial laminates at low and high temperatures and the transverse fatigue properties of uniaxial laminates.

For the experimental fatigue program for the thick laminates project, a design for a 30 MN test frame was made. For the fatigue behavior of thick laminates temperature effects are expected to be significant. The relation between visco-elastic heating and fatigue life at various temperatures is part of the ongoing research. To study the temperature build-up inside thick laminates during dynamic loading, an investigation to relate the temperature build-up with the energy loss factor observed during the fatigue test was started. Loss factors are measured experimentally and used as input for thermal Finite Element simulations.

**Output until 31 December 2011**

- Nijssen, R., Westphal, T., Stammes, E., ‘Strength and fatigue data from the UPWIND project’, EWEA 2011 conference, PO.265
Generally it can be consider as thick laminates those with thicknesses over 10mm. In wind turbines blades, thick laminates can be found in different parts, such as the root or the cap. For an actual 40mts long blade, thicknesses between 30 to 50 mm might be expected 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 100-150mm might be expected.

Actually, blade designs are based on static and fatigue 1-5mm thick coupon test, some safety factors establish by the certification entities and a full scale blade test. A very few work on thick laminates testing has been publish in order to compare the properties differences between thin and thick laminates weather on fatigue or static testing. Therefore, on account of the increasing presence of thick laminates on the main parts of the present and future wind turbines blades and on the aeronautical industry, more comprehensive study on thick laminates behavior, testing and properties is required in compassion 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 fatigue life prediction, design rules, scaling effect on laminates, 3D-effects on main blade subcomponents testing, self heating or the manufacturing processes influence on the final laminate properties, are a matter of interest for these work.

It is known, that manufacturing process has a stronger influence on thick laminates final properties than in thin laminates. Because of the temperature gradients that appear through the thickness during the curing cycle, each lamina cure with a relative different cycle. It is suspected that the non-uniformity on the curing cycles for each lamina is related with residual stresses and the mechanical properties variability through the thickness. Moreover, it is necessary to understand the influence of residual stresses and how does the lamina mechanical properties varies through thickness, in comparison with small coupon tests, in order to determine the thick laminates mechanical properties statistical variability, and related with different sources.

During the mechanical dynamic cycling of composites a self-heating occurs because of non-reversible mechanical processes during the loading and the unloading. As the temperature rise is governed by the poor laminate thermal conductivity properties, the geometry and in particular the thickness, an attempt to understand the origin of this temperature rise and its possible relation with damage growth would be carried out. In order to understand the influence of the temperature rise during fatigue loading and it influence on mechanical properties.
Moreover, the influence of thickness on fatigue for the blade subcomponent bottleneck design parameters, such as the bearing allowable on a T-bolt joint connection and the resin shear stress that rules scarf joints, would be studied. In conclusion, the main key factor that influence thick laminates design for wind turbines blades studied in the present work are:

- 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 on thick laminates and its influence on mechanical properties
- fatigue forecasting on thick laminates

**Research until 31 December 2011**

The research activities that has been carried out until December 2011 are related with the development of an in-house utility to manufacture thick laminates, and the study of the temperature build up and the fatigue testing of thick laminates. Ten millimeters thick coupons (see figure 1) has been manufactured by vacuum infusion for further fatigue testing on $R=-1$ in order to related its damping ratios or mechanical loss ratios with the temperature raise models observed on thicker coupons tested during the Optmat project (see figure 2).

![Figure 1: R=-1 10mm thick tested coupons](image1.png)

Additionally, measurements of the loss factor during delamination growth onset mode I fatigue test and infrared monitoring on mode I static test (figure 3) has been carried out, in order to observe the damping ratios or mechanical loss ratios that appears during crack growth.
Figure 3: DCB specimen, IR photo on static test 10 mm/min.
Time: 0.33 sec. Heat release during the fracture
Solar Cells and Modules

In the field of photovoltaic solar energy it has become very clear that materials development is key to further performance enhancement and cost reduction. The challenge is to select promising options from the broad range of opportunities offered by new active and passive materials, many of which are based on the use of nanotechnology. Within the ADEM-program research projects focus on materials for light absorption (the heart of any solar cell), coatings for reduction of electrical losses and spectrum converters for optimum use of sunlight, but also on materials used to construct modules from cells and on light-material interaction during advanced laser processing.

During 2011 the ADEM research theme on Solar Cells and Modules got company from the program on “Efficient generation of sustainable energy” within NanoNextNL, the national program on nanotechnologies for a wide range of applications. Another adjacent program is the FOM/Nuon Helianthos Industrial Partnership Program “Joint Solar Program”. To ensure maximum impact of these programs a form of organization and coordination of the solar energy research sector and its industrial partners will be developed in the course of 2012. The need for that has only grown with the recent preparation of the Innovation Contract Solar Energy, as part of the new government policy which aims to enhance the effectiveness of the innovation system.

2011 marked the acceleration of ADEM research activities. In the following pages young researchers inspired by the great potential of solar energy and determined to contribute to realizing that potential share their project results with you.

Theme coordinator

Prof.dr. Wim C. Sinke
The efficiency of single junction solar cells is severely limited by thermalization losses caused by absorbed photons with an energy that is in excess of the band gap of the cell. In addition, a high difference between photon energy and the band gap leads to high recombination losses of charge carriers. A method is investigated to fabricate thin layers of luminescent material on top of solar cells that down convert high energy photons to one or more lower energy photons. To avoid additional steps in the cell production process, the luminescent compound is integrated in the anti-reflection coating of the solar cell. As such coating often consist of SiNx, our focus is on the fabricating of Ca$_x$Si$_y$N$_z$O$_p$ type materials. When doped with Er$^{2+}$ ions, these materials absorb UV light followed by broad band emission due to Er$^{2+}$ 5d-4f transitions. Phosphor powder material studies have shown that the emission wavelength of this material can be tuned from blue to red by changing the stoichiometry of the material. By placing a thin film of such a material on top of the solar cell the cell efficiency can be increased from several percent to more than 10% point. This process is illustrated in figure 1.

Figure 1: The principle of a spectral converting thin film applied to a solar cell. High energy UV and blue light from the solar spectrum is absorbed by the spectral converting layer and re-emitted as red light, whose energy more closely matches the band gap of a silicon solar cell.

Research until 31 December 2011
Fabrication of Ca$_x$Si$_y$N$_z$O$_p$:Er$^{2+}$ layers is performed by using an AJA Orion 5 magnetron sputtering system. This thin film deposition system is capable of sputtering two semiconducting or insulating materials and two conducting materials simultaneously. This is done by applying a radio frequency controlled voltage or a DC voltage, respectively.
In this setup three sputtering materials are used. Calcium (99%) and silicon (99.999%) targets are sputtered with a rf-voltage source to produce thin films with a thickness of 200-500nm. A europium (99.99%) target is sputtered with a DC voltage source. C-cut Al₂O₃ or SiO₂ substrates are placed above these targets. The centre of the sputtered atom flux is aimed at a specific border of the substrate for each target, to create a composition gradient of calcium and silicon on the substrate. This combinatorial co-sputter deposition is performed in an atmosphere containing nitrogen to induce nitridation of the deposited material. Europium is simultaneously sputtered at a lower power to dope the film with a concentration gradient of europium, between 0-10%. This process is schematically shown in figure 2.

The performance of the combinatorial sputtering process is studied by doing thickness measurements on films deposited with single-target sputtering. After interpolation of the measurements it is found that the thickness of a single sputtered target material decreases linearly when measuring further away from the centre of the sputtered atom flux, as shown in figure 3.

Figure 2: Schematic representation of the combinatorial sputtering process, using Si, Ca and Eu targets. An actual substrate with a sputtered film is also shown. Each target is aimed at a specific border of the substrate in such a way that the sputtered atom flux is highest at that point. Ca and Si are aimed at opposite sides to create a composition gradient of the materials.

Figure 3: Cubic spline interpolation of the thickness of sputtered material from a single target. The centre of the sputtered atom flux is aimed at position x=0cm, y=3cm on the substrate. The interpolation shows a decrease in thickness when measuring away from the centre of the atom flux.
Sputtered films show a gradual color change over the gradient. To induce crystallization and activate the luminescence, the films are annealed for several hours at 1100°C in a N₂/H₂ atmosphere with an unknown concentration of air. The result is formation of areas of diffuse white film and transparent film. As shown in figure 4, UV excitation of the films (λ=360 nm) shows a blue and yellow emission in the transparent part of the film that is deposited on the Al₂O₃ and SiO₂ substrate, respectively.

Photoluminescence excitation and emission measurements show broadband emission around 570 nm from the film deposited on the SiO₂ substrate and broadband emission around 500 nm for the film deposited on the Al₂O₃ substrate, as shown in figure 5.

**Figure 3:** Two deposited films on an Al₂O₃ substrate (left) and a SiO₂ substrate (right) under normal light (A) and UV light (B) illumination. The film deposited on SiO₂ shows a yellow luminescence on the part of the film with the highest Si-Ca ratio. The film deposited on Al₂O₃ shows blue luminescence in the centre of the substrate and on the part of the film with the highest Si-Ca ratio.

**Figure 4:** Excitation and Emission spectra of the thin films shown in figure 3. Top: excitation and emission spectrum of the film deposited on Al₂O₃. Bottom: Excitation and emission spectrum of the film deposited on SiO₂.
X-ray diffraction analysis of the luminescent parts is performed to determine the crystal structure of the deposited films. The XRD pattern of the film that was deposited on Al$_2$O$_3$ shows crystal structure phases. A close match is found with the compounds Eu$_{4.67}$(SiO$_4$)$_3$O and Ca$_2$Eu$_8$(SiO$_4$)$_6$O$_2$. The film that was deposited on SiO$_2$ is tentatively assigned to Ca$_6$(SiO$_3$)$_6$(H$_2$O) (figure 5).

Figure 5: XRD measurements of the film deposited on a c-cut Al$_2$O$_3$ substrate (top) and a SiO$_2$ substrate (bottom). The top pattern shows a combination of crystal phases from Ca$_2$Eu$_8$(SiO$_4$)$_6$O$_2$ and Eu$_{4.67}$(SiO$_4$)$_3$O, while the bottom pattern closely resembles Ca$_6$(SiO$_3$)$_6$(H$_2$O).

It is assumed that the small air leak in the ceramic tube of the furnace caused oxidation and hydration of the different films, which resulted in luminescent oxides and oxide hydrates. New films will be annealed in a new tube for which it is expected that they result in the formation of compounds that more closely resemble silicon nitride materials.

The observed luminescence does not originate from the targeted Ca$_x$Si$_y$N$_z$O$_p$:Eu$^{2+}$ type of materials, but instead originates from calcium, silicon and europium containing oxides or oxide hydrates. The luminescence that is measured from these materials has not yet been reported and will be investigated further.

Industry activities until 31 December 2011
None

Output until 31 December 2011
- Mention Physics @ FOM poster
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 current solar cells 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 tandem (often also described as multi-junction) solar cell concept. The stability of the materials used as absorber layers under light exposure is of high importance.

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 nanostructured silicon-based materials is characterized by the formation and embedding of nanoparticles of crystalline silicon in an amorphous silicon host matrix, with the important aim of increasing their stability. The tailoring of several sizes of nanoparticles and variations in their ordering in the amorphous matrix leads to a broad range of materials, spanning the range from nanostructured to nanocrystalline silicon layers.

The challenge is to develop deposition technology that enables us to gain control over the formation and concentration of the ordered silicon nanoclusters 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 characterization and positron annihilation methods. The stability of the developed materials will be tested in solar cells.
Research until 31 December 2011

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. This 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), none of which have yet succeeded in providing convincing experimental evidence for their correctness. On the road towards SWE reduction we therefore present the latest insights in the a-Si:H nanostructure using Doppler broadening positron annihilation spectroscopy (DB-PAS) and Fourier Transform Photocurrent Spectroscopy (FTPS).

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. As is demonstrated by DB-PAS, vacancies are agglomerating into larger vacancies up to 400 °C. Above 400 °C the largest vacancies are released at the surface of the sample. This conclusion is supported both by earlier conducted and new hydrogen (H) effusion experiments.

Revolutionary insights in the defect states have been obtained by the first ever measurements on the occupation of various defect states in a light soaked a-Si:H p-i-n junction device under biased conditions using FTPS. Under forward bias conditions (normal solar cell operation) evidence has been found for the existence of at least four defect distributions in the band gap of a-Si:H. This shows that the dangling bond is not the dominant defect in a-Si:H, since dangling bonds are modelled to have no more than three singly charged states (1+/0/1-). Not fully H-passivated divacancies (and multivacancies) can however have both single and double charges, which makes the divacancy a more plausible defect candidate to represent the dominant defect states in a-Si:H. Furthermore, we make the point that under typical solar cell operating conditions the states far away from midgap are most likely to represent the dominant recombination states.

Output until 31 December 2011

1) Paper accepted for publication (http://dx.doi.org/10.1016/j.jnoncrysol.2012.01.037)
2) Abstract submitted to IEEE PVSC 38 conference in Austin, TX, United States of America concerning the relation between vacancies and the dominant defects in hydrogenated amorphous silicon
3) Abstract planned to be submitted ICPA-16 conference in Bristol, United Kingdom concerning the use of positron annihilation spectroscopy in monitoring vacancy agglomeration in hydrogenated amorphous silicon during temperature annealing
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 α-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], as illustrated in figure 1. 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.

Figure 1: Schematic overview of a Silicon Rich (SiR) and Carbon Rich (CR) multilayer of amorphous hydrogenated SiC before annealing (left) and the intended formation of QD’s after annealing (right).
Laser annealing of silicon carbide (SiC) multilayers might open up possibilities to increase the 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 afterwards apply the technology in functional devices.

**Research until 31 December 2011**

A study on the deposition conditions and characterization of a-SiC, the base material for the quantum dots, has been performed. A relation has been investigated between the atomic composition of SiC at different deposition conditions (using the XPS system and help of ADEM PhD candidate ir. R.J. Lancée) and various measurement techniques such as Raman, FTIR and Spectroscopic Ellipsometry. In addition, both single layers as well as multilayers of SiC have been annealed using continuous wave, excimer and ultrashort pulsed lasers with the aim of forming quantum dots (the latter with the help of ADEM PhD candidate D. Scorticati MSc and dr. J. Bosman at ECN). Measurements show strong indications of quantum dot formation and indicate a dependency between the supplied laser energy and crystal dimensions. This is indicated by a growing peak in the Raman spectra in figure 2 as the supplied laser energy increases.

**Figure 2.** View of the Raman spectra of the as deposited SiC multilayer, and after irradiation with the excimer laser source at different fluencies.
However, measurements contain a fair amount of variance because of errors in laser spot overlap, non-uniform energy distribution of the laser spot, material ablation and redeposition of ablated material. Currently conducted experiments aim to reduce these sources of variance.

**Extra information**

A study on the macro economic effects of a national solar cell investment fund has been conducted for a Dutch Member of Parliament. This has been used for their preparation for the parliament energy debate (Dutch: Wetgevingsoverleg Energie) with the minister which was held on November 21, 2011.

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 2011

Experimental work included:

1. Silicon Solar Wafers and Solar Cells breakage issues

The purpose of this work is to understand the fracture behavior of multicrystalline silicon wafers and to obtain information regarding the fracture of solar wafers and solar cells. The effects on silicon wafer strength of saw damage and of grain size, boundaries and triple junctions are investigated. Also the effects of surface roughness and the damage layer removal process are considered. Significant changes in fracture strength are found as a result of different silicon wafer crystallinity and surface roughness. Results indicate that fracture strength of a processed silicon wafer is mainly affected by the following factors: the saw-damage layer thickness, surface roughness, cracks/defects at the edges and the number of grain boundaries, which all serve as possible crack initiation points. Also the effects of metallization paste type and firing conditions on the strength of solar cells are considered. It is observed that the aluminum paste type and firing conditions influence the strength of solar cells.

Breakage issues and mechanical strength of mc-silicon wafers and solar cells were investigated using a combination of four-point bending test, bowing measurements, confocal microscopy, Raman spectroscopy and X-ray computed tomography. The study showed that:

- Multicrystalline (mc) silicon wafer crystallinity has a significant effect on the mechanical strength.
- Surface and edge defects, such as microcracks, grain boundaries and surface roughness, are the most probable sources of mechanical strength degradation.
• There is a relationship between aluminum paste composition, mechanical strength of a cell and amount of cell bowing.
• When loaded in tension, the aluminum layer improves the strength of a solar cell. The eutectic layer within this structure probably shows some plasticity and can also serve as a bridge for possible critical microcracks at the silicon wafer surface.
• Drying aluminum paste at low temperature (250 °C) yields a better mechanical strength of mc silicon solar cells than drying at higher temperature (350 °C).
• There is a strong correlation between maximum firing temperature, bowing and fracture strength of solar cells; the higher the firing temperature the higher the fracture strength and the Effect of maximum firing temperature on the characteristic stresses at fracture and amount of bowing of silicon solar cells greater the bowing (table 1).

<table>
<thead>
<tr>
<th>Firing temperature (°C)</th>
<th>Characteristic stresses at fracture (Al under tension)</th>
<th>Bowing of a complete cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>149 (MPa)</td>
<td>6.48</td>
</tr>
<tr>
<td>860</td>
<td>171 (MPa)</td>
<td>1.16</td>
</tr>
<tr>
<td>840</td>
<td>187 (MPa)</td>
<td>1.40</td>
</tr>
<tr>
<td>960</td>
<td>193 (MPa)</td>
<td>1.43</td>
</tr>
<tr>
<td>950</td>
<td>205 (MPa)</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 1

• Thickness of the eutectic layer as well as uniformity (fewer defects) of the aluminum back contact layer can be considered as important parameters controlling mechanical stability of silicon solar cells.
• There was developed a model allowing to predict deformation and bending stresses (figure 1 and 2).

Figure 1: Example of Digital Image Correlation (DIC) data used to determine strain and displacement for solar cell specimens loaded at 3N with 4-point bending setup.

Figure 2: Developed Ansys simulation of bending stresses. DIC data and experimental 4-p bending results were used for verification of the model.
2. X-ray Diffraction Stress Characterization

The residual stresses and stresses resulting from bending in multicrystalline silicon cells were investigated using the X-ray diffraction technique, bowing measurements and bending tests. The study showed that:

- The thickness of the eutectic layer as well as the uniformity of the aluminum 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;
- It was found that it is possible to measure bending stresses by X-ray diffraction using an in-situ bending clamp specially designed for thin solar cell specimens. The resulting data give valuable information about the stress state development during different processing steps of multicrystalline silicon solar cells;
- It was found that holding samples at the load 2÷3N results in a stress relaxation effect due to plasticity/creep or cracking of Ag layer (figure 3).

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 behavior and stress states of silicon solar cells.

![Figure 3: Stress relaxation in Ag layer as a result of 10 hours holding time](image)

3. Raman Spectroscopy characterization of residual stress in multicrystalline silicon solar wafers and solar cells:

The residual and bending stress of mc-Si were investigated using Raman spectrometry, bowing and 4-point bending tests. The study showed that:

- Residual stresses at the grain boundaries are 50–70 MPa higher than within the grain;
- Grain boundaries are the most probable sources of mechanical strength degradation of mc-Si wafers;
- An α-Si phase was found only in the smooth grooves of the as-cut wafer (figure 5);
- Saw-damaged layer is in tensile stress of ~500 MPa (figure 6);
• 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 silicon matrix.

Based on the results, it should be possible to find a connection between silicon microstructure, processing conditions, defects and mechanical stress. The results will be used to build a multiscale model, which integrates the behavior of the silicon and the layers in order to predict stress development.

Figure 5: Representative Raman shift for the as-cut wafer, showing a local indentation-induced transformation of Si into a-Si.

Figure 6: Representative Raman shift for as-cut, textured and polished neighboring wafers.
Industry activities until 31 December 2011

Industrial activity has included collaboration with ECN for sample preparation and modeling of the relationship between the mechanical properties of the cells and the microstructure of the metallization pastes. The results of this collaboration have provided back-ground knowledge to ECN. This has been used by ECN in consultancy projects with industrial partners including cell manufacturers and metallization paste suppliers. The further work with ECN will look at the effect of changes in processing, including type of metallization paste and firing temperature, on the mechanical properties of the cells. The influence of soldering interconnection tabs to the bus-bars on the mechanical properties the cells will also be investigated. Soldering of increasingly thinner cells is becoming more and more critical. The thinner cells are highly susceptible to damage by the soldering process. This, in combination with high-density metallization pastes, has resulted in increasing yield losses during module manufacture. A better understanding of the source of the yield loss and how it can be avoided is of great importance to the industry.

Output until 31 December 2011

1. V.A. Popovich, M. Janssen, I.J. Bennett, I.M. Richardson, “Breakage issues in silicon solar wafers and cells”, Photovoltaics international, Volume 12, 2011, pp. 36-42
5. V.A. Popovich, A. Yunus, M. Janssen, I.M. Richardson, I.J. Bennett, Effect of silicon solar cell processing parameters and crystallinity on mechanical strength, Solar Energy Materials and Solar Cells, Volume 95, Issue 1, January 2011, Pages 97-100
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 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 nano-crystals 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 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 straightforward wet-chemical synthesis and the possibility for solution-processing. Their relatively high dielectric constant is beneficial for efficient exciton dissociation.

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 for improvement of material performance in solar cells.

Figure 1: TEM pictures of PbSe nanocrystals, quantum dots (left) and nanorods (right), synthesized in our lab.
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. If sufficiently ‘hot’ the excited electron can create an extra electron-hole pair by carrier multiplication, which is in competition with thermal relaxation (figure 2).

**Figure 2:** An energetic photo-excited state can induce a second excitation via carrier multiplication, which occurs in competition with thermal relaxation.

Carrier Multiplication is a well-studied process in PbSe quantum dots in colloidal dispersion. However, two or more excitons 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 another quantum dot, 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 3). 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 3:** The quantum yield increases with photon energy due to carrier multiplication. The band gap is equal to $E_g = 0.63$ eV.
We have extended our studies on the dynamics of (multiple) photoexcited charges to PbSe nanorods (figure 1). Nanorods are of interest because of the efficient charge transport along the rod. We will investigate the efficiency of charge generation and carrier multiplication in PbSe nanorods. We found that mutual Coulomb interactions between charges within a nanorod have a strong influence on their motion and decay by recombination. These properties are significantly different from that of spherical QDs.

Output until 31 December 2011


The c-Si solar cell technology is leading the solar cell market to date. To maintain this position and compete with emerging technologies, the cost per watt ratio needs to be driven downward through time. Thin films have become more and more important to increase efficiency of c-Si solar cells, by acting as (anti-)reflection coatings and/or passivation coatings. By using combinations of different material properties such as in stacks, it is possible to yield a higher trade off in optical and passivation properties, which can increase the efficiency over a single thin film. The plasma-enhanced chemical vapor deposition (PECVD) technique has found an increasing number of applications in c-Si photovoltaic devices processing.

Most common systems used for optical and/or passivation purposes, are silicon dioxide, either deposited (SiO$_x$) or thermally grown (SiO$_2$), amorphous silicon nitride (SiN$_x$), amorphous silicon (a-Si:H), aluminum oxide (Al$_2$O$_3$) and stacks of SiO$_x$/SiN$_x$. Each of them has specific advantages and disadvantages, depending on the temperature of the deposition, the deposition rate, the refractive index and the surface passivation quality of the films. In my research discussed below, I have mainly investigated the passivation properties of the SiO$_x$/SiN$_x$ stack system, for c-Si solar cell applications, deposited on the ETP-PECVD industrial deposition platform (DEP) developed by OTB-Solar, which yields a high deposition rate. Besides ETP-PECVD of SiN$_x$ and SiO$_x$/SiN$_x$ stacks, I also investigated ETP-PECVD deposited a-Si:H for c-Si passivation purposes. ICP-PECVD of SiN$_x$ and a-Si:H for c-Si passivation purposes have also been studied for benchmarking and for a comparison with the ETP-PECVD deposition technique.

The following research questions will be addressed:

1. What is the ruling passivation mechanism of the different thin film materials/stacks proposed? What is the role of electric-field passivation by built-in charges and chemical passivation of surface defect states and how do both passivation mechanisms contribute to the overall passivation effect? How is this related to the atomic composition and bonding configuration and to the thickness of the passivation films used? How does it depend on the doping of the silicon and on the doping profile/concentration?

2. How is surface passivation affected by the processing of the thin film material? What is the role of growth rate, temperature and ion bombardment on the passivation quality? What is the influence of the deposition method, surface pretreatment and anneal on the passivation quality?

3. Which additional benefits over single films can be obtained by stack systems? How can the surface passivation level and passivation mechanism be tailored for optimum solar cell performance?
Research until 31 December 2011

With respect with the above mentioned research questions, most research was carried out on SiO$_x$/SiN$_x$ stacks deposited by the ETP-PECVD method on the OTB DEPx industrial deposition platform.

- Field effect passivation is only possible in conjunction with chemical passivation. It is not possible to sufficiently passivate c-Si by an intrinsic charge in thin films or stacks deposited when there is no chemical passivation present.
- Chemical passivation is obtained by hydrogen diffusion out of the bulk of the material or stack that is deposited on c-Si towards to c-Si interface.
- Both ETP-PECVD SiO$_x$ and SiN$_x$ have a fixed positive charge when deposited on c-Si. On n-type c-Si this field effect passivation has a beneficial effect. On p-type c-Si, these films are not the ideal candidate because the fixed positive charge will lead to parasitic shunting. SiN$_x$ deposited on SiO$_x$ as part of a SiO$_x$/SiN$_x$ stack for c-Si passivation will not contribute additional fixed positive charge. All the fixed positive charge present in the SiO$_x$/SiN$_x$ stack stems solely from the SiO$_x$.
- SiO$_x$ thickness increase in SiO$_x$/SiN$_x$ stacks will lead to higher c-Si wafer lifetimes, up to 200 nm of SiO$_x$ thickness. When SiO$_x$ increases in thickness, the field effect passivation becomes more pronounced because an increase in fixed positive charge density in these stacks.
- Besides fixed positive charge contribution, SiO$_x$ also acts as a hydrogen reservoir that supplies hydrogen towards the c-Si interface when SiN$_x$ is deposited and when complete SiO$_x$/SiN$_x$ stacks are annealed.
- Firing SiO$_x$/SiN$_x$ stacks result in higher passivation quality than SiN$_x$ only.
- Firing SiO$_x$ prior to SiN$_x$ deposition results in low passivation quality of complete SiO$_x$/SiN$_x$ stacks.
- SiN$_x$ has higher hydrogen content of ~18 at. % than as-deposited SiO$_x$ with hydrogen content of 8 at. %. This hydrogen concentration gradient in the SiO$_x$/SiN$_x$ stacks drives hydrogen from the SiO$_x$ towards the c-Si interface when SiN$_x$ is deposited and when complete SiO$_x$/SiN$_x$ stacks are annealed.
- After annealing, cross-linking of Si-O in SiO$_x$ and Si-N in SiN$_x$ occurs. This can be observed by a small change in refractive index and increase in the Si-O and Si-N bond densities.
- After annealing the hydrogen content of SiO$_x$ and SiN$_x$ decreases to 3 and 12 at. % respectively, which could also be observed by a decrease of Si-H and N-H bond densities.

Besides SiO$_x$ and SiN$_x$ surface passivation, a-Si:H films deposited by ETP-PECVD have also been investigated for passivation purposes. Lifetimes in the ms range were obtained on c-Si wafers. These have been used for light soaking experiments done at the Delft University of Technology by Arno Smets.

A new remote plasma deposition reactor (ICP-PECVD) was acquired by the PMP research group. The surface passivation of SiN$_x$ and a-Si:H deposited by ICP-PECVD was investigated. This SiN$_x$ and a-Si:H material will be used as benchmark material and will be compared to similar material deposited by other deposition techniques. Because of the lower growth rate, good process control, and better material uniformity obtained by this deposition technique compared to ETP-PECVD, intrinsic material properties and passivation mechanisms can rigorously be studied.
Industry activities until 31 December 2011
There is a collaboration with OTB-Solar for ETP-PECVD depositions of SiNₓ and SiOₓ/SiNₓ stacks and firing of these materials. Meetings with OTB-Solar scientists have been arranged and joined posters and conference proceedings have been presented.

Output until 31 December 2011
- SiliconPV conference oral presentation in Leuven (BE). Abstract has been accepted for this conference which will take place in April-2012.
**Project:**
Laser material interactions for PV applications

<table>
<thead>
<tr>
<th>Name PhD-candidate: Davide Scorticati</th>
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<tr>
<td>Affiliation: University of Twente</td>
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<td>Start date: 15 Jan 2011</td>
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<tr>
<td>Project leader(s): Prof. Dr. Ir. A.J. Huis in ’t Veld, UT</td>
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<tr>
<td>Dr.ir. G.R.B.E. Römer, UT</td>
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<tr>
<td>Other personnel: Dr. Arthur Weeber, ECN</td>
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Ultra Short Pulsed Lasers (USPL), with pulse durations in the ps and fs range, offer innovative possibilities to create efficient PV cells at industrial production rates. The laser–material interaction is characterized by non-thermal processes, allowing real 3D machining of the PV cell, such as scribing, drilling, and texturing. The focus of this project is to study the fundamentals of laser–material interaction for PV cells. The effect of laser parameters, such as wavelength, pulse duration, overlap, fluence, polarization, etc. on the processing results is studied and modeled. The aim is to gain basic knowledge and understanding which is needed to develop industrial processes with a high quality, accuracy and selectivity. The modeling will therefore be extended to simulation of real processes/applications using lasers.

**Research until 31 December 2011**

During the first year of research, the main focus was laser texturing of thin layers with ultra short laser pulses for enhancing light trapping in thin film solar cells. Large areas of grating constituted by highly periodical ripples with different periodicities were produced on 400nm molybdenum layer deposited on soda lime glass without cracks and delamination. Samples were provided by TNO and are the same used for the backcontact of CIGS solar cells.

Cooperation with TUDelft lead to a joined paper accepted for an oral presentation at the European SPIE conference in Bruxelles in april 2012 (title: “Surface processing by Ultra Short Laser Pulses (USLP) of thin metallic film on glass”). In addition, also a feasibility study of texturing was performed on different TCO layers.

**Figure:** SEM picture showing an area of a sample covered by highly periodical ripples. The length of the ripples is not limited by the spot size (~30μm). These ripples have a periodicity of 890 nm and are produced on 400 nm molybdenum layer deposited on soda–lime glass.
The topic of surface texturing of thin films for PV applications won’t be continued. Interesting scientific results were obtained, while applicability to PV industry was shown very limited because of economical reasons due to the large time required for laser texturing compared to nano-imprinting techniques (102-103 times higher). Moreover, FIB (Focused Ion Beam) has more freedom than laser micromachining for making a master with 3-D features down to 100nm.

From March 2012 Laser Doping for selective emitter is started as new research topic, and will be studied in close cooperation with ECN Petten (contact person: A. Weeber). In 2012 the knowledge acquired during the first year on the laser-material interaction will be used to study laser doping.

**Output until 31 December 2011**

Cooperation with Tu Delft for a joined paper accepted for an oral presentation at the European SPIE conference in Brussels in April 2012.
Catalysis, Membranes and Separations

Various research projects in the Catalysis, Membranes and Separations (CMS) cluster are working hard on catalytic conversion technology and separation technologies, some of which are based on membranes. Their applications cover the domains of clean fossil as well as biomass. The past year was characterised by high enthusiasm and commitment of the involved scientists, but also by severe delays and disappointment because financial commitments failed to materialise, which were needed to realise the research facilities and new positions.

Moreover, other research initiatives such as BatchBio and various European programmes have been launched and are making progress. This is particularly true for the biomass domain and to a lesser extent for the clean fossil domain. The subsequent initiatives obviously strengthen the research agenda of the ADEM programme and the planned ADEM investments may also be of essential importance to realising innovations based on these adjoining programmes.

Theme coordinator

Prof. dr. ir. Leon Lefferts
Biomass will be a valuable and sustainable source of chemicals and fuels in the future. 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 system, sand is used to transfer heat from an oxidation reactor to the gasification or pyrolysis reactor. In the latter biomass reacts with steam to a mixture of mainly methane, synthesis gas and some CO\textsubscript{2}. The unconverted biomass fractions, including tar, are fed into an oxidation reactor to heat up the sand to the reaction temperature needed for gasification. The sand subsequently enters the gasification reactor to provide the necessary temperature. This procedure offers the advantages of a nitrogen-free product gas which can easily be upgraded to substitute natural gas (by cleaning and methanation) with a high thermal efficiency.

The aim of this project is to build catalytic and chemical looping functions into the sand bed, to enhance the gasification efficiency and to reduce the formation of heavy tars during gasification. The natural mineral olivine ((Mg,Fe)\textsubscript{2}SiO\textsubscript{4}) is a promising material for this as it not only can serve as heat carrier but also has catalytic functionality for the degradation of tar. Moreover, the iron oxide in olivine can switch valence from Fe\textsuperscript{2+} to Fe\textsuperscript{3+} and is capable of transferring oxygen from the oxidation zone to the gasification zone.

This project will:

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

Research until 31 December 2011

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 (20% O\textsubscript{2} in Ar) and reduction (CO, H\textsubscript{2} and H\textsubscript{2}O mixtures), both at 750 °C. The resulting changes in the olivine catalysts’ bulk composition were characterized using X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD). Surface chemistry and morphology changes were characterized using X-ray Photoelectron Spectroscopy (XPS) and Secondary Electron Microscopy (SEM). At last, Thermo Gravimetric Analysis (TGA) was used to quantify the chemical looping capability of olivine.
The main changes in the \((\text{Mg,Fe})_2\text{SiO}_4\)–catalyst composition after exposure to high temperatures concern the Fe. In the oxidizing environment, \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_3\text{O}_4\) phases are observed to segregate out of the bulk mineral. On the catalyst surface, formation of crystallites is observed and the amount of Fe at the surface is more than doubled. The catalyst entering the gasification zone is thus best described as a largely Fe-depleted olivine with the inclusion of \(\text{FeO}\) phases.

After exposure to reducing conditions (\(\text{H}_2 + \text{CO} + \text{H}_2\text{O}\)) the \(\text{FeO}\) phases are reduced to FeO and Fe\(^0\), both in the bulk and at the surface. The surface content of Fe is reduced to roughly half the amount present after oxidation and the surface crystallites decrease in size. In CO containing gases significant carbon deposition is observed, some of this in the form of nano-fibers. All observed changes in the surface composition are significant already after one minute.

**Figure 1**: XPS spectra of the Fe 2p region show that the oxidation state of Fe in olivine changes from Fe\(^{2+}\) to Fe\(^{3+}\) upon oxidation. The surface Fe is present as Fe\(_2\)O\(_3\) (hematite).

**Figure 2**: SEM pictures show formation of crystallites after oxidation (left), which have disappeared to a large extent after 1 min. reduction (middle). Carbon fiber formation is observed after reduction in syngas (CO/\(\text{H}_2\))

After exposure to reducing conditions (\(\text{H}_2 + \text{CO} + \text{H}_2\text{O}\)) the Fe\(_2\)O\(_3\) phases are reduced to FeO and Fe\(^0\), both in the bulk and at the surface. The surface content of Fe is reduced to roughly half the amount present after oxidation and the surface crystallites decrease in size. In CO containing gases significant carbon deposition is observed, some of this in the form of nano-fibers. All observed changes in the surface composition are significant already after one minute.
Apart from its catalytic activity in tar cracking, olivine also serves as an oxygen-carrier, transporting oxygen from the combustion zone to the gasification zone. To quantify the oxygen transport, TGA measurements were performed (figure 4). Oxidation and reduction times were taken as 3 and 1 minute, respectively, comparable with the average residence times of olivine in the relevant reactors in the MILENA gasifier. Olivine can take up 0.4% percent of its mass as oxygen. It can be calculated that 16% of all iron present in olivine contributes to the oxygen transport.
Industry activities until 31 December 2011
ECN will, together with its partners waste- and energy company HVC, Ballast Nedam, Taqa Energy, the province of Noord-Holland, the municipality Alkmaar and Gasunie, establish the Dutch center of expertise in biomass gasification. A 12 MW MILENA gasifier will be constructed as a demonstration plant, which will produce 5 million m$^3$ SNG per annum. In 2017, ECN expects that a commercial plant based on the MILENA technology can be constructed with a capacity of 50 – 100 MW.

Output until 31 December 2011

- **Poster:** Physical Characterization of Catalytic Bed Materials used in Indirect Biomass Gasification. Remco Lancee, Hans Fredriksson, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  *Presented at:* The Netherlands’ Catalysis and Chemistry Conference, 28 February – 2 March 2011, Noordwijkerhout, The Netherlands
  North American Catalysis Society Meeting, June 5 – 10 2011, Detroit, MI, USA

- **Presentation:** Surface Properties of (Mg,Fe)$_2$SiO$_4$-catalysts for Indirect Gasification of Biomass. Hans Fredriksson, Remco Lancee, Peter Thüne, Hubert Veringa, Hans Niemantsverdriet
  *Presented at:* North American Catalysis Society Meeting, June 5 – 10 2011, Detroit, MI, USA
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 facilitates coke gasification 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 the first part of the project, CO oxidation on Rh/CeO$_2$ was studied. Using the DFT+U approach, we studied possible structures for small Rh oxide clusters (from 1 to 4 Rh atoms) and larger Rh clusters on CeO$_2$(111) surface. Reaction energies for the oxidation process for each species were calculated to determine the relative stability of Rh$_n$O$_m$ clusters (figure 1). It can be seen that the RhO$_3$, Rh$_2$O$_6$, Rh$_3$O$_6$, Rh$_4$O$_9$ are stable structures. The average atomic O/Rh ratio for these species are: 3, 3, 2 and 2.5, which are very close to the experimental values for Rh/CeO$_2$ under CO oxidation conditions. These results point to complete oxidation of the Rh cluster.

**Figure 1:** Calculated reaction energy for the oxidation process with reference to the Rh cluster and O$_2$ in gas phase.
In conclusion, by computational modeling, we have found evidence that the ceria-supported RhOx clusters are the active sites for CO oxidation. CO oxidation involving O from the metal oxide followed by reoxidation of the clusters by ceria is the dominant pathway. Finally, O$_2$ dissociatively adsorbs to regenerate the catalyst. This mechanism is preferred over the Eley-Ridael mechanism.

For one of the candidate structures, two reaction paths were computed with DFT (Figure 3): (a) CO reacts with O from Rh$_3$O$_m$ followed by O spillover process from ceria to reoxidize Rh$_3$O$_{m-1}$, and (b) CO from gas phase reacts with adsorbed O$_2$ (Eley-Ridael). In situ Raman spectroscopy strongly supports the former mechanism. These results are also corroborated by kinetic modeling of the reaction with the DFT derived kinetic parameters (manuscript II in preparation).

In Figure 2, shown which species are the candidate catalytic structures for CO oxidation: RhO, RhO$_2$; Rh$_2$O, Rh$_2$O$_2$; Rh$_3$O, Rh$_3$O$_2$; Rh$_4$O, Rh$_4$O$_2$. These results show that highly dispersed Rh oxides are the dominant species under CO oxidation conditions (manuscript I in preparation).

Figure 2: Calculated Gibbs free energy change for the oxidation and reduction process.

Figure 3: Reaction energy diagram for CO oxidation on ceria supported Rhodium oxide particle.

Two further lines are currently being explored: (i) the exploration of cluster chemistry on (110) and (100) surfaces of ceria and (ii) the catalytic reactivity of these systems in the water-gas shift reaction as a model for reforming. Part of these studies involves computation of IR spectra to support the interpretation of experimental efforts by the Lefferts group in Twente. For this purpose, we will include adsorbed OH and its interaction with CO to form carbonate, formate and hydrogen carbonate.
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 $H_2O$ is conceptually a promising alternative to generate $H_2$ from bio-oil. It is reported that $H_2O$ is able to regenerate hydroxyl groups on oxides like ceria, which increases $H_2$ yield and catalyst lifetime.

It has been suggested that by tuning the dimensions and the morphology of $CeO_2$, its catalytic performance can be greatly enhanced. Several investigators have reported the successful synthesis of $CeO_2$ nano-shapes like rod, cube, wire, etc. and their enhanced reactivity towards CO oxidation. To best of our knowledge, so far much attention has been focused on synthesizing and testing the reactivity of these nano-shapes but there is no work focusing on in-depth characterisation of surface species actually responsible for enhanced activity of nano-catalyst. The goal of this project is to determine structure - performance relationships: 1) the influence of the ceria surface on water dissociation activity and 2) the reactivity of different types of surface hydroxyls towards model coke compounds. For this reason, ceria morphology will be tailored for investigating the effect of defect sites and hydroxyls on the above-mentioned reactions.

**Results & Discussion:**

In this project, ceria oxides with distinct morphology, rods & cubes were successfully synthesized using hydrothermal method. TEM images of the ceria nano-materials used in the present study are shown in figure 1.

![TEM images of the CeO$_2$](image1.png)
Raman spectroscopy revealed that different ceria morphologies show different amounts of oxygen defect sites and oxygen displacement (figure 2). In figure 2, the inset shows peaks at 258 and 594 cm\(^{-1}\), which can be assigned to the displacement of oxygen atoms from ideal fluorite lattice positions, and oxygen vacancies in the lattice, respectively. Clearly these bands are much higher in the ceria rods and cubes than in the reference sample.

Figure 2: Normalised (with 462-465 cm\(^{-1}\) peak) Raman spectra of fresh ceria cube (blue), rod (red) and reference (ref-black spectrum) obtained at room temperature using 532nm laser at power level of 2mW.

To study the relation between the typical -OH groups and their reactivity towards CO, FTIR spectroscopy (Fourier Transform Infrared Spectroscopy) was performed in-situ for the different ceria samples (figure 3). In figure 3, the types of -OH species present (3800-3000 cm\(^{-1}\) range) are similar but the relative intensities are different, indicating that the amount of active -OH groups present differs in all the samples. Subsequently, in the presence of 33vol% CO/He (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 H\(_2\)O at 200°C, the carbon intermediates start decomposing, thereby reproducing most of the active -OH groups, see figure 4 (blue-spectra). In addition, the bands in the region 1800-800 cm\(^{-1}\) start decreasing in the presence of H\(_2\)O, leaving behind the stable formate and carbonate species. To summarise, in the reference sample, carbonate species decompose completely leaving behind only stable formates, whereas in the cube sample, along with the stable formates, carbonate species co-exist as well. The rod sample displays intermediate behaviour between the reference and cube sample.

Figure 3: FTIR spectra of ceria (a) reference, (b) rod and (c) cube sample at 200°C in He flow (black spectrum) followed by 33vol% CO flow (red spectrum). The green dots indicate the formate peaks in the 1800-800 cm\(^{-1}\) region.
Conclusions and future plans

From the results it can be concluded the types of –OH species present are the same for each morphology, but with different relative intensities. Interestingly, the carbon surface species formed during exposure to CO clearly depend on the ceria morphology, as does the water activation and oxide surface re-hydration. In the following year these studies will be extended towards platinum supported ceria morphologies and the results will be compared to theoretical studies performed in the related ADEM project (TU/e).

Output in 2011

- Poster: Tailored ceria nano-particles for highly reactive –OH species: Green Future
  S.Agarwal, B.L. Mojet, M. Kovačevič L. Lefferts, Netherlands’ Catalysis and chemistry Conference-XI, Noordwijkhout, Netherlands, 28th February-2nd March 2011
- International workshop on “Understanding Structure & Functions of Reducible oxide systems”, ZCAM-Zaragoza (Spain), 20-23rd June 2011
- Paper: Effect of morphology of ceria towards the interaction with CO and H$_2$O regeneration: detailed in-situ characterisation by infrared spectroscopy, S.Agarwal, B.L. Mojet, L. Lefferts (Manuscript in preparation)
**Project Background**

Biomass has become an appealing alternative to decrease the use of fossil fuel in the power production. In the ECN Milena process, biomass is converted by the coupling of two separated reactors in order to produce substitute natural gas. 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 methane for power generation. The gas produced is nitrogen free, avoiding the NO$_x$ production and post processing of the gas to separate it from N$_2$. 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.

**Objectives of the project**

*Apply fundamental of chemical looping 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.

**Progress within the report period**

*Experimental approach*

It is well known that hydrodynamics parameters of a fluidized bed reactor are influenced by the temperature, aside from the macroscopic gas properties, such as density and viscosity. In order to improve the reactor performance, it is required a better understanding of the gas-solid interaction at high temperatures. The lack of hydrodynamics studies at high temperature, basically relies on the difficulty of measurement at elevated temperatures.
Particle Image Velocimetry (PIV) coupled with Digital Image Analysis (DIA) has been used to characterize the hydrodynamics of fluidized bed reactors at low temperatures. PIV/DIA is a non-invasive technique. However, it requires visual access to the system; therefore, it is restricted to pseudo 2-D beds. In this project, PIV/DIA will be extended to high temperatures, in order to investigate the effect of temperature on the hydrodynamics of bubbling fluidized beds.

![Figure 1: High temperature endoscopic PIV/DIA](image)

Figure 1 shows a schematically representation of the proposed system. A pseudo 2-D quartz column is placed inside a furnace capable of operating up to 1000°C. To acquire the required images, a high-speed (HS) camera is coupled to a high-temperature endoscope. A double pulsed ND:YAG laser provides the required illumination for the recordings. The laser is triggered together with the camera shutter to allow less than 2 milliseconds delay between consecutive images (adequate to run PIV/DIA analysis). Time-average information of both bubble behavior and solids circulation fluxes is estimated by cross-correlation and image processing of 1000 pairs of images.

Trials with the endoscope supplier were done to determine if the proposed system would be capable of running PIV/DIA experiments. There is a loss in light and spatial resolution due to the use of the high-temperature endoscope in front of the HS camera. This loss is overcome by the use of the double pulse Nd:Yag laser as a light source. Although exposure time was increased from 0.08 ms (without endoscope) to 2 ms (with endoscope), it is possible to run PIV/DIA experiments. In figure 2 is shown the output of the trials with the endoscope supplier.

![Figure 2: Pseudo 2-D bed image without endoscope (left) and with endoscope (right)](image)
Currently, the optical endoscope has been designed and acquired; characterization of the endoscope is still in progress. As for the laser endoscope, we are still working on the design. Regarding the image post processing, a Matlab script is being developed to determine the bubble properties and solids circulations fluxes. Regarding the effect of solids circulation in the hydrodynamics, a cold flow model was built up. Feeding and extraction points along the height of the column are located. The aim of this set up is to investigate the influence of external solids circulating rate and position of the feed/extraction points in the hydrodynamics of bubbling fluidized beds.

Theoretical Approach
A phenomenological model will be developed to obtain fundamental understanding of the prevailing phenomena in chemical looping and the influence of operating conditions in the reactor performance. It is critical for the description and optimization of the process to describe the rate of heat and oxygen transported between the two interlinked reactors as well as the internal solids mixing (i.e. particles residence time distribution). Currently, a literature survey of the phenomenological models used to describe chemical looping is in progress. An existing phenomenological model will be extended to account for noncatalytic reactions and external solids circulations.

Planning within 2012
Experimental
- Construction of high temperature endoscopic PIV/DIA.
- Effect of temperature in hydrodynamics: experiments for different temperatures, gas velocities and particles.
- Experiments of feed/extraction of solids, effect in the hydrodynamics.
- Influence of gas production in hydrodynamics: experiments at reactive conditions, methane reforming.

Theoretical approach
- Phenomenological model for a pseudo 2-D fluidized bed reactor.
  Validation of the model with experimental work at high temperatures.
- Validation of the phenomenological model for noncatalytic reactions with external solids circulation.

Knowledge transfer and co-operation
Oral presentation at ISCRE-22 in Maastricht (September 2-5, 2012) “High temperature hydrodynamics of fluidized beds for chemical looping process”.
As described in the previous year report, the research contributes to the development of a ceramic membrane reactor, enabling hydrogen production with CO$_2$ capture. Integration of the mixed ionic-electronic conducting oxygen separation membrane into the reactor eliminates the need for costly oxygen. Aim of this project 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 until 31th of December 2011
Synthesis of powders and ceramics of different compounds based on strontium ferrate doped on either A- or B-site with A = Mg, La, Ce and B = Al, Ti, Nb, respectively. Besides doping on either A- or B-site, co-doping on both sites was also done. These compounds were used in stability tests in CO$_2$-containing environments using thermogravimetry, but also in sintering studies to determine optimal sintering programs. In addition, research on creep behavior of sintered cylindrical samples is conducted in cooperation with The Forzungszenrum Juelich (FZJ), Germany. Exploration of possibilities for thin film production on porous supports made of the same materials has started, with a special focus to spray pyrolysis. A permeation set-up was designed (not yet constructed) to conduct permeation experiments under high oxygen gradients and in studies towards partial oxidation of methane. Literature studies on POM reactors and creep mechanisms have been performed.
The growing energy demand combined with increasing concerns about greenhouse gas emissions is driving the research towards the development of processes with integrated CO\textsubscript{2} capture. The present research aims at the development of ceramic membranes for use in a reactor concept, enabling hydrogen production with integrated CO\textsubscript{2} capture, commonly referred to as pre-combustion carbon capture.

**Research until 31 December 2011**

Literature study has been conducted to select candidate materials for hydrogen selective membranes. One of these materials is 1,2-bis(triethoxysilyl)ethane (BTESE). Membranes were fabricated via dip-coating a sol and characterized via single gas permeation measurements. These membranes have a typical H\textsubscript{2} permeance of 4 x 10\textsuperscript{-7} mol m\textsuperscript{-2} Pa\textsuperscript{-1} s\textsuperscript{-1} and a H\textsubscript{2}/CO\textsubscript{2} selectivity of 4, which is below the corresponding Knudsen value of 4.7.

To improve the H\textsubscript{2}/CO\textsubscript{2} selectivity of the membranes, Niobia and Zirconia were incorporated into the material by altering the sol-gel synthesis. Membranes doped with Zirconia led to an increase in H\textsubscript{2}/CO\textsubscript{2} selectivity from 4 to 10 in comparison with plain BTESE membranes while the permeance only drops to 3 x 10\textsuperscript{-7} mol m\textsuperscript{-2} Pa\textsuperscript{-1} s\textsuperscript{-1}. 
Hydrogen Production and Fuel Cells

Fuel cells are “smart devices” that convert electro-chemical energy into direct electric current and offer new opportunities for a clean and energy efficient society. From the beginning, hydrogen fuel cells have been associated to the idea of vehicle transport and these devices positioned themselves as a key player in a near future hydrogen society. During the past year, four ADEM PhD students researched fundamental and technological aspects of fuel cells, ensuring a strong and enthusiastic start within the program. Fuel cells are, however, not limited to hydrogen and can be seen as an attractive energy supplier for many other applications and products. The advent of mobile devices during the last years and the increasing diversity of small household, industrial or medical equipment, have pointed to the possibility of fueling autonomous small machines with fuel cells. And the fuel itself can be abundant and cheap: researchers at Case Western University have found a way of converting a cockroach’s food intake into electric current, with the bug functioning as a fuel cell and generating electricity. As eccentric as those new fuel possibilities could sound, the fact remains that The Netherlands is still a leading green society in the world and original solutions like the above one can only be achieved with sustained National research efforts, with the ADEM program being a key component.

Theme coordinator

Dr. hab. Eduardo Mendes  
Associate Professor Delft University of Technology
Fuel cells are considered to be the green power sources of the 21st century and represent the way through which the “hydrogen economy” could become a reality. The main driving force for the fuel cell research is the increasing concern about global pollution due to the consumption of fossil fuels as well as the need of reducing the economic and political dependency on global oil suppliers. Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are simple devices in which hydrogen and oxygen electrochemically react to form water, by producing electricity and heat. Their biggest advantages over internal combustion engines are no or low CO$_2$ emissions depending on the hydrogen source, efficiency up to 80%, silent and low temperature operation, no moving parts and thus long mechanic-life time and no need of lubricants. These advantages make PEMFCs promising alternatives to fossil fuel combustion engines both for portable and stationary combined heat and power applications.

However, improvements in durability and cost reduction are still necessary in order to enhance their competitiveness on the market. This 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 structure grown on platinum or platinum group metals particles (figure 1). Carbon nanotubes have already been proven to enhance the durability of PEMFC electrodes, but this approach is novel since the carbon nanotubes 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.
Proton conduction is realized by a second continuous phase around the nanotubes network. The third continuous phase is the porous structure allowing the reactants to reach and the products to leave the catalyst active sites.

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. CNNs are Multi-walled carbon Nanotubes with narrow size distribution, forming chemical networks between each other, enhancing CNTs properties such as electric and thermal conductivity. They can be obtained by Chemical Vapor Deposition catalyzed by nanoparticles synthetized in bicontinuous microemulsions (BMEs). Microemulsions have been widely employed as template to synthesize metallic nanoparticles and they were proven to allow size control, stability, versatility. However, just low yields can be achieved by this synthesis route since in MEs the water content, where the synthesis is actually taking place, is normally < 15% in weight. With BMEs instead higher yield can be achieved because of the higher water content, up to 40-50% in weight. Additionally, higher stability and monodispersity can be obtained because of the different phase structure.

In summary, this project aims to optimize the CNNs concept in PEMFC electrodes, by investigating (i) the optimal carbon nanostructure regarding porosity, conductivity, proton conduction and stability, (ii) BMEs method to synthesize alternatives to platinum both as precursor of this structure and as more stable, active and cheap catalyst for oxygen reduction reaction and (iii) membrane electrode assembling (MEA) procedure to achieve the best performance.

Research until 31 December 2011

Bicontinuous Microemulsions Method for Nanoparticles Production
Bicontinuous microemulsions has been confirmed 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 nanoparticles, including platinum, nickel, cobalt and core-shell combinations thereof, are produced in these templates having a size range spanning from 2 to 5 nm, with a very narrow size distribution. Size is tuned by metal precursor and reducing agent concentrations. Insight on the mechanism of particles formation was investigated. Nanoparticle coalescence is prevented by the microemulsions structure, allowing the attainment of a very high level of colloidal stability at high concentrations (figure 2).

In addition, a relatively low cost, in situ technique based both on turbulence 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 2: TEM-Platinum Nanoparticles
Carbon Nano-Networks for Fuel Cells Electrodes

In preliminary tests, CNNs grown on platinum nanoparticles synthetized in bicontinuous microemulsion (figure 3) resulted to be active as fuel cell catalyst and performed even at very low loadings (figure 4).


Output until 31 December 2011

- Fuel Cells – Kick off meeting, Delft (11 May 2011)
  Presentation: “Nanostructured, Tricontinuous Carbon Network Electrode”
- ADEM Conference, Amersfoort (26–27 May 2011)
  Presentation: “Nanostructured, Tricontinuous Carbon Network Electrode”
- European Colloidal and Interfaces Conference – Berlin, Germany (4–9 September 2011)
  Poster: “Carbon Nano-Networks for PEM Fuel Cells”
- Thesis Proposal Defence, Delft (26 October 2011)
  Presentation: “Carbon Nano-Networks for PEM Fuel Cells”
- Chains 2011, Maarsen (28–30 November 2011)
  Poster: “Carbon Nano-Networks for PEM Fuel Cells”
Project:
Fuel oxidation on ITSOFC anodes and its influence on system performance

Name PhD-candidate: Hrishikesh Patel
Affiliation: TU Delft
Start date: 1 June 2010
Project leader(s): Dr P V Aravind, TU Delft

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 several reasons. Influence of contaminants on anode reactions is also equally important. Such information is useful, for example, for selecting suitable anode materials, for optimizing anode microstructure of SOFCs to be operated with different fuels, for identifying anode zones which are susceptible to degradation, for helping to form clear assumptions regarding reaction zones when detailed combined CFD & thermo-mechanical stress modeling is carried out (this is a very important issue for stack development), for developing gas cleaning systems, and for developing concepts for high efficiency systems using SOFCs with low temperature anodes. The objective 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.

Research until 31 December 2011
Setting up of Fuel Cell Systems Lab at the Process and Energy dept. Various equipments include impedance test station, cell and stack test station. Preliminary experiments with hydrogen and ammonia fuels with Nickel GDC symmetrical cell anodes using electrochemical impedance spectroscopy.
Making of Nickel pattern anodes with well defined triple phase boundary lengths for accurate estimation of kinetics in a model electrode.

**System Calculation on SOFC GT systems using Cycle Tempo.**

High efficiency SOFC - GT system fueled with different biofuels like methane ammonia ethanol and methanol is a promising alternative. The study of the influence of individual components on the overall system is critical in designing of real systems as well.

It was found that the system efficiency with methane is highest and least with methanol. The split between fuel cell and gas turbine power is a major factor in deciding the overall efficiency though the fuel cell efficiency alone is determined more by the per pass utilisation. The overall efficiency does not always follow the fuel cell efficiency.
The amine-process currently used for CO₂ capture is extremely expensive and suffers many drawbacks as amines are corrosive, degradation sensitive and volatile. Some of these problems can be circumvented 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 CO₂ solubility.

The aim of my project is to selectively capture CO₂ with a suitable ionic liquid from flue-gas streams, either at pre-combustion, post-combustion or natural gas reservoir conditions. A suitable ionic liquid should have a high CO₂ solubility, selectivity and a low viscosity. Preferentially, the ionic liquid should be biodegradable, non-toxic and cheap. The currently known ILs are performing still insufficient regarding these properties, which obstruct the application of ILs at a large scale. Therefore, the aim is to find/design an ionic liquid with improved characteristics with respect to the mentioned properties. The work is experimental based and the facilities in the high-pressure lab of the Process & Energy department are used to perform the experiments.

Research until 31 December 2011
The literature of the past decade on CO₂ capture with ionic liquids has been screened and the achievements and recent developments in this field have been addressed in our review article [1]. Furthermore, CO₂ solubilities in two inexpensive ILs have been measured experimentally [2].

Output until 31 December 2011
Solid Oxide Fuel Cells (SOFCs) are potentially able to replace the conventional combustion system by a higher efficient and environmental friendly system based on electrochemical reactions. However, there are still several drawbacks to be solved in order to be competitive in the energy market.

In the particular case of the SOFC anodes, the challenge is to have a long life material while keeping a good performance vs. methane reforming. The classic Ni/YSZ cermet suffers short durability when working with methane. On one hand, Perovskites are a promising material to substitute the Ni/YSZ cermet due to their stability vs CH₄. However, a better understanding is needed in order to obtain valuable materials with high power output. On the other hand, the microstructure has to be tuned in order to maximize the efficiency of these materials. Therefore, this project is divided in two parallel ways: “investigation of Perovskite materials under SOFC anode working conditions” and “tuning anode microstructure”.

Research until 31 December 2011

Investigation of Perovskite materials under SOFC anode working conditions

The basic requirements for an anode material can be listed as below:

- High ionic (O²⁻/H⁺) and electronic conductivity over a wide range of pO₂.
- Good thermal/chemical compatibility with electrolyte and interconnect materials including TEC.
- Good chemical and mechanical stability under SOFC working conditions.
- Good catalytic activity to oxidize fuels.
- High oxygen exchange kinetics.
- Low cost.

It has been proven that Perovskites can potentially achieve all these requirements. However, there is still room for improvement as there is still lack of knowledge on the materials properties under strong reducing conditions. Hence, the goal of this subproject is to make a full study of a potential material in order to obtain deeper understanding of its working principle. Perovskite is an oxide with the generic formula ABO₃. By convention, the A cation is bigger than the B, generally has a 2+ valence and is placed in the corner of the unit cell. Whereas B cation generally has a 4+ valence and is placed in the center of the unit cell (figure 1). However, the valences can be both 3+.
According to literature, there are two basic perovskite materials useful for SOFC anodes: La\(_{x}\)Sr\(_{1-x}\)TiO\(_3\)-\(\delta\) and La\(_{x}\)Sr\(_{1-x}\)Cr\(_y\)Mn\(_{1-y}\)O\(_3\)-\(\delta\). La\(_{x}\)Sr\(_{1-x}\)TiO\(_3\)-\(\delta\) has been selected as material for this study. Furthermore, it has been published that A site deficiency might increase the oxygen mobility, Mn doping on the B site might also increase oxygen conductivity and addition of CeO\(_2\) enhances the catalytic activity. Therefore, materials with these different compositions and/or deficiencies have been synthetized. Thus, Ce\(_{0.1}\)La\(_{0.2}\)Sr\(_{0.7}\)Ti\(_{0.9}\)Mn\(_{0.1}\)O\(_3\)-\(\delta\) is the material which includes all of these. Results of XRD analysis for the different synthetized products are shown on figure 2.

The XRD results show that all synthetized products have the Perovskite structure, even when applying A-site deficiency or B-site doping (STO, S7L3TO, S7L2TO, S7L3T0M1O, S7L2T9M1O). However, the Ce doping leads to a segregation of CeO\(_2\) secondary phase besides the Perovskite. This can be seen in the peaks at 28° and 56° 2\(\theta\) for CLST and CLSTM. Thus, it can be stated the desired products for this study were successfully synthetized.

The next planned actions are the study of the properties in order to see the influence of each chemical composition to their performance. Therefore, the catalytic methane reforming, oxygen permeation and ionic/electronic conductivity will be investigated.
Tuning of the anode microstructure
Apart from the material itself, another important factor for the anode efficiency is the microstructure. This is due to the so-called triple phase boundary (TPB). The TPB could be defined as the amount of area where electrons, ionic oxygen, and fuel are in contact. They are all needed to carry out the reaction. Hence, the larger the TPB area, the higher the efficiency of the anode.

For the classic Ni/YSZ anode, the desired properties for a high TPB can be listed as follows:
- High porosity and interconnected pores in order to get a high gas transport through the electrodes.
- Small pore size are needed to increase the surface area of contact between the fuel gas and the oxygen ion coming from the electrolyte.
- Nickel must be available on the surface where there is the TPB. Otherwise, it is useless as the reaction cannot take place.
- Nickel should be interconnected in order to enhance the electronic conductivity to the current collector.

Thus, the state of the art focuses on using pore formers such as graphite, carbon black, rice starch, potato starch or corn starch. However, there are several drawbacks related to this technique:
- Pore size: high porosity can be achieved by the addition of higher amount of pore former. However, bigger pores are formed in that case leading to less active area.
- Interconnection: Using this method the pores are formed in a cluster-like manner, resulting in a lack of connectivity between them.
- Nickel is not available in the small pores.

Consequently, a new method is needed to create the desired microstructure. In addition, this technique should be cheap and easily reproducible. This can be done by combining two different techniques: electrospinning and templating. Electrospinning is a well-known method to create micro/nano polymeric fibers. It is normally used in the biomedical field. However, it could also be used as pore former or as template in this case.

This templating consists on having an “antimold”, the electrospun fibers in this case, which are filled with the metal precursor. Then the infiltrated sample is annealed at high temperature. Thus, the fibers are burnt out and the desired pattern is formed. The electrode would be made as shown in figure 3. The first step would be to grow the electrospun fibers on top of the electrolyte, figure 3c. Then, the YSZ precursor would be infiltrated in the electrospun scaffold and dried to form a gel, figure 3b. Finally, the infiltrated fibers would be annealed at 850°C (figure 3a). Thus, the YSZ would be formed and the polymeric fibers would burn out forming the desired micro/nanochannels.

Figure 3: Electrospun template preparation method.
- a) annealed product, b) infiltrated fibers, c) fibers deposited on substrate
The next step would be to control the deposition of the Ni onto the surface of the channels. It could be done by growing electrospun fibers containing Ni or NiO nanoparticles. Thus, when the polymer is burnt out the NiO would be properly deposited. This is shown on figure 4.

Figure 4: Theoretical electrospun templated product when Ni particles are added

Up to now, the concept has been proven by preparing templated YSZ thin films with electrospun fibers without adding Ni. The wetting and drying of precursor in the fibers scaffold and the shrinkage while heat treatment have been studied and improved. At the same time, the directionality of the fibers have also been studied and improved by obtaining straight aligned fibers. The obtained results are shown on figure 5. It can be seen that straight aligned nanochannels are formed. Subsequently, it can be stated that the concept has been proven.

Figure 5: YSZ templated with straight aligned nanochannels.

However, there are still some other problems related to the preparation which have to be solved. First of all, samples suffer from cracking. Secondly, the directionality of the fibers must be vertical. Finally, Ni has to be added. Thus, these will be the next steps to be done in order to obtain a valuable electrode.
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, 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.
1. **YSZ sol-gel precursors**

1.1 **Recipes**
Two different sol-gel recipes have been tested: (1) based on 2-methoxyethanol and acetic acid stabilization; (2) based on acetylacetone stabilization in 1-propanol. Recipe (1) is used for thin film preparation using spin-coating, whereas recipe (2) will be used for mister vapor deposition. This method needs a more “friendly” (less toxic and corrosive) precursor.

Stabilization of the precursors have been monitored with: FTIR, TGA-DSC, and XRD.

1.2 **Aging Effect**
Aging has a significant effect on sol-gel precursor. The condensation of the polymer chains has continued to a much more advanced stage, and more M-O-M bonds have been formed. This has an effect on the viscosity and cracking behavior. In gels, during aging, condensation continues, and surface modification as well as syneresis takes place, resulting in a more compact and rigid gel.

HRSEM pictures (figure 1) show that aging (in this case) has no significant effect on the microstructure of the obtained thin film. However, clear differences between the densification of 3YSZ (tetragonal) and 8YSZ (cubic) films are observed.

2. **Densification behavior YSZ thin films**

2.1 **Microwave-assisted Rapid Thermal Annealing (RTA)**
YSZ is used as an electrolyte material in SOFCs. In order for the SOFC to function properly, the electrolyte material should have a high ionic conductivity and it should be impermeable for gasses. Rapid thermal annealing enables very high heating rates, and thus sintering occurs at much lower temperatures as for conventional heating methods. Furthermore, due to the porous nature of the deposited sol-gel films and the driving force to reduce surface area, the temperature of sintering is lower than for bulk materials. (No HRSEM pictures of comparison between conventional and RTA heated thin films available yet).
2.2 X-Ray Reflectivity (thin film density determination)

X-Ray reflectivity (XRR) is an X-ray technique that probes the surface of a thin films by using very low angles of beam 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. For sol-gel films however, this is not straightforward. When an X-ray beam impinges the surface at very low angles, total external reflection occurs; however, as the angle increases to above the critical angle, the intensity drops dramatically. This critical angle of total external reflection is solely dependent of the electron density (and thus the material density). If the thin film and the interface with the substrate are very smooth, the material acts as a mirror ($\beta/\delta = 0$), and the critical angle is easily determined (figure 2). If the thin film shows defects, the absorption coefficient changes, and the determination of the density becomes more and more difficult. (Note: the density will also be measured using Rutherford Back Scattering, in order to validate the new method).

Figure 2: Fresnel reflectivity with different absorption coefficients.

A simple method has been developed to accurately determine the critical angle, without modeling the data with a full-curve fit. The density of sol-gel derived thin films can easily (within 15 min) be determined.

2.3 Densification behavior measured with XRR

Thin films of 3YSZ and BYSZ have been prepared by spin-coating. Subsequently, they were heat treated for different times at fixed temperatures. Thin film density was determined by the method described above.

Figure 3: Densification behavior of BYSZ thin films annealed for different times at 650, 850 & 1000 °C.
3. Patterning YSZ structures by means of micro-molding in capillaries (MIMIC)

An increase in the total surface area of the electrolyte material can be beneficial for the performance of the fuel cell. One method to achieve this by depositing a very porous layer on top of a highly dense YSZ film (using the information of the abovementioned method). Also, patterning techniques can be used to increase the surface area. Different YSZ structures (sizes and dimensions) have been patterned by means of micro-molding in capillaries (figures 4-5).

Figure 4: HR-SEM pictures of cross- and ring-shaped structures after annealing at 850 °C for 1 hour, a) overview of a larger patterned area of cross-shapes; b) cross pattern at higher magnification. Pictures a-b have been taken in-lens at 2.0 kV for higher topographical resolution; c) overview of a larger patterned area of ring-shapes; d) ring pattern at higher magnification. Pictures c-d have been taken with secondary electrons at 2.0 kV.

Figure 5: HR-SEM pictures of patterns obtained from square-shaped molds. All images are taken after heat treatment at 850 °C for 1 hour (in air). a) overview of large patterned area. A continuous, crack-free, film was obtained; b) the continuous film at higher magnification. Sharp edges and uniform size and shape of patterned film are clearly visible; c-d) square line-patterns were obtained for 20 times diluted sols on volume. A small amount of PDMS residue is visible; e) overview of a large patterned area of “dog-bone” shapes. The continuous film was deliberately cracked by addition of extra sol precursor during the drying stage; f) the “dog-bone” shaped structure at higher magnification. The place of crack formation is clearly visible (as indicated with the arrows) and the shape of the structure follows the curvature of the crack. Pictures a, c and e have been taken with secondary electrons at 1.3 kV. Pictures b, d and f have been taken in-lens at 1.3 kV for higher topographical resolution.
Output until 25th March 2011

Batteries

This program is on hold

Theme coordinator
Prof. dr. Peter H.L. Notten