Annual Report
2014

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Colophon
This report takes a look back at activities carried out under the banner of ADEM in 2014. In response to the needs of industrial partners, ECN, DUT, TU/e en UT are conducting research into new materials for energy applications. The acronym ADEM stands for ‘Advanced Dutch Energy Materials - Innovation Lab’ - also referred to as the ADEM Program. This annual report provides an impression of the content of and progress made on all ongoing research projects, past and current investments in the joint research infrastructure and projects approved in 2014. The research is funded by the Ministry of Economic Affairs to the tune of €30,000,000. The participating companies together also contribute more than €3,000,000.

Since 2013, the Program Board has been made up of representatives from the participating companies, from the Hightech Systems & Materials and Energy Top Teams and from the Ministry of Economic Affairs. Its primary remit is to formulate the needs of industry and subsequently to advise the Steering committee on the allocation of resources to proposals submitted and infrastructural investments. Based on a long-term vision, the Board also has the task of identifying opportunities for new synergy between planned and ongoing projects and in doing so makes use of its industrial network.

In 2013 and 2014, the Steering committee submitted all not yet committed research projects and research infrastructure (and investments in it) to the Program Board. A total of 31 proposal submitted (21 PhD positions and 30 investments) were then evaluated. In 9 cases, this resulted in a recommendation for the proposals to be modified and in 10 cases for them to be rewritten and resubmitted. The Program Board endorsed the Steering committee’s proposal to withdraw 3 major investments and redeploy the resources.

In the wake of this phase of critical assessment and review of the ongoing Program, there is now room for the Board to focus on its secondary task: making use of the wide range of networks in the industry that its members represent. These networks can help to flesh out and substantiate the broad contours of the ADEM research. If there is to be a follow-up to the current Program, the indispensable and most valuable areas for material research will need to have been clearly defined. In this, the Board will have an important role to play in also representing those stakeholders who are not represented in the Board itself.

Large corporations have the capacity required to roll-out innovations on a large scale and over a longer period. SMEs, on the other hand, have the wherewithal to develop innovations on a smaller scale quickly. As new technologies are developed, so new industrial players are entering the arena.

The Program Board and the ADEM organisation are in favor of involving innovative SMEs and these new industries in the ADEM research programs.

Herman Kuipers

Chair of the ADEM Program Board
2014: results and plans

The Netherlands has an excellent track record in materials research, particularly in (nano)materials for use in energy conversion devices. This is a broad range of devices, which encompasses electricity generation and storage devices (wind, solar cells, batteries), heat transfer and storage devices, (solar-powered) chemical conversion devices, etc.

The Dutch government made a large investment in the ADEM Innovation Lab. Half of the funds is going to material research projects, the other half is used to install new advanced research facilities.

With the help of industrial partners, who are offering significant financial support, the Innovation Lab started with 10 PhD students in 2010, followed in 2011 by 14 others, and up to 2014 again 14 new PhD students were recruited.

In the past year, 5 PhD students have graduated and most of them found a continued career, again in energy-related jobs, in The Netherlands. We wish Vera Popovich (TUD), Shilpa Agarwal (UT), Emanuela Negro (cum laude, TUD), Remco Lancee (TUE), and Weiyu Song (TUE) all the best on their career paths and hope to meet them in another capacity at future ADEM meetings. In the current year, 2015, we expect another 8 PhD students to obtain their degree.

In 2014, 10 ambitious PhD students have joined our program: Yaolin Xu, Petra Dral, Luc Raijmakers, K. Coenen, Bas van de Loo, Peter-Paul Harks, Niek de Klerk, Gianluca Limodio, Norah Hornsveld, V. Reddy Paida.

The ADEM Shared Innovation Lab expanded in the same period to a valuable research infrastructure that facilitates sharing of facilities for research on materials for conversion, storage, and transport of energy.

In 2014 we upgraded an NMR (TUE), we installed a new advanced ion implanter and anneal-oxidation oven (ECN), and an E-Beam evaporation system (ECN). In total 7.3 M€ have now been invested in experimental equipment. We presented our shared facilities at our annual ADEM Conference with posters, now included in this annual report. The online version is freely accessible and ADEM partners can use the equipment for none or reduced costs. 4 M€ investment projects are granted in 2014, to be realized in 2015. Another 2 M€ proposals for investments in shared infrastructure will follow in 2015.
Up to now, we have realized 2.5 M€ worth in industrial participation, cash or in kind. Another 2.7 M€ has been committed for the coming years. The Ministry of Economic Affairs midterm approval of ADEM’s program in 2013 offered the opportunity to start projects in the Theme Batteries. The first projects have indeed started in 2014 and are already included in this report. In 2015 more projects will start in the Batteries Theme.

We have appointed new Theme Coordinators for two ADEM research themes. Louis Winnubst (U. Twente) has succeeded Anton van Steenhoven (TU/e) as Theme coordinator for Heat. Theo van der Meer (U. Twente) has succeeded Arian Nijmeijer (U. Twente) as Theme coordinator for Catalysis, Membranes and Separations (CMS).

2014 has been my last full year as your Scientific Director. In the past three years we have established an effective relationship with the government as our biggest sponsor, we have installed an ADEM Program Advisory Board consisting of key persons from large and medium-sized companies and from two Top Sectors who have a clear vision on the energy future of our country. We have ensured that there is an industrial demand for the advanced research facilities we have invested in, by securing hard commitments to co-invest in these facilities and in the research projects that are conducted with the help of these tools. Moreover, we have promoted and installed a Facility Sharing program, that provides an instrument to link researchers to advanced materials analysis tools and to facilitate the effective utilization of them, as well as to bundle the related expertise. And last but not least, we have re-established a consistent series of annual ADEM Conferences, offering an information and networking platform for both internal members and external parties.

I hope to meet all of you all in future energy research programs and related events, to jointly build a sustainable energy future.

Ruud Schropp,
Scientific Director of ADEM
Within the broad theme of Heat, the ADEM activities are in the area of materials for compact heat storage and compact heat engines. Limiting the focus to two system components; which have resembling processes and deploy similar techniques (synthesis of sorption materials, molecular analysis and TGA-DSC measurements), strongly enhances the coherence within the theme.

ADEM Projects embedded in the research groups

All four projects are in their final stage, with PhD defences to be expected in 2015. The relatively new research line on heat storage at TU Eindhoven started in 2007 with a Master’s study. At the end of 2014, seven PhD-students were appointed to work on this topic. The work is carried out in close collaboration with ECN via joint supervision of several PhD students (Prof. Zondag from ECN has been appointed as part-time professor at TU Eindhoven). Close contacts exist with Prof. van Duin (Penn State University) who is the initiator of the reactive force field model. The results obtained within this research line are integrated into IEA SHC task42 (International Energy Agency Solar Heating and Cooling) on Compact Thermal Energy Storage in which Dr. Rindt is leader of the working group on Numerical Modeling. The good contacts established European wide have led to participation in the FP7-project SAM.SAA (Sugar Alcohol based Materials for Seasonal Storage Application). A spin-off of this research line is sorption cooling. The Energy Technology group participated in a KIC InnoEnergy project on Energy Storage in which collaboration was established with the start-up company Ares-RTB on the development of a sorption cooler.

Metal-Organic Frameworks is a central theme within the section of Catalysis Engineering aimed at energy efficiency, catalysis, adsorption and separation. Adsorption heat pumps fit perfectly well in this portfolio. Within the group of Engineering Thermodynamics there is a strong collaboration on this topic of heat pumps as well as on the molecular modelling activities. Both teams have an excellent reputation in these areas and are active in new proposals within Horizon2020 in this field.

The research on heat transfer enhancement by carbon nano fibers in the Thermal Engineering group of the University of Twente has strong links with the research line on thermo-acoustic engines with a team of 3 PhD’s. In the last phase of the project the CNF’s will be applied to a regenerator of a thermo-acoustic engine. Within this topic there is close cooperation with the research groups Structural Dynamics and Acoustics and Energy, Materials and Systems.
ADEM facilities

The most important facility within the Heat theme is the Setaram high pressure TGA-DSC with mass spectrometer and microbalance, which is operational at ECN. This system has been used for several other projects within ECN and is also available as an ADEM facility.

The Rubotherm high-pressure thermo-balance, installed in the Engineering Thermodynamics group at TU Delft, has been used by Martijn de Lange (Project TUD-P08) for cyclic adsorption-desorption experiments.

Theme Coordinator

Prof.dr. ir. Theo van der Meer
University of Twente
Introduction

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

![Figure 1: Representation of the thermochemical seasonal heat storage system based on the water vapour sorption process in salt hydrates, integrated into an individual house.](image-url)
In order to develop adequate sorption materials for this application, this project focusses on establishing the effect of the operating conditions of the system (temperature, vapour pressure) and of the structural and material properties on the heat- and vapour transport during the sorption process. Within this line of research, an experimental material characterization has been carried out at different scales of the material (crystal, grain and powder bed) to identify the influence of these system and material properties. First, the study was carried out on model salts Li₂SO₄·H₂O and CuSO₄·5H₂O which present simple and well established water vapour sorption processes, in order to identify a suitable methodology of research and relevant material characterization techniques under the practical conditions of the seasonal heat storage. Next, these experiments have been extended to other salt hydrate materials ((MgSO₄·7H₂O, MgCl₂·6H₂O, CaCl₂·2H₂O), selected at ECN for their more promising performance as thermochemical materials for seasonal heat storage application in the residential sector.

Research results from 1 January until 31 December 2014

In the previous years of this ADEM project, issues related to slow kinetics and material stability were identified for respectively the sulphate and chloride materials, reducing their performance for long-term heat storage. Improvements of the material properties and system conditions are required to develop a suitable salt hydrate material for a packed bed sorption system. Therefore, the effect of adjusting the operating conditions and changing the material properties by means of chemical mixtures was investigated on micro-scale by thermal analysis. Subsequently, lab-scale reactor tests were carried out to estimate their performance for long term heat storage in a packed bed system. Then, first semester of 2014 focused on finalizing the experimental characterization of several sulphate (Li, Cu, Mg) and chloride (Mg, Ca, Sr) salt hydrates by thermal analysis, X-ray analysis, Raman spectroscopy and microscopy (optical, SEM) to identify and improve the properties of the materials and operating conditions of the (de)sorption process of the salt hydrate materials for heat storage application. Additionally, in 2014, the collaboration with Shuiquan Lan, an ADEM PhD student from the Eindhoven University (TU/e), was continued to characterize the kinetics of reaction of the salt hydrate materials identified by thermal analyses according to nucleation and growth models. The second part of the year was mainly focused on the writing of the dissertation that will close the research project. The highlights of the thesis are the following.

First, an extensive investigation of the thermodynamics, kinetics and transport phenomena was carried out for the dehydration and hydration reactions over thermal cycles of the two model salts Li₂SO₄·H₂O and CuSO₄·5H₂O, presenting simple and well-studied water sorption processes. It showed that stability of the thermodynamical properties depends on the preservation of the molecular structure of the material over multiple cycles. On the other hand, the rates of reaction depend both on the conversion rate of the material (intrinsic kinetics) controlled by the system conditions (T-p(H₂O)), and on the transport phenomena (e.g. diffusion) influenced by both the material grain structure and system conditions. This investigation also highlighted the uniqueness of the thermal behaviour of each salt hydrate material, due to the unique evolution of its structural properties (crystal, grain) over thermal storage cycles.

Next, for two salt hydrate materials (MgSO₄·7H₂O, MgCl₂·6H₂O), selected at ECN as potentially interesting thermochemical materials for seasonal heat storage, the limiting conditions (system, material) were investigated to improve their thermal performance for long term storage. For MgSO₄·7H₂O, a slow reaction rate was found during the rehydration process inducing a non-efficient release of the stored heat during the dehydration. This phenomenon is associated to slow reorganization of the material structure, evidenced by an amorphization of the material, under the operational conditions of the system. A thermal analysis study of the (de)hydration reactions under different conditions of water vapour pressure, identified an optimum in the reaction rates for a water vapour pressure of 50 mbar. However, up-scaling of these conditions in a lab-scale reactor test showed only a small improvement of the overall thermal performance of the material. Additionally, the p(H₂O) value of 50 mbar is not feasible for the end-goal application of seasonal heat storage in the residential sector. The investigation on MgCl₂·6H₂O showed that the degradation of the thermal performance over various cycles was mainly caused by hydrolysis (HCl formation) of the material.
This process is influenced by both material properties and open-sorption design of the storage system, and the desorption temperature. The structural characterization of the material permitted to identify that the presence of Mg-ions in the material structure favoured the formation of HCl vapours, due to the acidic properties of the hexa-aqua-magnesium ions \([\text{Mg(H}_2\text{O)}_5\text{(OH}^-)]^+\) in presence of water vapour. This research has led to an explanation of why in open-sorption systems, in which the HCl vapours are evacuated from the material, the hydrolysis reaction is promoted, particularly for the lower hydrated phases (2-hydrate, 1-hydrate) where the equilibrium depends strongly on the HCl pressure. When the material is only dehydrated between the 6-hydrate and 4-hydrate phases, the hydrolysis of the material is prevented. However, this way of stabilizing the thermal material properties reduces its storage capacity is reduced by half, and then the interest for this material for the end-goal application.

Alternative chloride materials (CaCl\(_2\)·2H\(_2\)O and SrCl\(_2\)·6H\(_2\)O), with structural properties and energy storage densities similar to the Mg-salts, were preliminary investigated in this project. The first results on these materials showed an improvement on the long term stability compared to the Mg-salts, but kinetic issues for SrCl\(_2\)·6H\(_2\)O and melting at low temperature for CaCl\(_2\)·2H\(_2\)O, limit their use as suitable thermochemical heat storage materials. From this research project, it is concluded that none of the materials investigated presents sufficiently good properties to allow a direct implementation in an open-sorption domestic storage system. The most promising perspective is given by CaCl\(_2\)·2H\(_2\)O, if its physical stabilization at low temperature can be realized by a suitable carrier material or chemical modification.

**Industrial collaboration until 31 December 2014**

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

**All output from 2014**


**Other**

The ADEM project 4.2. aimed to be finalized in the course of 2015.
Project: TUE-P01

Development of micro- and meso-scale models for heat and vapor transport in storage materials

Name PhD-candidate: Shuiquan Lan
Affiliation: Eindhoven University of Technology/Mechanical Engineering/Energy Technology group
Start date: 15 Sep 2010

Project leader(s): Dr. C.C.M. Rindt
Other personnel: Prof. H.A. Zondag, Prof. A.A. van Steenhoven

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

Research results from 1 January until 31 December 2014
Development of heating stage microscopy system:
The dehydration reaction of Li$_2$SO$_4$.H$_2$O monocrystals was investigated by in situ observations in terms of nucleation and nuclei growth processes. Optical observation was carried out in a heating stage facility using a Zeiss microscope (SteREO Discovery.V20). As shown in Fig. 2, the experimental conditions including temperature and water vapor pressure in the reactor are precisely controlled and the reaction is recorded photographically by the camera system. In order to measure the growth rate in-depth, measurements on encapsulated crystals were also carried out. Typical
results of surface nucleation and interface propagation in the bulk are shown in Fig. 3.

**Figure 2:** A schematic drawing of the heating stage in combination with the microscope.

**Figure 3:** Microscopic observations of surface nucleation (left column) and growth in the bulk of Li₂SO₄·H₂O crystals (right column).
Development of sharp interface model:
A sharp interface model was developed for describing the dehydration reaction of Li$_2$SO$_4$.H$_2$O single crystals. It includes the intrinsic chemical reaction and mass diffusion simultaneously at an elementary level. The mathematical framework is based on a conservative formulation of finite difference method. The code implemented in Matlab was verified successfully by the problem of the interface motion of transient liquid phase (TLP) bonding of nickel and mass conservation was observed as shown in Fig. 4 (right).

![Figure 4: Code verification by comparing current result with reference (left) and comparison of various mass flux (right).](image)

The interface propagation experiment shown in the right column of Fig. 3 was simulated by our model. The water concentration profile as a function of dimensionless time for various Damköhler number values (Da) is shown in Fig. 5. Both microscopy experiments and TG measurements were carried out in order to validate the sharp interface model and gain deeper insight into the reaction interface.

![Figure 5: Profiles of water concentration distribution in a plane sheet for various Da values indicated in figure titles. Dehydration starts at the surface and Δt denotes the time difference between two profiles in each figure.](image)

Industrial collaboration until 31 December 2014
None
All output from 2014


**Introduction**

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

**Research results from 1 January until 31 December 2014**

Based on a thorough literature review, the most promising MOF-working fluid pairs have been selected, based on their capacity, adsorption behaviour, enthalpy of adsorption and stability of MOFs with regard to the working fluid of choice. Eligible working fluids are water, methanol, ethanol and ammonia.
Figure 1: Total amount of energy released in the condenser (at 298 K), $Q_{\text{con}}$, when the full working fluid capacity is condensed, both per unit MOF volume (black bars, left $y$-axis) and per unit mass (red bars, right $y$-axis). For the last three adsorbents methanol is the working fluid, for the others this is water.

From this, a set of MOF-water and MOF-methanol pairs showed potential for application in adsorption driven heat pumps and chillers. Subsequently, the performance of these working pairs has been compared to those commercially available and often researched in scientific literature. Of these benchmark materials, the AQSOA™ series (zeolites used by commercial devices of Mitsubishi plastics in conjunction with water) stand out. In Fig. 1 the energy that can be generated in a condenser when the full adsorption capacity of a material is used is shown. Clearly, per unit volume of materials, MOFs show better performance than either the aforementioned AQSOA series or silica gel (water) or activated carbon (methanol). Furthermore we found that MOFs can be regenerated at lower temperatures than conventional solids which makes that sustainable energy can be more easily employed (E.g. solar thermal energy, industrial waste heat. Furthermore, in general MOFs show enhanced thermodynamic efficiencies, clearly indicating the potential that these materials hold for the application at hand.

Previous study is based on thermodynamic ('static') material properties. Though these are important for an assessment of feasibility, mass and heat transfer should be high to ensure a high specific power. Last year we already reported a method to creating coatings of one particular MOF, CAU-10(Al)-H, directly on aluminium interfaces without the aid of a binder, to enhance the heat transfer especially, which is often the rate limiting step in adsorption driven heat pumps and chillers. CAU-10(Al)-H is of special interest as it has very suitable adsorption characteristics (Fig. 2, left) and its constituents, aluminium and isophthalic acid, are both produced on an industrial scale and thus abundantly available.
Figure 2: H$_2$O adsorption isotherm (288, 298 K) on CAU-10(Al)-H (left), cyclic gravimetric water adsorption measurements upon temperature step changes between 45 and 75 °C, at a fixed water vapor pressure (26 mbar) directly synthesized on an anodized aluminium plate (right) and SEM images of the MOF coating on those plates (scale bar represents 100 μm, bottom).

The aforementioned coatings, reported in the 2013 ADEM report, contained minor amounts of unwanted byproducts, inhomogeneous crystal size distribution and incomplete coverage. We therefore optimized the coating method. Adding an anodized aluminium oxide layer on the surface of metallic aluminium significantly enhanced crystal attachment and growth. This as this layer is more reactive. This is of prime importance as our synthesis protocol revolves around leaching some of the aluminium ions from the support to build up the MOF structure. Furthermore, separation of crystal nucleation and growth creates superior coatings, devoid of the aforementioned issues (SEM image in Fig. 2, bottom). Cyclic adsorption measurements performed with the Rubotherm magnetic suspension balance (acquired with ADEM budget, Fig. 2, right) indicate clearly that stability is not compromised when this MOF is coated on a substrate, a feature indispensable for application in adsorption driven heat pumps and chillers. Furthermore, the response of the amount adsorbed on a temperature step change is significantly more rapid for the coated sample than for bulk CAU-10(Al)-H, indicating that heat and mass transfer are enhanced when a coated substrate is employed, in comparison to powder. The loading, however, expressed per unit mass of sample, is significantly lower for the substrate than for the bulk powder. This is because the aluminium substrate has a thickness of ~ 0.5 mm, whereas the coatings have a thickness in the order of 60-120 μm (SEM images), so most of the sample mass comes from the bulk aluminium. For application in AHP/ADC devices a thermodynamic optimization analysis of the coating thickness with respect to the support thickness should be performed, considering not only capacity, but also heat and mass transport. The improved layer, lastly, can adsorb 20% more water per square meter than the coatings reported previously.
Lastly, in contrast to previous claims in literature, we determined, with the aid of X-ray diffraction and subsequent refinement, that the steep step in water adsorption (Fig. 2, left) is not due to structural changes. This is very beneficial as it is known that these structural changes often lead to significant variations in crystal unit cell of the MOF. The latter would make it very challenging to retain the shape (in our case coatings) upon adsorption.

**Industrial collaboration until 31 December 2014**

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

**All output from 2014**

5. Goesten, M.G.; Szécsényi, A.; De Lange, M.F.; Sai Sankar Gupta, B.; Kapteijn, F.; Gascon, J.; Sulfonated Porous Aromatic Frameworks as solid acid catalysts. *Journal of Catalysis, under revision*
12. De Lange, M. F., Vlugt, T. J. H., Gascon, J., Kapteijn, F., Adsorptive characterization of porous solids: Error analysis guides the way. *Faculty Colloquium*, Zhejiang Normal University, Jinhua, China, 8 April, 2014 (oral)

**Other**

Mariëlle Wiegman received the 2014 NPS award for best bachelor thesis, working on this particular project.
Introduction
The advancement of high performance thermal systems has stimulated interest in methods to improve heat transfer rates. Considerable efforts have been made to increase heat transfer rates by implementing passive convective heat transfer enhancement methods that require no direct consumption of external power. This is mainly achieved by modifying heat exchanging surfaces which either plays a role in disrupting the flow field without increasing surface area (effect of surface roughness) or by increasing surface area and in some cases even both. As a result, surface covered with layer of carbon nanofibers (CNFs) results in high surface area, rough surface morphology and extremely high thermal conductivity which makes it ideal candidate for enhancing heat transfer. These properties of CNFs results in a substantial improvement of the exchange of heat between the surface and the surrounding fluid flow. The aim of the project is to study in depth the effect of carbon nano-fibers deposited on heat transfer surfaces in minimizing exergy losses in heat exchangers. For instance, in thermo-acoustic and thermo-chemical heat pumps which have a large influence on their final application.

Research results from 1 January until 31 December 2014
From previous work, we have determined that high crystallinity of the carbon nano-fibers resulted in better heat transfer (HT) performance. Moreover, the influence of the different structural morphologies and surface roughness of the deposited layer significantly influences the HT performance. It was concluded that the permeability of the deposited layers plays a significant role on the heat transfer enhancement of the samples. However, these experimental investigations were only performed on 50µm wire subjected to a cross flow from a nozzle. In the current study, the HT performance of the nano-structured surfaces was investigated using two rectangular microchannels (H=125µm and H=200µm). The focus on 2014 was to determine heat transfer performance of nano-structured surfaces on a flat substrate. The samples used in the current study were designed to exhibit higher crystallinity than the previously made investigations.

Material synthesis and characterization
Prior the synthesis of the nanostructured layers, the substrate silicon samples were coated with 10nm Ta adhesion layer and 5nm Fe layer respectively. The thin film layer was reduced using $H_2$ by increasing the temperature from ambient to 720°C at a rate of 10°C/min and maintaining the temperature for 1.8hrs. This process results in de-wetting of the thin Fe film. Initially the possible oxide layer that exists on the thin film reduces to pure metal. This is followed by the rearrangement of the 5nm Fe thin film in to clusters of nanoparticles.
After the treatment process, a controlled synthesis of a highly porous layer of CNTs was successfully achieved using Thermal Catalytic Vapour Deposition (TCVD) process at 720°C, see Figure 1. By varying the synthesis period, the thickness of the CNTs was controlled. Two different layers were obtained after exposing the wetted sample to the reacting hydrocarbon environment (C\textsubscript{2}H\textsubscript{4}). Samples exposed for 45min possess an average layer thickness of 6µm, where as an exposure of 90min resulted in a 20µm thick layer of CNTs. Vertically alignment of the layers was achieved during the synthesis process. This alignment is attributed to van der Waals forces between the crowding nanotubes. The CNTs diameters were measured by post processing the SEM images using image processing software ImageJ. The average diameter of the CNTs synthesized for a period of 45min and 90min are 35nm and 32nm respectively. The smaller the average diameter creates a denser morphology, see Figure 1-b & Figure 1-d. The difference of fibres diameter with relatively high porosity results in a flow permeability ratio between the two samples to be less than an order of magnitude. As a result, the two fiber layers can be assumed to have more or less similar response to flow penetration.

![Figure 1: SEM images of the deposited layer of two thick layer of MWCNTs (a,b) 6µm thick layer with synthesis duration of 45min and (c,d) 20µm thick layer with synthesis duration of 90 min.](image)

In order to determine the surface information of the each sample, a thorough investigation of the sample surfaces was made by using the data obtained by confocal microscopy. Samples were scanned point by point from a selected depth (optical sectioning) and a 3D topology of the CNFs sample is reconstructed using the data with the inbuilt computer program (VK analyzer). The data was processed to obtain surface information such as surface roughness and external surface area. For both samples a similar structure of the surface was expected, because only the synthesis period was different. However, the mean and root-mean-square surface roughness of the sample synthesized at 45min and 90min were found to be (S\textsubscript{a}=1.062µm, S\textsubscript{q}=1.333µm) and (S\textsubscript{a}=0.717µm, S\textsubscript{q}=0.954µm) respectively. The difference of surface roughness data between the two samples is attributed to the fiber diameters, which creates different density of layers of fibers, resulting in a smooth the top surface. Large enhancement of the external surface area was achieved for both samples. The external surface area ratio between the surfaces produced compared to the projected area of the sample is 7 and 7.1 times, for 45min and 90min synthesis period respectively.
The friction factors obtained for the bare silicon sample are used as a benchmark to determine the flow characteristics of the samples covered with CNTs. For the 125µm channel height, the 6 and 20µm thick layer of CNTs resulted in 12% and 26% increase in friction factor respectively. Friction factors obtained from the 200µm channel height show a similar trend with an increase of 6% and 16.4% for 6 and 20µm CNTs layer thickness respectively. The vertically aligned CNTs layers successfully enhance the heat transfer performance of the sample inside the rectangular microchannels. An average heat transfer enhancement of 19% and 74% is obtained inside the 125µm height microchannel with 6µm and 20µm CNTs layer thickness respectively. Whereas, the average heat transfer enhancement of 22% and 62% are obtained inside the 200µm channel with corresponding CNTs layer thicknesses of 6µm and 20µm. Since the nanostructured layer composed of highly porous strands of CNTs, the method of enhancement are separately studied by reviewing the structural characteristics of the samples. The relative surface roughness of both samples is less than 1% which results in negligible influence in heat transfer. The samples exhibit comparable improved external surface areas ratio. This surface area can increase the heat transfer only if the layer exhibits low porosity, which will result in high effective thermal conductivity. The CNTs layer exhibit extremely high internal surface area, which is highly dependent on the height of the layer, resulting in significantly larger internal surface area of 20µm than 6µm thick sample. However, the extremely high porosity of the CNTs can insure heat transfer only with partially or fully flow permeable layer. Different heat transfer and pressure drop results were obtained for the same samples under different channel height. Figure 2 shows the average enhancement heat transfer and friction factor for each measurement with respect to the CNTs layer thickness ratio \( \frac{h_{\text{CNT}}}{D_h} \). Result shows an increase in friction factor with an increase of the CNTs layer thickness ratio. This is attributed to the flow restriction, created by the CNTs layer, resulting in higher pressure drop. In contrast, an increasing trend in heat transfer can only be guaranteed for samples measured with the same channel height. For instance, for smaller difference in height ratio, even though the samples tested exhibit exactly similar layer morphology and topology, lower heat transfer performance was obtained for the channel height of 125um compared to 200um, see Figure 2. This is mainly attributed to the scaling effect induced by the structured surface which increases the local viscous dissipation. The local viscous dissipation competes with heat transfer resulting in lower heat transfer enhancement compared to the bigger channel size.
Industrial collaboration until 31 December 2014
This project has a strong link to the thermo-acoustic project in the laboratory of thermal engineering at the university of Twente which is funded by Nefit/Bosch. A PhD student is investigating a heat engine which makes use of a thermodynamic cycle similar to Stirling, but with less moving parts, therefore having a much higher reliability. Thus, the student focuses on the optimization of the novel engine generator for application within a micro-CHP appliance. The last step in this ADEM project is to apply the CNF’s on a regenerator for the thermo-acoustic engine. We will use the experimental facilities of the thermo-acoustic project.

All output from 2014

Other
The research work was originally intended to investigate the heat transfer performance of the nanostructured materials in the thermal engineering group led by Prof. van der Meer with a PhD candidate and the production of the materials in the Catalytic Processes and Materials group (CPM) led by Prof. Lefferts with the help of post-doc. Due to the withhold of the fund, the allocation of the post-doc was not possible during the course of the PhD work. However, the PhD candidate devoted much of his time, with the support of the CPM researchers from the group of Prof. Lefferts, to the synthesis of the materials than it was anticipated. With the availability of the post-doc funding, the PhD candidate is currently appointed on post-doc basis to finalize the heat transfer research by applying carbon nano structured material in actual regenerator with support of CPM group.
This report of the ADEM theme Wind Energy presents the state of the art of the initiated R&D projects. The last couple of years the Wind Energy Industry has been hit hard due to the crisis and as well as due to global energy policy changes. The prospects for the coming years will be more flourishing according to various market studies. However, the competitiveness of the various companies have increased and subsequently the performance of their turbines. Cost of Energy is a main design driver for wind turbines and its components like blades. It is becoming more and more challenging to improve the design of the blades to obtain a competitive cost of energy. A strategy to meet this challenge is to create a thorough and profound understanding of the behaviour of composite materials in order to create a weight efficient design. The full glass fibre design of the current 70+ m blades by Senvion and LM illustrates what still can be obtained with a full glass blade without the need to switch to carbon.

ADEM projects

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

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

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

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

Theme coordinators

Dr.ir. Harald Bersee
Prof.dr. Rinze Benedictus
Delft University of Technology
Introduction
Thick laminates are increasingly prevalent in the main parts of the present and future wind turbine blades and in other industries. A comprehensive study on thick laminates behaviour, testing, design and properties is required.

The aim of the project is to identify and quantify effects of large laminate thicknesses. Topics covered are thick laminates static allowable and fatigue life prediction, and the relation with current design rules, scaling effect on laminates, 3D-effects in blade thick subcomponents testing, self-heating in fatigue loading, or the manufacturing process influence on the final laminate properties, are investigated in this work.

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

Research results from 1 January until 31 December 2014
The approach followed in the present work is to identify the main factors involved in the thickness effect, and to evaluate each factor’s contribution to the thickness effect independently. The factors considered in the present work are:

Self-heating effect during dynamic loading. This was related with the material energy loss factor. During dynamic loading a certain rate of mechanical energy is dissipated into heat, leading to a rise of the material temperature. When the material temperatures approaches the maximum service temperature a fatigue life reduction can be observed. This effect was successfully studied and a FEM methodology was proposed in order to forecast it (see Figure 1).
**The manufacturing process influence.** Through-thickness lamina properties study is on-going. For this purpose 70mm thick plates were manufactured and sub-laminates were extracted and tested in order to study the mechanical properties through the thickness (see Figure 2). In addition different curing cycles were applied in order to observe the effect of the temperature gradient through the thickness (see Figure 3).

![Figure 1: 'S77' coupon temperature field and FE model (h = 10 W m⁻¹°C ).](image1)

*Figure 1: ‘S77’ coupon temperature field and FE model (h = 10 W m⁻¹°C ).*

![Figure 2: Sub-laminates methodology to study the properties through the thickness.](image2)

*Figure 2: Sub-laminates methodology to study the properties through the thickness.*

![Figure 3: Ultimate compression stresses through the thickness.](image3)

*Figure 3: Ultimate compression stresses through the thickness.*

**The scaling effect and the coupon geometry influence.** The scaling effect was studied for compression coupons via FEM with cohesive elements and fracture mechanics, in order to minimize the scaling effect during thick laminates coupon testing. Thick laminates fatigue life prediction in comparison with thin laminates coupons was studied in scaled compression tests up to 20mm thick.
Static tests of scaled compression coupon for 4, 10 and 20mm were performed, showing no thickness effect in the ultimate strength. In addition, Poisson ratios in direction 12 and 13 were measured showing comparable values. Stress gradients through-the-thickness as predicted by FEM models were observed in the tests. While the scaled geometries did not show a reduction of the ultimate strength due to the thickness, they showed a decrease in fatigue life S-N curves slopes with the thickness, such test were compared with the S-N guidelines standards (see Figure 4). Further scaled coupons with higher thicknesses need to be tested in fatigue to confirm this trend.

![SN-curves (R=10) for 4, 10 and 20mm. Least-square regression.](image)

**Figure 4:** SN-curves (R=10) for 4, 10 and 20mm. Least-square regression.

**Industrial collaboration until 31 December 2014**

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

**All output from 2014**

5. Lahuerta F, Nijssen RPL, Meer FP van der, Sluys LJ. “Experimental-computational study towards heat generation in thick laminates under fatigue loading” Int Journal of Fatigue 2014 (Submitted).

7. Lahuerta F, Nijssen RPL, Meer FP van der, Sluys LJ. “Static and dynamic through thickness lamina properties of thick laminates” in 20th International Conference on Composite Materials. Copenhagen 2015 (Submitted).


Other

N/A
Introduction

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

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

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

Research results from 1 January until 31 December 2014

Results were shared from another PhD project started in May 2014 (a follow-up of the former micromechanical work, partly supervised by Tim Westphal).

Industrial collaboration until 31 December 2014

None
All output from 2014
One of the top challenges to be solved for future generations is to guarantee the availability of sufficient, affordable energy from renewable energy sources. Photovoltaic (PV) technology, which directly converts sunlight into electricity, will play an important role in the future to provide useful energy. The Solar Cell cluster of the ADEM program focuses on the enhancement of efficiency and reduction of costs of solar cells, in which the energy conversion takes place.

Although the energy transition is a slow process, mainly driven by cost reduction in energy providing services, the PV industry has grown rapidly in recent years. It has succeeded in significantly reducing the prices and cost of PV technologies. This price reduction has resulted in so-called grid parity in consumer prices of electricity in many parts of the world including the Netherlands. Further reduction of the cost of PV systems is expected to increase the installations of PV systems world-wide at this unprecedented rate. Improving conversion efficiency, reduction of the material consumption, and long-term stability of solar cells and modules are key factors for reducing their costs. Therefore novel concepts for increasing the efficiency are investigated and tested within the Solar Cell cluster of the ADEM program.

The program aims to materialise innovations in technologies in close collaboration with industry. In 2014 the Analysis of 3D volume organization of polymer-based photovoltaics devices programme has been granted to TU Eindhoven and a PhD candidate has been attracted. The Solar cell surface engineering program has been granted to TU Twente and a PhD candidate will be recruited. TU Delft was granted and a PhD student who started working on the project Implantation and low-temperature diffusions steps for solar cells.

At TU Delft two PhD’s have successfully finished their research work and theses have been delivered on Advanced stable silicon based materials and on Mechanical properties of crystalline silicon solar cells that determines the handling of thin waters, production and cell reliability. At TU Twente and TU Delft three PhD students are in their final phase to finish work on Spectroscopy on optic active coating materials, on Mechanism of energy- and loading transport in advanced photovoltaic materials and on Laser material interaction.
Besides the already mentioned research, research is ongoing on **Coating for surface passivation**, **Materials for ‘all-silicon tandems’** and **Thermo-mechanical stresses and failure behavior as function of connection technology in solar cells**. These and newly granted PhD projects will result in additional expertise in solar cell processing and are carried out in cooperation with FEI, Tempress, and ECN.

The ongoing research is actively communicated and receives attention at international conferences. One of the PhD candidates, Michiel Aerts, who is a student at TU Delft, received attention with an article in the prestigious magazine Nature Communications on the topic of ‘Highly efficient carrier multiplication in PbS nanosheets’, about a new nanostructured material. Jimmy Melskens has received the Best Student Presentation Award during the 40th IEEE Photovoltaic Specialist Conference in Denver, USA for his research on stability of amorphous silicon.

Stefan Roest, founder and CTO of Eternal Sun, presented his company at the ADEM conference 2014 and showed researchers his way to a successful commercial implementation of research results.

**Theme Coordinator**

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

Research results from 1 January until 31 December 2014
The focus in 2014 was on two topics: 1) charge transport in PbS nanosheets and 2) terahertz spectroscopy measurements on PbSe nanorods and quantum dots.

Charge transport in PbS nanosheets
In our 2014 paper we establish that in thin lead sulfide nanosheets the efficiency of carrier multiplication is much higher than for quantum dots, nanorods and bulk material. The next step is to study the photoconductive properties of these nanosheets using terahertz spectroscopy. These properties, such as the mobility and lifetime of photogenerated electrons and holes are vital regarding their application as a solar cell material. We find that the sum of electron and hole mobilities reaches 500 cm²/Vs for nanosheets of 4 nm thickness and increases to values on the order of 800 cm²/Vs for the thickest sheets measured (see Figure 1).
The measured values are very high for colloidal nanocrystals synthesized via wet-chemical techniques, and are approaching lead sulfide bulk values for the thickest sheets. The frequency dependent conductivity points to an increasing importance of backscattering with decreasing sheet thickness.

Terahertz spectroscopy on PbSe nanorods and Quantum Dots

Of great importance for the application of semiconductor nanomaterials in (opto-)electronic devices are their optical and electronic properties. Many of those properties will vary with the size, shape and the degree of quantum confinement of the nanocrystal, in addition to the material of which it is made. In optoelectronic devices, often electric fields are used to deliver or extract charge carriers and one of the most important fundamental properties is thus the behavior of charges under an applied electric field.

For this study we present time-resolved terahertz spectroscopy measurements on PbSe quantum dots and nanorods. For the large PbSe quantum dots ($d = 11.6$ nm) we measure a purely real change in the dielectric function. However, this is contrary to the signal that is predicted by taking into account effective medium theory. For the short, quasi-1D PbSe nanorods ($L = 11.5$ nm, $d = 4.3$ nm) the THz response per electron-hole pair is a surprising factor 80 times higher (see Figure 2). Both these observations can be qualitatively explained by stating that the measurement is not sensitive to the electronic response inside the particle, but rather is measuring the response to the electric field of the portion of the electron and hole wave function that penetrates into the ligand shell on the nanocrystal surface.

Figure 2: THz probe field $E_p(t)$ (black line, left axis) and $\Delta E(t)/E_{max}$ per electron-hole pair or the QDs (blue lines) and NRs (yellow line).
The group of prof. Siebbeles has an ongoing collaboration with Toyota Motor Europe (Zaventem, Belgium) on nanomaterials for photovoltaics. Toyota provides funds for a postdoc at TU Delft and Dr. Sachin Kinge from Toyota has a part-time appointment as guest assistant professor at TU Delft.

All output from 2014
4. Poster Presentations at Physics@FOM 2014, Veldhoven on “Auger recombination in PbSe Nanorods: transition from cubic to bimolecular decay” and QD 2014, Pisa, Italy and the ADEM conference, Ermelo on “Efficient Carrier Multiplication in colloidal PbS Nanosheets”
5. Press release on Nature Communications paper: “Loodsulfide: het ideale nanomateriaal voor betere zonnecellen?”

Other
Introduction
The majority of solar cells produced today (>90%) uses crystalline silicon as absorber material. At the Si surface, the crystal lattice terminates, and hence defects exist. These defects can act as recombination centres for light-generated electron-hole pairs, limiting the conversion efficiency. In this project, we search for thin films or film stacks capable of passivating these defects for both p and n-type doped Si surfaces. The latter is required for e.g. the next generation high-efficiency solar cells, where all contacts are located at the back side. Furthermore, research focusses at fundamental understanding of passivation processes, the physical interplay between passivation layers and the silicon solar cell, and the stability of passivation schemes during solar cell manufacturing.

Research results from 1 January until 31 December 2014
It was found that we can accurately control the fixed charge density and polarity in the passivation layer by precisely tuning the SiO$_2$ interlayer thickness in SiO$_2$/Al$_2$O$_3$ stacks, prepared by atomic-layer deposition (ALD), making this a suitable scheme for back-contacted solar cells. By studying the passivation behaviour of these SiO$_2$/Al$_2$O$_3$ stacks on several Si base types, we have gained fundamental understanding about the working principles, such as the role of texture and surface doping concentration on the passivation properties.

Industrial collaboration until 31 December 2014
Tempress Systems: study of applicability of B$_2$H$_6$ as p-type doping source for Si solar cells, passivated by ALD Al$_2$O$_3$. (to be published as: “Emitters Doped with Boron from B$_2$H$_6$ and Passivated with ALD Al$_2$O$_3$ for Crystalline Si Solar Cells”).
Levitech: investigation of industrial viable ways to create “zero-charge” passivation schemes based on ALD Al$_2$O$_3$. Assistance in corona-charge experiments.

All output from 2014
Paper:
Conference contributions:
2. “Excellent Chemical Passivation of $p$+ and $n$+ Surfaces of Silicon Solar Cells by Atomic Layer Deposition of Al$_2$O$_3$ and SiO$_2$/Al$_2$O$_3$ Stacks” B.W.H. van de Loo, H.C.M. Knoops, G. Dingemans, I. Romijn, W.M.M. Kessels, AVS symposium, Baltimore, 2014

Conference proceedings:

Other
-
**Project: TUD-P15**

**Advanced nanostructured silicon-based films for stable absorber layers**

**Name PhD-candidate:** Jimmy Melskens

**Affiliation:** Photovoltaic Materials and Devices, Faculty of Electrical Engineering, Mathematics and Computer Science, Department of Electrical Sustainable Energy, Delft University of Technology

**Start date:** 1 Oct 2010

**Project leader(s):** Prof. dr. ir. M. Zeman

**Other personnel:** Dr. ir. A.H.M. Smets, Dr. S.W.H. Eijt, Dr. H. Schut, Prof. dr. E. Brück

**Introduction**

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

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

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

**Research results from 1 January until 31 December 2014**

Thin-film silicon solar cells have attracted a lot of attention since the first report on the fabrication of a hydrogenated amorphous silicon (a-Si:H) solar cell in 1976. However, a-Si:H-based solar cells suffer from light-induced degradation (LID) which can only partially be recovered by annealing. This issue has become known as the Staebler-Wronski effect (SWE). In this work it is aimed to fundamentally improve the understanding of the a-Si:H nanostructure and the defects in this material to finally enable a reduction of the SWE.
Unfortunately, the SWE has proven to be a notoriously difficult problem due to the complexity of the a-Si:H nanostructure. Because of this complication, the first aim is to improve the fundamental understanding of the nanostructure and the defects in a-Si:H and then the SWE and the nature of metastable defects are studied to pave the way towards a reduction of the SWE.

A wide range of material characterization techniques is used to conduct systematic defect studies on both a-Si:H films and solar cells. From the studies conducted on films with widely varying nanostructures it has become clear that Doppler broadening positron annihilation spectroscopy (DB-PAS) and Fourier transform infrared (FTIR) spectroscopy are powerful complementary tools when trying to determine the dominant type of open volume deficiency in the material. For high quality a-Si:H it is concluded that divacancies are the dominant open volume deficiencies, while the dominant type of open volume deficiency can get as large as nanosized voids when the deposition rate is increased sufficiently.

When investigating the electrical properties of defects in a-Si:H films and solar cells, Fourier transform photocurrent spectroscopy (FTPS) is used to quantify the sub gap absorption. By using voltage biasing, in situ light soaking, or in situ annealing on an a-Si:H solar cell it is possible to manipulate the occupation and density of states in the bandgap of the absorber layer and monitor any induced changes. This accuracy has enabled the observation of four sub gap contributions in the absorber layer bandgap of an a-Si:H solar cell. Considering the apparently important role of open volume deficiencies in the a-Si:H nanostructure and the fact that there are more than two distributions in the a-Si:H bandgap, it is unlikely that the commonly assumed continuous random network (CRN), in which isolated dangling bonds (dbs) are the dominant defects, is an accurate description of the nanostructure. Instead, the disordered network with hydrogenated vacancies (DNHV) is proposed as a nanostructural description which is more likely to be correct.

When using annealing as a probing tool to study the nanostructure of the as-deposited state, it is shown that a-Si:H films deposited at increased hydrogen dilution are characterized by an increased hydrogen passivation degree of small open volume deficiencies. Irrespective of the used hydrogen dilution, three different processes are observed by means of DB-PAS during annealing: vacancy agglomeration, hydrogen effusion, and crystallization. Since these processes take place at higher temperatures when the a-Si:H film is deposited at increasing hydrogen dilution, a reduced mobility of open volume deficiencies is linked to an enhanced light soaking stability. Finally, FTIR spectroscopy results indicate that the hydrogen effusion is a two-stage process, in which hydrogen initially mostly effuses from the small open volume deficiencies and only secondly predominantly from larger open volume deficiencies.

Using all these new fundamental insights into the a-Si:H nanostructure, the nature and kinetics of LID in a-Si:H films and solar cells are investigated. It is concluded that the most stable type of a-Si:H is deposited at a low deposition rate, which is associated with the smallest type of dominant open volume deficiency, i.e. a well hydrogen-passivated divacancy. The four observed sub gap contributions have different light-induced defect creation rates during light soaking and do not follow a single time dependence $t^\beta$. More specifically, it does not generally hold that $\beta = 1/3$ or $\beta = 1/2$, as has been repeatedly reported in literature.

Since these findings call for a more advanced SWE model, which involves defects related to open volume deficiencies in addition to the dbs present in the CRN, a new nanoscopic description of the LID is given based on results obtained from DB-PAS and electron paramagnetic resonance (EPR) spectroscopy. It appears that there is a long term process in the LID which does not depend on the a-Si:H nanostructure. More importantly, it is found that there are defect types with short and long spin relaxation times, which are predominantly linked to defects created in small and large open volume deficiencies, respectively. This newly found link between LID and the a-Si:H nanostructure is an important step on the road towards fully understanding and further reducing the SWE and it once again shows that the DNHV is a more appropriate description of the nanostructure than the CRN.
Figure 1: S-W diagram with normalized values obtained from VEPFIT. The error bars for S/S_{c-Si} are not visible because they do not exceed the width of the markers. The arrows indicate an increase in deposition rate (r_d). Three different types of positron traps are distinguished: divacancies, multivacancies, and nanosized voids. The corresponding values of the nanostructure parameter K are indicated for each of these three types of dominant open volume deficiency. The second listing of sample a5 in the legend refers to the same sample after annealing (a.a.).

Figure 2: (a) Fitting a sum of four error functions to the sub gap FTPS-EQE spectrum. (b) Fitting a sum of four Gaussian functions to the derivative of the sub gap FTPS-EQE spectrum. Some data points (○) have been omitted for presentation purposes only; the actual data values are more closely spaced.

Figure 3: VEPFIT results for a dense a-Si:H film on a glass annealed at subsequently increased annealing temperatures showing the evolution of the (a) S/S_{c-Si} and (b) W/W_{c-Si} parameters of the top and bulk layers of the film. Note that the annealing treatment at T_a = 500 °C was conducted twice with a break of 3 months in between.
Figure 5: Increase of the fitted error function amplitudes as observed during in situ light soaking of an a-Si:H p-i-n solar cell with (a) white and (b) blue light (1 kW/m$^2$ at 25 °C). For each of the fitted subgap contributions, a power law slope can be fitted to the error function amplitude increase to obtain the time dependence $\sim t^\beta$.

Figure 6: Schematic representation of a new nanoscopic model of the LID in a-Si:H. The black arrows indicate light-induced changes and the dashed blue ellipses indicate spin interaction, which is strongly distance-dependent. The green and red arrows are only used to indicate different species and do not visualize an effusion process. The dominant defect configurations in small and large open volume deficiencies after prolonged light soaking are marked in a blue rectangle. The gray area represents the CRN-like material in which the open volume deficiencies are embedded.
Industrial collaboration until 31 December 2014
None.

All output from 2014
5. Presentations at the IEEE PVSC 40 conference in Denver, CO, United States (oral presentation; Best Student Paper Award), the PSD-14 workshop in Kyoto, Japan (oral presentation), and the EU PVSEC 29 conference in Amsterdam, the Netherlands (poster presentation).

Other
• Winner of the Best Student Paper Award for the presentation entitled “The nature and the kinetics of light-induced defect creation in hydrogenated amorphous silicon films and solar cells” at the IEEE PVSC 40 conference in Denver, CO, United States.
Introduction

An alternative use of ultra-short laser sources, as a future prospect, can be found in thermal processing, e.g. extremely selective annealing, laser doping, etc. The benefit of using ultra-short laser pulses for thermal processing relies on the possibility to be highly selective in depth of the laser induced transformations. This can be exploited for processing thin films or very shallow regions on the top surface of materials. This progress report summarizes the research not only of 2014 but also of the previous three years.

Research results from 1 January until 31 December 2014

Results from 15 January 2011 until 31 December 2013

We studied the ultra-short laser pulses-material interaction on different thin layers adopted for the fabrication of thin film solar cells for different processes.

In the first year of research, thin molybdenum films (thickness ~ 150-400 nm) deposited on glass were textured by ultra-short laser pulses. On the surface of the films, nano-sized gratings formed which are known as Laser-Induced Periodic Surface Structures (LIPSSs). These structures modify the optical properties of the films by increasing the scattering of light in the near infra-red part of the spectrum. Focusing on the technical side of laser nano-fabrication of long regular LIPSSs on thin brittle molybdenum films, the aim of this work was also to give an understanding of the correct laser parameters to apply during laser texturing of these thin films, in order to avoid or minimize thermal damage. It was found that the brittle-ductile transition must be taken into account when optimizing the laser parameters during laser processing.
Fig. 1 a) Picture of laser textured samples showing the colorful effect and the effective feasibility of large area nanogratings on 400 nm Mo layer. b) Angular intensity distribution (AID) shown from spectrophotometer measurements as function of the scattering angle $\theta$ and the wavelength $\lambda$ of the incident light. Measured data fit the grating equation for 390 nm periodicity.

![Figure 1](image1.png)

Figure 2. Transmittance of three different samples as function of the wavelength in the working range of a solar cell. Compared samples are, respectively: the SnO$_2$ material as-deposited, the SnO$_2$ treated at with a low laser fluence and the SnO$_2$ treated at with a high laser fluence. The transmittance was inspected using a spectrophotometer equipped with an integrating sphere.

![Figure 2](image2.png)

The second and third year of research were mainly focused on thermal annealing by ultra-short laser pulses of SnO$_2$ thin films (thickness $\sim$1 $\mu$m).

First, the effect of the laser annealing on the electrical and optical properties was studied. A marked increased optical transmittance of light in the visible-UV range and a simultaneous modest decrease of the electrical properties of the laser treated films were found. Combining these two contributions via the so-called Figure of Merit, an overall improvement of the performance, up to 59%, of the films after the laser treatment was observed. At high laser fluence levels, modification of the surface texture of the films was also observed.

Second, an explanation, at a microscopic level, of the observed changes in the SnO$_2$ thin films was given. That is, it explained, at a microscopic level, the origin of the measured macroscopic changes. The increased optical transmittance was mainly attributed to the removal of the thin interfacial carbon-reach layer present in the as-deposited samples and to the new surface morphology, while the small decrease of the electrical performance was ascribed to the generation of laser-induced defects, upon laser processing, especially in the molten-resolidified region.
**Results from 1 January until 31 December 2014**

In the fourth year of research we investigated the effects of ultra-short pulsed laser treatment on Al-doped ZnO thin films (thickness ~130-800 nm) deposited by industrially scalable deposition techniques, such as sputtering and plasma enhanced chemical-vapor deposition. The conductivity of the films increases sharply after laser exposure from 1 and $10^{-3}$ Ω·cm to $10^{-2}$ and $10^{-4}$ Ω·cm, while keeping an excellent transparency in the visible range (85-90%). The morphology and nanostructure of the films was analyzed in detail. The doping efficiency of Al atoms is improved by laser exposure, which promotes their incorporation in the ZnO lattice via the creation of zinc vacancies. The scalability of this process was also experimentally proved. Based on parameters studied in this chapter, the time required for processing of a surface of 1 m², using for example a 1 kW laser source, lies between 80 and 150 seconds with a calculated energetic cost of about few cents Euro/m², hence showing the potential for industrial applications.

A journal paper on the ultrafast annealing of Al:ZnO is under review.

**Industrial collaboration until 31 December 2014**

TNO/Solliance, TUDelft, ECN/Solliance, Roth&Rau

**All output from 2014**

1. D. Scorticati et al., Thin film surface processing by ultrashort laser pulses (USLP), *Proc. SPIE* 8438, Photonics for Solar Energy Systems IV, 84380T (June 1, 2012); doi:10.1117/12.922270


**Other**

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**Project: TUD-P16**

Silicon based nanoparticles for efficient solar-spectrum conversion in all-silicon tandem solar cells

**Name PhD-candidate:** Martijn van Sebille

**Affiliation:** TU Delft, Photovoltaic Materials and Devices

**Start date:** 6 Aug 2012

**Project leader(s):** Prof. dr. Miro Zeman and dr. René van Swaaij, TU Delft

**Other personnel:** -

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**Introduction**

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

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

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


Research results from 1 January until 31 December 2014

We developed a fast, nondestructive measurement and simple analysis method for obtaining the absorption coefficient of silicon QDs embedded in an amorphous matrix. This method enables us to pinpoint the contribution of silicon QDs to the absorption spectrum of QD containing films. The DOS of the amorphous matrix is modeled using the standard model for amorphous silicon while the NCs are modeled using one Gaussian distribution for the occupied states and one for the unoccupied states. For laser annealed a-Si$_{0.66}$O$_{0.34}$:H films, our analysis shows a reduction of the QD band gap from approximately 2.34 to 2.08 eV indicating larger mean QD size for increasing annealing laser fluences, accompanied by a reduction in QD DOS distribution width from 0.28 to 0.26 eV, indicating a narrower size distribution.

Industrial collaboration until 31 December 2014

The PVMD research group has an enduring collaboration with HyET solar, with significant interaction on the field of thin film silicon solar cells. HyET Solar shows interest in our research within this field, including the projects carried out by Martijn van Sebille.

All output from 2014

1. Poster presentation: PhD Poster event EEMCS 2014, TU Delft, The Netherlands
   Title: Optical Characterization of Embedded Silicon Quantum Dots;
   Authors: M. van Sebille$^1$, R.A. Vasudevan$^1$, R.J. Lancee$^2$, R.A.C.M.M. van Swaaij$^1$ and M. Zeman$^1$
   $^1$ Photovoltaic Materials and Devices, Delft University of Technology, The Netherlands
   $^2$ Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, The Netherlands

2. Poster presentation: MRS Fall Meeting 2014, Boston, MA, USA
   Title: Optical Characterization of Embedded Silicon Quantum Dots;
   Authors: M. van Sebille$^1$, R.A. Vasudevan$^1$, R.J. Lancee$^2$, R.A.C.M.M. van Swaaij$^1$ and M. Zeman$^1$
   $^1$ Photovoltaic Materials and Devices, Delft University of Technology, The Netherlands
   $^2$ Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, The Netherlands

Other

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Introduction

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

ADEM projects

Within the theme of biomass conversion into Substitute Natural Gas (SNG) an optimised olivine-based catalyst is developed as a result of an in-depth study on the behaviour of olivine structure under different gas environments resulting in a better insight in the mechanism of oxygen transport by olivine. On this subject Remco Lancee defended his PhD thesis at TU/e on November 26, 2014: “Characterization and Reactivity of Olivine and Model Catalysts for Biomass Gasification” In a second SNG-related project a combined theoretical and experimental approach is followed to improve reactor design and operation performance for a chemical looping combustion process.

On April 3rd, 2014 Shilpa Agarwal defended her PhD thesis at the University of Twente (UT): “Surface chemistry of tailored ceria nanoparticles: interaction with CO and H₂O”. The structure of these ceria catalysts was revealed by techniques such as aberration-corrected electron microscopy (AC-TEM), FTIR, Raman spectroscopy, and it has been demonstrated that the nature of the exposed surfaces affects the catalytic steam reforming of bio oil. Another project on catalytic materials concerns the development of robust catalysts, including detailed mechanistic studies, for e.g. the catalytic oxidation of bio-ethanol to acetaldehyde. This opens promising routes for valorisation of biomass into many important chemicals. On this subject Weiyu Song defended his PhD thesis at TU/e on September 11, 2014: “Computational studies of catalytic reactivity at the metal-reducible oxide support interface”

At UT an integrated autothermal reforming reactor is being developed for natural gas conversion into hydrogen with integrated CO₂ capture, consisting of two different membranes: an oxygen membrane and a hydrogen selective ceramic membrane. Dense, mixed ionic-electronic conducting ceramic membranes with high oxygen flux and stable in CO₂ environment were fabricated using a tape casting/sintering technique.
A new micro-porous silica hybrid-based membrane is developed with improved H₂/CO₂ permselectivity and good hydrothermal stability. In a new project, started in 2014, a more fundamental study has been started to explore the dynamic nature of these hybrid systems. Finally, attention is paid to the search for alternative materials for CO₂ capture. The currently used amine process suffers from drawbacks such as corrosive behaviour and sensitivity to degradation. Within this ADEM project specific ionic liquids (ILs) for natural gas sweetening are designed.

**Industrial Involvement**

Together with HVC and Gasunie, ECN has initiated the Groen Gas 2.0 demo project to demonstrate large-scale green gas (SNG) production. Chemical looping combustion technologies, as developed in the CMS cluster, are included in this process. In the field of micro-porous silica hybrid membranes, narrow collaboration exist with PERVATECH BV (Rijssen), one of the key players in the production of these hybrid ceramic membranes.

**Plans**

In 2015 several PhD theses will be issued by the first tranche of PhD students. The green light to execute the planned program to full extend includes the opportunity to start essential additional and new research.

**Equipment**

Examples of equipment from the first tranche of ADEM investments, which are of importance to CMS and shared with different partners, are: Vertex 70 FTIR & MS, Conversions Inspector for Gas Separationsse, XRF and XPS (0.5 micron resolution)

**Theme Coordinator**

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

Sustainable Bio-oil Steam Gasification

- Bio-mass promises renewable energy and chemicals production

![Figure1: Schematic overview of bio-oil steam gasification]

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

Research results from 1 January until 31 December 2014
Steam reforming of bio-oil combined with the gasification of coke deposits in the presence of water is a conceptually promising alternative to generate hydrogen gas. H$_2$O can be activated in the gasification stage to form hydroxyl groups (-OH) on oxide-supported (like ceria) metal catalysts, which increases both the H$_2$ yield and the catalyst's lifetime. The reactivity for the water dissociation as well as the reactivity of resulting hydroxyl groups can be further improved by altering the shape and size of ceria support. Based on the recent studies, ceria nanoshapes exhibit excellent redox properties and high specific activity/selectivity in comparison to the bulk ceria particles.
However, the knowledge related to the surface species actually responsible for enhanced catalytic activity of ceria nanocatalysts so far remain lacking. The work presented in this thesis highlights the fundamental aspects of ceria nanoshapes, with emphasis on the effects of surface planes on overall catalytic performance. The main objectives of this work are to investigate the true exposed facets, as well as to understand the reactivity of hydroxyl species and the role of defects on the ceria nanoshapes.

In the first part of this project, definitive information on the nature of the exposed surfaces in these CeO₂ nanoshapes is provided using aberration-corrected transmission electron microscopy (AC-TEM) and high-angle annular dark field imaging (HAADF). Prior to the present work, discrepancies in literature existed related to the exposed planes on these ceria nanoshapes. For instance, it was the common belief that rods showed enhanced activity due to the exposure of active {110} and {100} planes. These findings were reported prior to the recent advancements in TEM (of AC and HAADF), and thus the results were unclear. Furthermore, our initial FTIR results suggested that ceria rods and octahedra share similarity in terms of exposed planes. This spurred us to re-examine rods with up-to-date TEM equipment. From the AC-TEM results it is apparent that ceria octahedra and rods both expose {111} surfaces, whereas ceria cubes mainly expose {100} surfaces.

Additionally, H₂-reduced ceria nanoshapes were examined for water gas shift (WGS) reaction to evaluate the structure performance relationship. It is observed that the WGS activity normalized with surface area (m²) was identical for ceria octahedra and rods, whereas ceria cubes were found to be much more active. Further, to understand the interaction of surface species with CO during WGS catalytic reaction, H₂-reduced ceria nanoshapes were analyzed using FTIR spectroscopy at 350°C. Similar to WGS results, the FTIR spectra specifically, the hydroxyl (-OH) vibration bands and their interaction with CO, for rods and octahedra were observed to be the same. On the other hand, cubes with {100} planes exhibited different relative amount of the surface –OH species and their interaction with CO resulted in different spectral features in comparison to rods and octahedra. It is clearly demonstrated in present work that the nature of the exposed surfaces affects the WGS activity as well as interaction of surface sites with CO. Due to the presence of the same {111} exposed planes, ceria rods and octahedra show similar WGS activity, as well as similar interaction of –OH species with CO obtained using FTIR spectroscopy. Interestingly, cubes with more active {100} surface planes have different –OH bands and interactions with CO, resulting in a higher WGS activity per m².

It is known that the hydroxyl species are the active sites in CeO₂ supported catalytic reactions such as WGS, and steric constraint can lead to different amounts of hydroxyl species on different exposed planes. In the second part of this work, the role of different types of active hydroxyl (–OH) species on the nanoshapes (wires, octahedra and cubes) and their respective reactivity towards CO and extent of regeneration of –OH species with water has been investigated using in situ FTIR spectroscopy at 200°C. All three ceria nanoshapes showed similar –OH stretching bands although with different relative intensities. Likewise rods, wires resemble octahedra in the hydroxyl range of FTIR spectra. The bridged hydroxyl species (–OH3641) on ceria wires and cubes were found to be reactive towards CO, whilst only limited interaction with CO was observed for octahedra. In addition, the formation of hydrogen carbonates was observed only in case of octahedra and the relative amount of defects detected follows the trend: Wires > cubes > octahedra. Based on these observations, it is suggested that both the presence of defects as well as the shape of ceria nanoparticles influences the interaction of specific hydroxyl groups with CO. Finally, subsequent exposure to water vapor at 200°C showed a clear shape dependent water activation to –OH species, resulting in removal of different relative amounts of formates and carbonates formed in either ambient or CO.

It is well known in the literature that the presence of intrinsic defects, as well as the ease of formation of defects during the reaction, strongly influences the ceria-catalyzed reactions. To understand the involvement of defects in ceria rods during the formation of specific formate and carbonate surface species at 200 and 350°C is investigated using a combination of in-situ Raman and FTIR spectrosopies.
It was observed at 200°C that the majority of formates and carbonates formed in CO do not form vacancies in the ceria lattice, whilst at 350°C formation of both formates and carbonates (mono/bidentate) result in the creation of vacancies. In addition, formation of stable polydentate carbonates was observed at 350°C. These polydentate carbonates were stable in water vapor as well as not forming vacancies in the ceria lattice. It must be noted that based on temperature the Raman signatures of the defect peaks arising in CO were very similar. However, their chemical origin seems to be different since at 350°C the addition of H₂O is needed to remove the vacancies, while at 200°C the majority disappeared already in He flowed immediately after CO flow. In the present work, it is also proposed that apart from the reported defects, such as anion Frenkel pair and oxygen vacancies, other CO-induced defects, e.g., vacancy clusters, interstitial and Schottky disorder might also form in the ceria lattice. Further theoretical studies are highly recommended for specific defect identification and corresponding peak assignment in the Raman spectra.

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

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

**Industrial collaboration until 31 December 2014**

None

**All output from 2014**


**Oral presentations**

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

Other
Project: TUE-P12
Fundamentals of Chemical Looping for Biomass Gasification

Name PhD-candidate: Ildefonso Campos Velarde
Affiliation: Chemical Process Intensification (SPI), Chemical Engineering and Chemistry, Eindhoven University of Technology
Start date: 2 May 2011
Project leader(s): Prof. Dr. M. van Sint Annaland, Dr. F. Gallucci
Other personnel:

Introduction
With the increasing energy demands, biomass is becoming a valuable and sustainable source for the future chemicals and fuels production. Conversion of biomass into Substitute Natural Gas (SNG) is an appealing opportunity to decrease anthropogenic CO$_2$ emissions. Biomass can be efficiently converted to SNG by the use of indirect biomass gasification technologies.

Indirect biomass gasification is a process carried out in two coupled/interconnected reactors. In this integrated system, a solid bed material (sand or oxygen carrier) is used to transfer heat (and/or oxygen) from an oxidation reactor to the gasifier, where biomass reacts with steam (and oxygen) and is converted into a mixture of mainly methane, synthesis gas and CO$_2$. The unconverted biomass fractions, including char and tars, are fed to the oxidation reactor, where they are combusted by air in order to heat up the bed material to the reaction temperature needed for gasification (> 800 °C). This operation allows an efficient production of a nitrogen-free syngas which can easily be upgraded to substitute natural gas. However, the tar produced by the gasification remains one of the main challenges in this technology, because of fouling issues in downstream equipment, decreasing of the overall process efficiency and increasing of the cost. Furthermore, to design these reactors, phenomenological models for gas-solid fluidized bed reactors have been developed. These models rely heavily on constitutive equations for the fluid dynamic characteristics (e.g. equivalent bubble size and bubble rise velocity, solids circulations etc.). These correlations have only been obtained and validated for fluidized beds operated at low temperatures. In order to improve both reactor design and operation, a better understanding of the prevailing phenomena occurring at higher temperatures is required.

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

In the present research a combined theoretical and experimental approach is followed. For the theoretical work, a phenomenological model has been developed and it has been coupled with Aspen Plus. This model allows the process analysis and optimization of indirect biomass gasification using an oxygen carrier.
As for the experimental approach, a novel endoscopic-laser Particle Image Velocimetry (PIV) coupled with Digital Image Analysis (DIA) technique has been developed to study the hydrodynamics of gas-solids fluidized beds at elevated temperatures. Additional work is being carried out on the use of oxygen carrier for tar reduction and on the influence of the temperature on the minimum fluidization conditions.

Research results from 1 January until 31 December 2014
The influence of the temperature on the minimum fluidization conditions is one of the key points to understand the prevailing phenomena in gas-solids fluidized beds operated at high temperatures. All other correlations to describe hydrodynamic of fluidized beds depend on the minimum fluidization velocity \( U_{mf} \). Experimental work and a literature research have shown that none of the 63 available correlations can predict the minimum fluidization velocity of different gas mixtures at elevated temperatures (see Figure 1). Furthermore, it was found that the estimation of \( U_{mf} \) depends heavily on the accurate estimation of bed porosity at minimum fluidization conditions (\( \varepsilon_{mf} \)). The three available correlations in open literature to estimate \( \varepsilon_{mf} \) have shown a poor accuracy in predicting the experimental porosity. Therefore, the experimental research has been focused on deriving a new correlation to predict minimum fluidization conditions. This correlation has been developed covering different particle and gas properties, as well as the influence of temperature. Moreover, the endoscopic-laser PIV/DIA has been applied to determine \( \varepsilon_{mf} \) at elevated temperatures, and has been compared to the widely used pressure transducer method (Figure 2). Endoscopic-laser PIV/DIA has shown to be a very powerful tool and the experimental results obtained with the technique confirm that the general understanding of high temperature fluidization is very limited and often rather inaccurate. This work has been submitted for publication in a peer reviewed journal. The next step in the experimental research is to carry out a systematic design of experiment to study the influence of temperature on the bubble properties, solids circulation patterns and solids hold-up using (nearly) spherical particles.

Concerning the use of an oxygen carrier for tar reduction, the candidate is comparing the reactivity of two important oxygen carriers (OC), olivine and ilmenite and to investigate the influence of the reactivity on the indirect gasification process. In this work toluene is used as a model component for tar. Finally, the experimental results from both streamlines will be implemented in phenomenological model developed in Aspen Plus to optimize the indirect biomass gasification process.

Industrial collaboration until 31 December 2014
None

All output from 2014
**Project: TUE-P05**

**Sorbent Development on the Basis of Kinetics and Mass- and Heat-Transport Phenomena in Sorption-Enhance Processes at Elevated Temperatures**

**Name PhD:** Kai Coenen

**Affiliation:** Eindhoven University of Technology/Chemical Engineering and Chemistry/Multiphase Reactors Group

**Start date:** 15 Apr 2014

**Project leader(s):** Prof. Dr. Martin van Sint Annaland

**Other personnel:** Prof. Dr. Emiel Hensen, Fausto Gallucci, Paul Cobden

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**Introduction**

The worldwide demand for hydrogen has steadily increased over the last years. More than 50 million tons of hydrogen is currently produced annually in the world, of which more than 80% is produced by conventional steam methane reforming. The sorption enhanced water-gas shift (SEWGS) process is a promising technology for hydrogen production with pre-combustion decarbonisation. The SEWGS process can yield higher capture ratios at lower efficiency penalties and at lower costs than other mature technologies using solvents. The SEWGS is a kind of pressure swing adsorption (PSA) process based on reversible \( \text{CO}_2 \) adsorption on solid materials at temperatures between 350 and 550 °C. The overall process directly converts syngas into separate streams of \( \text{H}_2 \) and \( \text{CO}_2 \), which makes the SEWGS process exceptionally suitable for pre-combustion \( \text{CO}_2 \) capture, mitigating anthropogenic greenhouse gas emissions.

Sorbents based on hydrotalcites are capable of capturing \( \text{CO}_2 \) at high temperatures (300-500 °C) and are therefore ideal candidates for use in high temperature pressure swing adsorption (PSA) systems in which reaction and adsorption occur simultaneously at high pressure (up to 40 bar) and temperature, followed by regeneration of the sorbent by release of the \( \text{CO}_2 \) at the same temperature but lower pressure (<5 bar). Hydrotalcites have a layered structure at low temperature and are available in a wide range of compositions. At higher temperatures the structure of the hydrotalcites changes and can be best described by mixed-metal oxides. Potassium promoted hydrotalcites, which have been widely studied in literature for SEWGS can be described as mixed magnesium–aluminium oxides with basic character. Although applications of these materials have been studied and shown to be feasible at a larger scale, there is still a lack of understanding of the fundamental interactions occurring with small gas molecules (\( \text{H}_2\text{O}, \text{H}_2\text{S}, \text{CO}_2 \) and other possible acidic species). In order to develop new and better materials for these applications, a deeper understanding of the physical and chemical properties including composition, morphology, microstructure and porosity, with the aim to better describe the kinetics, mass and heat transport phenomena, is necessary.

**Research results from 1 January until 31 December 2014**

In the first year of this ADEM project a new experimental setup has been designed, constructed and debugged that allows to carry out experiments at elevated pressures and with \( \text{H}_2\text{S} \). The setup (see Figure 1) combines the capability to do thermogravimetric analysis (TGA) and packed bed reactor (PBR) experiments at pressures up to 10 bar and temperatures up to 1000 °C. A gas feeding system capable to feed gases like \( \text{H}_2 \), \( \text{CO}_2 \), \( \text{CO} \), \( \text{CH}_4 \), \( \text{N}_2 \), \( \text{H}_2\text{S} \) and steam has been installed to feed different gas mixtures to the PBR or the TGA.
Two SICK gas analysing systems have been installed to monitor gas composition online. Proper operation of the setup has been validated by comparison with experiments performed in an already existing TGA at TUE with a similar gas-feeding system (but at atmospheric conditions and without H₂S). Preliminary adsorption experiments with CO₂ and steam have been carried out on potassium promoted hydrotalcites and alumina, and a standardized procedure to measure adsorption isotherms has been developed.

Figure 1 HOTSORB setup at TUE

Three different potassium promoted sorbents (two hydrotalcite based adsorbents and γ-alumina) have been screened with BET, HG-Porosimetry, SEM-EDX and TGA experiments to study the morphological structure and the adsorption behaviour of different components to be able to design further experiments. Experiments at 400 °C on these sorbents have shown that the cyclic CO₂ capacity, performing adsorption with CO₂ (1 hour) and regeneration with N₂ (1 hour), increases with an increasing basicity of the adsorbent. The sorbent with the highest magnesium-to-aluminium ratio of 2.95 (KMG70) showed the highest cyclic capacity, whereas KSORB (potassium promoted alumina) showed the lowest cyclic CO₂ capacity (see Figure 2). From the results it can be concluded in correspondence to literature that the sorbent with the highest surface area does not necessarily have the highest sorption capacity (see Figure 3).

Figure 2 Cyclic CO₂ capacity a 400°C for different sorbents
Figure 3 Surface area measured with BET and HG-porosimetry for different adsorbents

Due to mechanical stability issues with KMG70 in SEWEGS applications, it has been decided to start the detailed investigation with KMG30, which has already shown sufficient mechanical stability in PBR experiments at semi-industrial scale at ECN. The influence of temperature, cyclic time, and the effect of steam will be studied in detail for this sorbent. A model capable to describe the measured results will be developed. In a later stage, the influence of (competitive) H₂S adsorption and the material composition will be studied in detail and the adsorption kinetics models will be implemented in a reactor model to evaluate and optimise the SEWGS process.

Industrial collaboration until 31 December 2014

The object of this research is to understand and quantitatively describe the complex sorption kinetics of gas mixtures with different gaseous species during the different SEWGS processes. A model capable to describe the interactions between the sorbent and the gas molecules will make it possible to describe the sorption process better and to find the optimal operation conditions. This model will be used to optimize the SEWGS process and other projects at ECN using hydrotalcite based adsorbents to capture CO₂ and other acidic species.

All output from 2014

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Other

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**Project: UT-P08**

**Mixed-conducting ceramic membranes for oxy-fuel conversion**

**Name PhD-candidate:** Drs. ir. S.F.P. ten Donkelaar

**Affiliation:** University of Twente, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, Inorganic Membranes

**Start date:** 15 Feb 2011

**Project leader(s):** Prof. dr. H.J.M Bouwmeester
Prof. dr. ir. A. Nijmeijer

**Other personnel:** Prof. dr. A.J.A. Winnubst

**Introduction**

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

**Research results from 1 January until 31 December 2014**

In close collaboration with FZJ (IEK-1), asymmetric SrTi₁₋ₓFeₓO₃₋δ (STF) membranes were fabricated using an inverse sequential tape-casting technique. In this fabrication method the dense membrane layer is first cast followed by the casting of the porous support on top of the membrane layer. After cofiring (sintering of the asymmetric structure), a ~ 20 µm thick dense layer on top of a 700 µm thick porous support (porosity ~ 25 %) was obtained. The membranes show oxygen fluxes up to 2 ml/min at temperatures approaching 1000 °C using air as feed gas and argon as sweep gas. These oxygen fluxes are comparable with those obtained for asymmetric La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ (LSCF6428) membranes. Upon using oxygen as feed gas rather than air the oxygen fluxes increase by a factor of three. This result is interpreted to reflect the existence of concentration polarization in the porous support. A change in activation energy is discerned from the Arrhenius plot of the oxygen flux shown in Figure 1, indicating a change in governing mechanism. At low temperatures (< 800 °C) oxygen transport is judged to be governed by oxygen surface exchange.

In addition, creep tests were conducted on STF ceramics. Measurements were carried out in air at different stress values in the temperature range from 800 to 1000 °C. Observed activation energies and stress exponents point to diffusional creep as the predominant mechanism for creep in the STF system.

**Industrial collaboration until 31 December 2014**

None
All output from 2014

**Poster presentation** International Conference on Inorganic Membranes (ICIM 2014), Brisbane, Australia: Sebastiaan F.P. ten Donkelaar, Arian Nijmeijer and Henny J.M. Bouwmeester, Electrical conductivity relaxation on the SrTi$_{1-x}$Fe$_x$O$_{3-δ}$ system.

**Poster presentation** Mesa+ annual meeting 2014: Sebastiaan F.P. ten Donkelaar, Arian Nijmeijer and Henny J.M. Bouwmeester, Electrical conductivity relaxation on the SrTi$_{1-x}$Fe$_x$O$_{3-δ}$ system.

**Other**

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**Figure 1.** Temperature dependence of the oxygen permeation flux through supported thin-film STF membrane using air or pure oxygen as feed gas.
## Introduction

The hybrid microporous organosilica membranes based on carbon-bridged SiOₓ moieties that were developed in recent years [1] are much more stable under hydrothermal conditions than silica and methylated silica membranes. The high stability makes that this material is the first that can be operated in the dehydration of organic solvents under industrially relevant conditions for several years. Besides membranes, the material could also find use as substrate material in heterogeneous catalysis and because of its very high surface area for molecules smaller than nitrogen, e.g., carbon dioxide, it also holds potential as sorbent. The reason for the high stability of the microporous structure of this organic-inorganic hybrid material is not entirely clear at this moment. Long-term measurements of membranes under steady state operation conditions do not provide much insight into the degradation process of the material itself. The goal of this project is to look more closely at the degradation mechanisms of various silicas, methylated silicas and hybrid silicas in the form of powders, thin films and membranes from a more fundamental point of view.


## Research results from 1 January until 31 December 2014

A literature study was done on the performance of various hybrid microporous organosilica membranes in order to find clues on (degradation) processes in these materials. The studied membranes were commonly found to show a poorly understood slow flux decline on the time scale of months to years (not caused by fouling) related to the presence of water, accompanied by a steady selectivity and thus intact microporosity. This suggests that though the overall structural integrity of the material is not compromised by hydrothermal operating conditions, other structural rearrangements do occur. Experimental follow-up in this project further explored the dynamic nature of these hybrid systems and specifically of bis(triethoxysilyl)ethane. Though the material is generally assumed to be in a stabilized structural state after the commonly applied thermal treatment of 2-3 hours at 250-300 °C, detailed experimental investigations have shown that this assumption is not correct. Thin films, gels and powders of the material were investigated during thermal treatments at various temperatures (120-300 °C) for prolonged periods (days-weeks). In-situ monitoring of film thickness with X-ray reflectivity showed ongoing significant shrinkage for days, up to 20% and quantitatively depending on the temperature. Fourier-transform infrared spectroscopy of gels and powders during thermal treatment showed ongoing temperature-dependent changes in the vibration energy of siloxane and silanol bonds, reflecting ongoing changes in the molecular environment. Thermogravimetric analyses and differential scanning calorimetry showed ongoing temperature-dependent mass loss during annealing, accompanied by energy release. Preliminary experiments with hydrothermal annealing suggested that both a high pressure and the presence of water have a profound influence on the annealing process.
Preliminary experiments with exposure of annealed materials to a gaseous catalyst suggest that such treatments may be a fast alternative to 'age' or stabilize the material, as opposed to prolonged thermal treatments. The search for a coherent explanation for all combined results is in progress. Ongoing work in 2015 includes additional experimental analyses with silicon solid state nuclear magnetic resonance, ellipsometry, pycnometry and membrane permeation measurements.

This project proceeds in collaboration with multiple research groups at the University of Twente, involving ADEM-related as well as other researchers and equipment.

**Industrial collaboration until 31 December 2014**
Collaboration was started with Pervatech BV, located in Rijssen, The Netherlands. Pervatech BV produces the previously mentioned hybrid microporous organosilica membranes for industrial use. Their insight in industrial performance will be combined with our scientific approach and facilities to accelerate innovation on both sides.

**All output from 2014**

**Other**
No other remarks.
Project: UT-P09

Hybrid silica membranes for oxy-fuel conversion membrane reactors

Name PhD- candidate: Marcel ten Hove

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

Start date: 1 Feb 2011

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

Other personnel: -

Introduction

The growing energy demand combined with increasing concerns about greenhouse gas emissions is driving the research towards the development of processes with integrated CO$_2$ capture. The present research aims at the development of ceramic membranes for use in a reactor concept, enabling hydrogen production with integrated CO$_2$ capture, commonly referred to as pre-combustion carbon capture.

Research results from 1 January until 31 December 2014

Hydrothermal stability tests on BTESE (1,2-bis(triethoxysilyl)ethane) hybrid silica and Zr-doped BTESE membrane materials have been performed in cooperation with IEK-1 of Forschungszentrum Jülich. The membranes were subjected to a gas stream with a composition of 51%v/v H$_2$O, 31%v/v CO and 15%v/v H$_2$ for three days at 200, 300, 400 or 500°C. After treatment the membranes were characterized by single gas permeation measurements. For comparison a simple hydrothermal test was performed by putting a membrane above boiling water for three days. No change in permeation is observed for BTESE after hydrothermal treatment at 300°C, while at 400°C a more Knudsen type premselectivity is observed, as seen in 1. It is believed that at 400°C decomposition of the BTESE matrix takes place.

Figure 1:

Permeance versus kinetic diameter for BTESE before and after hydrothermal treatment. Data of single gas permeance was measured at 200°C with a pressure difference of 2 bar. The number in the sample code corresponds to the treatment temperature.
Also Zr-BTESE membranes show Knudsen type permselectivity after hydrothermal treatments at 400 and 500°C (see Figure 2), indicating decomposition of the BTESE matrix. After hydrothermal treatment at 200 or 300°C a drop in permeance is observed. Most interesting here is that the $\text{H}_2/\text{CO}_2$ selectivity increases from 10 to 30 after hydrothermal treatment. The exact reason behind this increase is not yet known and will be a further point of research.

From these hydrothermal stability tests it can be concluded that the maximum operating temperature for these type of membranes is less than 400°C. Although, after a hydrothermal treatment, the permeance of hydrogen of a Zr-BTESE membrane decreased by 40%, the $\text{H}_2/\text{CO}_2$ selectivity increased to 30, which is suitable for a water gas shift membrane reactor for pre-combustion carbon capture.

**Figure 2**: Permeance versus gas kinetic diameter for Zr-BTESE before and after hydrothermal treatment. Data of single gas permeance was measured at 200°C with a pressure difference of 2 bar. The number in the sample code corresponds to the treatment temperature.

In order to see whether or not stable values are achieved during hydrothermal treatment, in-situ hydrothermal stability tests were performed at 200°C for Zr-BTESE membranes. Figure 3 shows the time course for the permeance during hydrothermal treatment. There is an initial drop in permeance in the first two hours, after which the permeances reach stable values. The obtained stable values are in agreement with the static tests done for longer periods of time, indicating that there is no further decline in permeance after 2 hours of hydrothermal treatment.

**Figure 3**: Time course of permeance during in-situ testing of Zr-BTESE at 200°C, with a pressure difference of 2 bar.
Industrial collaboration until 31 December 2014
Collaboration with Shell in the field of exchange and discussions on obtained results.

All output from 2014

Other
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Introduction
To meet the increasing demand for renewable, CO₂-neutral energy, biomass (in particular waste products) can be used for the production of fuels, such as hydrogen, synthetic natural gas or Fischer-Tropsch diesel. Conversion of biomass to fuels can be performed using gasification as an initial step in the conversion. The resulting primary products CO, H₂, CO₂ and CH₄ can then easily be used within present infrastructure.

Amongst the different gasification techniques, fluidized-bed gasification is preferred for biomass. However, a major disadvantage of the conventional biomass gasification process is the high concentration of N₂ in the product gas, resulting from the partial combustion of biomass with air. This can be avoided by using indirect fluidized-bed gasification. In indirect gasification, the combustion and gasification take place in separate reactor vessels, which are coupled together. This type of reactor, where a circulating bed material is used to transport the heat from the combustion zone to the gasification zone, is therefore also referred to as a dual fluidized-bed reactor. Although this approach avoids the problems associated with N₂, one of the main problems of biomass gasification still remains, namely the formation of tars, that pollute the product gases and the reactor.

By using a catalytically active bed material during gasification, it is possible to improve the efficiency of the process and to reduce the content of tars in the product gas. Olivine (\((\text{Mg,Fe})₂\text{SiO}_4\)) is widely used as an active bed material for catalytic cracking of tars during gasification of biomass in dual fluidized-bed reactors. The elemental composition, addition of Fe and high temperature treatments influence the catalytic properties of this mineral. However, olivine is not a stable material under process conditions, relevant for biomass gasification.

Moreover, the exact catalytic function of olivine is not yet fully understood. The central questions of this project were thus: How does olivine change during exposure to the different conditions, representative for gas environments present in indirect biomass gasification reactors and how does this behavior relate to the performance of olivine as a biomass gasification catalyst?

Research results
The dynamic behavior of olivine under realistic model conditions, i.e. alternatingly oxidizing and reducing gas environments at 750°C, was investigated. Significant changes in phase composition of the material, depending on the gas composition and the duration of the treatments, were found using XPS, XRD, XAS and SEM. A large fraction of the iron, both in the bulk and at the surface olivine, is present as free Fe-phases, which are sensitive to changes in the gas environment. In addition, the elemental composition of the surface changes dramatically depending on the gas composition. After exposure to oxidizing environments, the amount of Fe at the surface is twice as high as after
reduction. Furthermore, the reduction of the iron oxides upon switching from oxidizing to reducing conditions shows that olivine can transport oxygen from the combustor into the gasifier. The capability of olivine to transport oxygen was studied with Mössbauer spectroscopy, which confirmed that during oxidation, iron segregates out of the olivine matrix, forming free iron oxide phases. Thermo Gravimetric Analysis (TGA) was used to quantify oxygen transport under alternating oxidizing/reducing conditions. The TGA results indicate that at least 18% of the iron, present in olivine, participates in the oxygen-transfer process, on the time scale of minutes. XPS, combined with depth profiling, provided further insight into the dynamic behavior of olivine under relevant conditions. Iron enrichment at the surface is observed after oxidation and upon subsequent reduction, the iron quickly redistributes in the olivine towards the original, more homogeneous distribution.

During long term, continuous use as bed material in biomass gasification, olivine gets coated by materials stemming from the biomass ash. The nature of this bed material coating and the influence of the coating on the catalytic reactivity was studied in detail. SEM-EDS analysis showed that already after 30 h of biomass gasification, a surface layer, containing calcium and potassium, is formed on olivine. XPS depth profiling showed that this Ca- and K-rich surface layer also contains carbonate species and is more than 0.5 micrometer thick. A mechanism for the coating of the bed material is proposed, involving iron segregation to the surface during the first stages of use of olivine as a bed material. Ash compounds are incorporated in this surface layer, in which Fe is still mobile and K is able to penetrate deep into the particles, because of its volatility. The WGS-activity of the ash-coated olivine is almost a factor 5 higher than that of uncoated material. Biomass ash compounds were also found to be WGS active and are known to be active towards tar reduction as well.

The research carried out in this ADEM project contributes with important information on the fundamental properties of olivine, used as catalytically active bed material in indirect biomass gasification. Significant changes in surface chemistry and morphology were observed. Iron, a well-known catalytic material, is highly mobile in olivine. This high mobility leads to the formation of free Fe-oxide phases, in turn resulting in redox behavior and oxygen transport. Moreover, during use in biomass gasification, a Ca- and K-rich layer forms on the bed material, which influences its reactivity.

These observations contribute to revealing the details of the catalytic processes in biomass gasification and will help selecting the optimal process conditions to achieve optimal performance of olivine as a catalyst in indirect gasification reactors.

**Industrial collaboration until 31 December 2014**

Together with HVC and Gasunie, ECN has initiated the Groen Gas 2.0 demo project to demonstrate how the MILENA biomass gasification technology developed by ECN can be used for large-scale green gas production.

ECN is currently working on the engineering of a 12 MW gasifier. This plant will be constructed as a demonstration plant, which eventually will produce steam for electricity and Substitute Natural Gas (SNG).

This plant uses the technology described in the Introduction of this project and the results of this ADEM project can be used to make the biomass gasification process more efficient and effective.

**All output from ADEM project**

**Journal Publications:**

Conference Presentations:

Oral:
1. North American Catalysis Society Meeting, Louisville, KY, United States, June 2013
2. Annual Meeting of the American Institute of Chemical Engineers, Pittsburgh, PA, United States, October 2012
   "Best Presentation of Session"-Award
3. Advances in Catalysis for Biomass Valorization, Thessaloniki, Greece, July 2012

Poster:
1. North American Catalysis Society Meeting, Detroit, MI, United States, June 2011

Other

Obtained PhD degree at November 26, 2014
Introduction

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 overcome by using ionic liquids (ILs), which are salts consisting exclusively of ions and have melting points lower than 100 °C. ILs bear some interesting properties, such as: low volatility, relatively high chemical/thermal stability, non-flammability, tunable properties and relatively high 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 IL should have a high CO₂ solubility, selectivity and a low viscosity. Preferentially, the IL should be biodegradable, non-toxic and cheap. The currently known ILs are performing still insufficient regarding these properties, which obstruct the application of ILs at a large scale. Therefore, the aim is to find/design an IL with improved characteristics with respect to the mentioned properties.

Research results from 1 January until 31 December 2014

Solubilities of CO₂, CH₄ and mixtures of both have been measured in a variety of ILs [1-3]. The aim was to assess the potential of ILs for natural gas sweetening. CO₂/CH₄ selectivities in the ILs were calculated and the results were compared with the conventional solvents used in the natural industry (e.g., Selexol). In addition to the experimental work also advanced Monte Carlo molecular simulations have been used to predict the solubility of several gases in ILs, see Figure 1 [4-7].
Industrial collaboration until 31 December 2014
none

All output from 2014

Introduction

Reforming of biomass to hydrogen provides an alternative for the production of hydrogen from fossil fuels. For this process one requires a metal function to activate the C-C, C-H and O-H bonds. Very often a reactive support is required to cope with catalyst deactivation. A well-known example is the use of ceria which limits carbon deposition during reforming. Ceria has redox activity which can gasify the coke deposits in the presence of oxygen or water. The goal of this project is to determine structure-performance relationships: how does the composition and surface structure of the ceria determine the reactivity for water dissociation as well as the reactivity of the resulting OH groups with model compounds representing coke deposits. The influence of metals on C-C, C-H, O-H and C-O bond activation will be investigated.

Research results from 1 January until 31 December 2014

Part I: alcohol selective oxidation

The catalytic oxidation of bio-ethanol to acetaldehyde entails a promising route for valorization of biomass into many important chemicals that are currently mainly being produced from fossil-based ethylene feedstock. Recently, we have found a highly efficient and robust catalyst: Au nanoparticle supported on MgCuCr$_2$O$_4$ support for gas-phase oxidation of ethanol to acetaldehyde (space-time yield of 311 g$_{acetaldehyde}$/g$_{gold}$·h$^{-1}$ at 250°C, stable for at least 500 h) (P. Liu and E. J. M. Hensen, J. Am. Chem. Soc., 2013, 135, 14032). In the first part of this subproject, we employ density functional theory calculations to understand the unprecedented synergy between gold clusters on the MgCuCr$_2$O$_4$ spinel support. The mechanism (Figure 1) points to the importance of the interface between gold and the subjacent support. Dissociative adsorption of ethanol is facile and takes place by cooperative action of a gold atom at the metal-support interface and a basic oxygen atom of the support. The oxygen vacancy formation energy is found to be a good performance descriptor for ethanol oxidation of Au/MgMeCr$_2$O$_4$ (Me = Cu, Ni, Co) catalysts. It also provides insight into Au-Cu alloy synergy for alcohol oxidation. The high selectivity towards acetaldehyde stems from the facile desorption of acetaldehyde as compared to the cleavage of the remaining -C-H bond in the product. The opposite holds for methanol oxidation, explaining why experimentally we observe complete methanol oxidation over Au/MgCuCr$_2$O$_4$ under conditions where ethanol is selectively converted to acetaldehyde.
Figure 1: Mechanism of oxidation of ethanol to acetaldehyde for the Au\textsubscript{10}/MgCuCr\textsubscript{2}O\textsubscript{4} model: (center top) reaction energy diagram, (center bottom) most important transition state structures and (periphery) reaction mechanism.

Part II: conversion of propylene to acrolein

The oxidation of alkenes constitutes a very important class of reactions in the chemical industry because the oxidized products are used to manufacture a wide range of commodities. Acrolein is another important chemical intermediate for many common industrial chemicals, mostly importantly acrylic acid, with an annual production around 500,000 tonnes. Currently, acrolein is produced by use of multicomponent metal oxide systems, the preferred ones comprising Bi and Mo. Our experimental results find high selectivity and activity of the Au/MgCuCr\textsubscript{2}O\textsubscript{4} towards conversion of propylene to acrolein. In the second part of this subproject, we report the theoretical study of high selectivity of gold nanoparticles dispersed on a MgCuCr\textsubscript{2}O\textsubscript{4} spinel support. First, we find that the adsorption of propylene on the interfacial Au leads to dissociation of the Au cluster. This is because of the strong interaction between the \(\pi\) bond of propylene and Au 6s orbital. We give our mechanism based on Au\textsubscript{1}/MgCuCr\textsubscript{2}O\textsubscript{4} (Figure 2). The adsorbed propylene first dissociates its C-H bond which is catalyzed by surface O or O\textsubscript{2} species. This is the rate-limiting step of the whole process. Then the C\textsubscript{2}H\textsubscript{x}* species tilt to the support O to form C-O bond, followed by a second C-H bond dissociation by surface O to form acrolein. The corresponding epoxidation of propylene process was also examined to understand the high selectivity towards acrolein product. It was found that the strong interaction between \(\pi\) bond of propylene and Au makes it more difficult to react with surface O species (O, O\textsubscript{2} and OOH\textsuperscript{+}).
Figure 2: Reaction energy diagram (middle) with elementary reaction steps for the oxidation of propylene to acrolein on the Au\textsubscript{1}/MgCuCr\textsubscript{2}O\textsubscript{4} model.

Industrial collaboration until 31 December 2014
none

All output from 2014

Journals

Conference contributions

Other
Obtained PhD degree at 11-09-2014
The ADEM program on fuel cells as performed by 5 PhD students at TU Delft and Twente University has been rather successful.

The PhD students in Delft who are finished & staying are: Emanuela Negro who obtained her doctor’s degree Cum Laude on the 14th of November 2014 (picture above); Miguel Córdova Chávez is continuing on track, working on hybrid PEM membranes; similarly Hrishikesh Patel is making nice progress in his studies of SOFC anode materials, which may be particularly useful for high-power stationary systems. At Twente University, PhD student Sjoerd Veldhuis gained his degree on the 4th of March 2015 i.e. just before this report was written; and PhD student Gerard Cadafalch Gazquez has reported a slight delay as he is busy setting up a spin-off company making use of results that were gained during his studies. He is expected to obtain his degree in December 2015. Anyway, it is clear that the program is in full flow.

Although the Fuel Cell program covers a diverse range of research topics there is considerable synergy to be found both inside and outside the ADEM theme. For instance there is a clear overlap and mutual interest in relation to Li-ion battery technology within the Battery Theme. Also, outside ADEM quite a few other studies are carried out that provide much synergy, e.g. there are at least 6 PhD - students in total working on fuel cell related topics at TU Delft, possibly even more. This synergy has been recognized by the ADEM Program Committee, which decided that the remaining PhD vacancy in Delft will cover Li-ion and fuel cell materials in combination, building on the expertise obtained thus far. The title of the revised proposal TUD-P03 is “Charge carrier dynamics of laminates formed by hybrid superionic conductive PEM fuel-cell membrane and carbon nano-networks” (applicants - Picken, Koper & Kelder).

Collaboration

In terms of equipment we are gaining experience with a new custom- built 4- Point Probe -in plane-measurement cell with temperature and humidity control; as well as making use of a fuel-cell testing station that is being set-up in close collaboration with the HyET company. The collaboration with and support by companies is also benefiting from the existing overlap with the Li-ion battery theme, as mentioned in the report on that topic.

In the past year(s) we have organised some discussions & seminars at TU Delft basically to inform each other about our mutual interests, which seems to attract some attention from industry and academia. Importantly, various SME activities are also benefiting from the expertise acquired in the Fuel-Cell theme, and vice-versa, involving companies such as mnxpolymers, Active Warmth, HyET, CarbonX and others for PEM based systems. Similarly, HyGear and GENSOS are involved in the work on SOFCs.
For fuel cell technology as a whole it seems that the Netherlands has rather unique expertise available that should provide a sensible contribution to reforming the energy economy. Although the volume of the individual economic activities with regard to FuelCell related research and development is still limited at the moment, there appears to be quite a large interest.

In terms of future developments we anticipate opportunities for alkaline PEMs, possibly including Li-ammoniates as a solid state proton conductor, and alternative fuels/storage systems such as NH$_3$, which might also become available via electrochemical processes. We anticipate that this may become a topic for future Fuel Cell related research, both inside and outside the ADEM program.

Theme Coordinator

Prof. dr. Stephen Picken
Delft University of Technology, section Advanced Soft Matter, ChemE
Introduction

SOFC anodes are normally made of a nickel yttria-stabilized zirconia (YSZ) cermet. During operation, the reduced nickel acts as catalyst for the oxidation of fuels with ionic oxygen transported from the YSZ. This reaction produces electricity. Figure 1 exemplifies this process. However, the nickel undergoes cycles of reduction and oxidation during operation, resulting in a volumetric contraction and expansion. This phenomenon results in internal stresses in the material, which can cause fracture. Moreover, when hydrocarbons are used, the carbon is deposited on the nickel and deactivates it.

The classic anode fabrication methods do not control the nickel deposition or location. This means that it can be located in the bulk of the material. Therefore, it cannot reach the surface and react with the gas, blocking the reaction and the catalyst becomes inactive. This leads to a poor use of catalyst that in some cases can result in damaging the integrity of the material.

We used electrospinning as alternative to form SOFC anode with optimized microstructure so less nickel is needed and the problem is reduced. Electrospinning is a well-known electrodeposition technique for fabrication of polymeric micro- and nanofibers mats which are currently used in different fields of technology, such as biological cell growth, advanced batteries and water treatment systems. Recently the research was extended to the applicability of the deposition technique into ceramic applications.

In this project, we investigated ceramic microstructures prepared by combining electrospinning and sol-gel. We propose methodologies that lead to the formation of nanochannel and nanofibers nanofiber anode. These architectures have certain characteristics that are beneficial for solid oxide fuel cell (SOFC) anodes. Moreover, such materials show enhanced properties that can also be applied to other fields such as tissue engineering or micro/nano-electronics.
Research results from 1 January until 31 December 2014

Nanochannels

The aim was to fabricate nanochannels with controlled nickel deposition on the pore wall. Therefore, the catalytic activity is increased due to better catalyst location, high porosity and, large surface area. We used polymeric microfibers loaded with nickel as template. Then, YSZ sol-gel precursor was infiltrated into the microfiber mat and later annealed. During annealing, the microfiber mat burnt out and formed nanochannel porosity (figure 2a). Moreover, unidirectional porosity was achieved (figure 2b) and the pore diameter could be varied.

![Figure 2: Scanning electron microscope of the prepared nanochannel material with (A) random and (B) unidirectional porosity.](image)

The nickel containing solution for electrospinning was prepared in three different routes: solution, dispersion and suspension. It was found that the suspension of nanoparticles resulted in an improved microstructure as the nickel was located on the pore of the wall, as shown in figure 3.

![Figure 3: TEM and elemental point analysis of: samples templated with fibers loaded with stearate solution (A,B), samples templated with fibers loaded with nitrate dispersion (C,D) and samples templated with fibers loaded with nanoparticle suspension (F,G).](image)

The catalytic activity, measured as active area, of the prepared material was similar to the commercial one. However, the amount of nickel of the present material (10.5% w.) was much less than in the commercial Ni/YSZ cermet (51% w.). Upon normalizing the active surface area over nickel content, the templated sample had an active surface area of 168 ± 1 cm²/g of nickel, which is 4.76 times higher than the commercial sample (35 ± 0.8 cm²/g of nickel). The results are presented on figure 4.
Figure 4: Chemisorption analysis of the templated sample compared with a commercial Ni-YSZ cermet. The black column is the absolute active area and the patterned column is the active area normalized by the nickel content.

The electrochemical performance of the material was studied. It revealed that the conductivity was mostly ionic, meaning a poor electronic conductivity. We believe that the electronic conductivity could be greatly improved. This can be done by introducing species that are electronically conductive under reducing atmosphere.

Nanofibers
We fabricated a YSZ nanofiber mat, which was later infiltrated with nickel oxide precursor. Thus forming a YSZ core surrounded by nickel oxide as shown on figure 5.

Figure 5: EDX elemental mapping of YSZ nanofibers coated with Nickel Oxide.

Electrochemical impedance of the anode was measured, resulting on a far too poor performance (figure 6). This was attributed to a too high porosity of the nanofibers mat.
Figure 6: Electrochemical Impedance Spectroscopy of the sample measured in a partial pressure of 9% H2 and 3% H2O.

Industrial collaboration until 31 December 2014
Ajayan Research Group, Rice University, Houston, Textas, U.S.
LEPMI, Grenoble, France
MERLN, University of Maastrich, The Netherlands

All output from 2014
1. Poster presentation, Electrospinning of Ceramics: a Facile Route to Produce Advanced Ceramic Nanofibres, NWO Meeting Chemistry in Relation to Physics and Materials Sciences, Veldhoven, The Netherlands, 10/02/2014.
2. Oral presentation, Electrospinning of Ceramics: a Facile Route to Produce Advanced Ceramic Nanofibres, E-MRS, Lille, France, 30/05/2014.
3. Oral presentation, Flexible and Osteoinductive Yttrium Stabilized Zirconia scaffold for bone regeneration, TERMIS, Genova, Italy, 12/06/2014.

Other
STW Take-off grant awarded to the project “ceramic nanofiber paper”. The main applicant was Gerard Cadafalch Gazquez.

First Poster Prize in the NWO Meeting Chemistry in Relation to Physics and Materials Sciences, Veldhoven, The Netherlands, 10/02/2014
Project: TUD-P02

Super ionic composite membranes for PEMFC

Name: PhD- Miguel E. Cordova Chavez
Affiliation: TU Delft, ChemE, OMI
Start date: 11 Nov 2011
Project leader(s): Prof. Stephen J. Picken
Other personnel: Dr. Erik Kelder

Introduction

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

Research results from 1 January until 31 December 2014

Chemical Modification of PEEK
**Membranes preparation**

The membranes were prepared by solvent casting. The polymer and the Inorganic filler were added at the same time in the DMAc at room temperature. The solution was then put in a heating plate at 125 °C until a homogeneous solution was obtained. This solution is then cast in a petri dish and put on a heating plate at different ranges of temperature for solvent evaporation in the fume hood. This goes from 40 to 55°C depending on the compositions. After a complete evaporation of the solvent (approx. 3 days) the membranes are separated from the glass with demineralized water. Put in the vacuum oven at 55°C for 24 hours to completely dry out the samples and take out the traces of the solvent. The sample is then proton activated by being soak in 1M H$_2$SO$_4$ solution for 24 hours. The sample is clean with demineralized water and its ready for testing.

The sample size is a rectangle of 1.5 cm x 4 cm.

**New 4 Point Probe -in plane- measurement cell with Temperature and Humidity Control**

This cell was modified to work at ambient pressure to avoid the changes as a consequence of the temperature raising.
The sample is goes through an stabilization process of 1 hour before start testing. The testing last around 5 hours and makes a measurement every 5 min. A potentiostatic measurement scan from 1 MHz to 1Hz at 20 mV. The outcome is a nyquist plot and a bode plot. The validity of the measurement is followed by looking at the lissajous plot. The first resistance obtained is related to the Proton Conductivity of the sample by the following equation:

\[ \sigma = \frac{l}{R_s S} \]

where \( l \) distance between the electrodes, \( R_s \) is resistance measure by EIS and \( S \) is the transversal section of the sample. The condition of the measurement are presented in the table:

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temp</th>
<th>Temp Water</th>
<th>Resistance (Ohm)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>105</td>
<td>95</td>
<td></td>
<td>#DIV/0!</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td></td>
<td>#DIV/0!</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td></td>
<td>#DIV/0!</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>80</td>
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<td>#DIV/0!</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75</td>
<td></td>
<td>#DIV/0!</td>
</tr>
<tr>
<td>sPEEK</td>
<td>105</td>
<td>95</td>
<td>2170</td>
<td>8.8E-03</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td>750</td>
<td>2.5E-02</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td>1180</td>
<td>1.6E-02</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>80</td>
<td>1880</td>
<td>1.0E-02</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>2265</td>
<td>8.4E-03</td>
</tr>
<tr>
<td>sPEEK +15% LiBPO4</td>
<td>105</td>
<td>95</td>
<td>750</td>
<td>1.8E-02</td>
</tr>
<tr>
<td></td>
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<td>3.3E-02</td>
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<td>2.1E-02</td>
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<td>692</td>
<td>1.9E-02</td>
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<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>850</td>
<td>1.6E-02</td>
</tr>
<tr>
<td>sPEEK +20% LiBPO4</td>
<td>105</td>
<td>95</td>
<td>727</td>
<td>1.6E-02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td>347</td>
<td>3.4E-02</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td>504</td>
<td>2.3E-02</td>
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<tr>
<td></td>
<td>85</td>
<td>80</td>
<td>690</td>
<td>1.7E-02</td>
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<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>850</td>
<td>1.4E-02</td>
</tr>
<tr>
<td>sPEEK +25% LiBPO4</td>
<td>105</td>
<td>95</td>
<td>727</td>
<td>1.6E-02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td>347</td>
<td>3.4E-02</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td>504</td>
<td>2.3E-02</td>
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<td></td>
<td>85</td>
<td>80</td>
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<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>850</td>
<td>1.4E-02</td>
</tr>
<tr>
<td>sPEEK +30% LiBPO4</td>
<td>105</td>
<td>95</td>
<td>523</td>
<td>4.7E-02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td>288</td>
<td>8.6E-02</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td>352</td>
<td>7.0E-02</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>80</td>
<td>455</td>
<td>5.4E-02</td>
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<td>80</td>
<td>75</td>
<td>566</td>
<td>4.4E-02</td>
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<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>579</td>
<td>4.3E-02</td>
</tr>
<tr>
<td>sPEEK +30% LiBPO4</td>
<td>105</td>
<td>95</td>
<td>1693</td>
<td>1.5E-02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>90</td>
<td>470</td>
<td>5.4E-02</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>85</td>
<td>900</td>
<td>2.8E-02</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>80</td>
<td>850</td>
<td>3.0E-02</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>830</td>
<td>3.0E-02</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>458</td>
<td>5.5E-02</td>
</tr>
</tbody>
</table>
the 5 degrees difference in the temperature in respect to the measurement temperature gives a 80% relative humidity. Although usually the humidification in the fuel cell system is higher we took a conservative approach. In the following graph the plots from the conductivity can be observe. Nafion was not measure yet but the approximate value for Nafion goes to 0.1 S/cm at the same condition.

From this graph we can change the plotting and use the equation below to calculate the Activation Energy related to the proton conduction in the sample

\[ \ln(\sigma) = \ln(\sigma_0) - \frac{E_0}{RT} \]

High values of this activation energy usually implies bigger changes in the proton conduction in relation to the temperature. Compare to Nafion, the sample shows a higher value and it can be seen that this values decrease with the increase of Inorganic compound that is added to the hybrid membrane. This could be because the inorganic compound is able to stabilize the water inside the membrane and this keep the conductivity more constant. The increment in the conduction related to the faster movement of the proton at high temperatures but it’s also link to the water content of the sample. There is a clear jump in the conductivity at 25%, this could be link to the percolation point of the sample. The preliminary values obtained for the 30% already show a lower conductivity which are likely to occur above the percolation point by the aggregation of the inorganic filler.
<table>
<thead>
<tr>
<th>Sample</th>
<th>r2</th>
<th>$E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>#</td>
<td>7.46 (reported 95% RH)</td>
</tr>
<tr>
<td>sPEEK</td>
<td>0.95</td>
<td>83.9714</td>
</tr>
<tr>
<td>sPEEK +15% LiBPO4</td>
<td>0.82</td>
<td>50.7154</td>
</tr>
<tr>
<td>sPEEK +20% LiBPO4</td>
<td>0.97</td>
<td>66.512</td>
</tr>
<tr>
<td>sPEEK +25% LiBPO4</td>
<td>0.997</td>
<td>50.7154</td>
</tr>
<tr>
<td>sPEEK +30% LiBPO4</td>
<td>#</td>
<td>#</td>
</tr>
</tbody>
</table>

**Industrial collaboration until 31 December 2014**
No Collaboration has yet been made.

**All output from 2014**

**Other**
New Measuring Conductivity Cell for 4 point probe was acquired as part of ADEM equipment which was more reliable than previous measurements and also allowed us to perform measurements at higher temperatures changing partially the behaviour of the samples and allowing us to get better results but at the cost of learning to use this new equipment and the need to re-do all the previous samples.
Introduction

Although Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are very promising alternatives to combustion engines in portable applications because of their higher efficiency and lower CO\textsubscript{2} emission, their large-scale introduction into the market is still hindered because cost and durability are not yet meeting the targets set by for instance the U.S. Department of Energy. These issues are strongly related to the platinum (Pt) catalyst required for the Oxygen Reduction Reaction (ORR). The currently employed catalyst consists of Pt nanoparticles (Pt NPs) adsorbed on high specific surface area carbon. Especially in non-ideal operation conditions, e.g. temperature and potential cycling, the electrochemically active surface area (ECSA) of the catalyst decreases, carbon corrosion being the major degradation mechanism that can cause catalyst detachment. Improving carbon support resistance to corrosion is thus a crucial challenge as it is the main cause of performance degradation in low temperature fuel cells. Recent studies have proven that graphitic materials, such as carbon nanotubes (CNTs), are significantly more resistant to carbon corrosion due to the higher stability of the sp\textsuperscript{2}-hybridized carbon. Within our group, we developed a novel carbon material that consists of networked carbon nanostructures, CNNs, and is currently produced by a TU Delft spin-off company Carbon X. CNNs are 3-D hyper-branched carbon graphitic structures organized in a nano-scale pattern, Figure 1. They can be easily produced by Chemical Vapor Deposition (CVD) of ethene over transition metal catalyst synthetized in bicontinuous microemulsions (BMEs). The formation of networked, sponge-like, carbon graphitic structures is due to the carbonization of the surfactant, being the primary carbon source. CNNs show attractive properties for catalysis of fuel cells such as high specific surface area, high electrical conductivity, great oxidation resistance, surface defects increasing the material ability to disperse in solution and to simplify integration into polymer matrices. The versatility and simplicity of the synthesis route promises a less costly production than CNTs.

Figure 1. CNNs imaged by (a) SEM showing branches and junctions, (b) TEM visualizing two junctions I and II, and (c) showing multiple walls with capped ends and a d-spacing of 0.3 nm. Around the branches a thin amorphous layer is visible.
My PhD research aims to implement CNNs use in PEMFC electrodes, by investigating CNNs as a catalyst support for both noble and non-noble metal catalyst. Additionally, since CNNs synthesis is not fully understood yet, part of my research is also dedicated to the understanding of template properties (BMEs) via Molecular Dynamics (MD) Simulations and to the formation mechanism of NPs in BMEs.

**Research Results from 1 January 2014 to 31 December 1014**

A computational microscope: coarse grain simulations of dense BMEs systems

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

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

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


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

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

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

Figure 4 Accelerated durability tests

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

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

Figure 5 Polarization and power density curves: a) in H₂ single cell at 30 °C and at 60 °C, 0.1 NLPM H₂, 0.2 NLPM O₂; b) in MeOH single cell, 2 M methanol as anode feed, 100 ml₂O min⁻¹ and 60 °C.

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

Industrial collaboration until 31 December 2014

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

All output from 2014


Published Articles

2. E.Negro, R. Latsuzbaia, M. dieci, I. Boshuizen and G. J.M. Koper, \"Pt Electrodeposited over Carbon Networks Grown over Carbon Paper as high performance Catalyst for PEM Fuel Cells\", accepted in Applied Catalysis B.

catalysts for low temperature fuel cells”, accepted in Applied Catalysis B.

Oral Presentations
1. Oct ’14 – “Pt-Decorated non-covalently functionalized carbon graphitic structures as durable catalyst for ORR”, Electrochemical Society Meeting, Cancun, Mexico
2. Feb ’14 – “Coarse Grained MD Simulations of Dense Microemulsions”, NWO Fluids and Interface, Veldhoven, The Netherlands

Poster Presentations

Other
PhD Thesis awarded Cum Laude.
Introduction
Multi-fuel oxidation on SOFC anodes is an important topic especially for working with real life fuels. In order to understand fuel oxidation, in this work, nickel and ceria pattern anodes of well-defined geometry are prepared and tested. Fuel mixtures of hydrogen and carbon monoxide and even the effect of contaminants like H$_2$S is tested. Electrochemical Impedance Spectroscopy (EIS) is used to obtain the various parameters giving information about contributions from diffusion, reaction etc which can be used as a basis for optimising the SOFC anode for different fuels. Realistic system parameters obtained from such studies also shall be used for development of thermodynamic concepts for high efficiency energy systems based on ITSOFCs such as ITSOFC- gas turbine systems which can produce electricity at efficiencies as high as 70-80%.

Research results from 1 January until 31 December 2014
Pattern cells with ceria/ nickel – preparation of pattern electrodes of nickel on ceria, ceria on YSZ and Nickel on YSZ, testing them with EIS

The cells prepared above are tested under CO, H$_2$ and syn gas atmospheres in wet and dry conditions in order to establish the preference of oxidation of H$_2$ or CO. In addition, influence of water gas shift reaction can be estimated by addition of small amounts of water in CO and H$_2$/CO.
It is observed that hydrogen gives much smaller resistance than CO for both nickel and ceria cells and that for mixtures, it is likely hydrogen is preferentially oxidized.

The influence of contaminants like H₂S on ceria and nickel pattern anodes is also tested. The relative kinetics of poisoning and recovery of ceria compared with nickel can help in designing and optimizing anodes for contaminants. We observe significant poisoning of ceria as well as nickel pattern cells.
Using the tests above, preliminary modeling of reaction mechanism is undertaken to propose a reaction mechanism to fit the obtained impedance.

**Industrial collaboration until 31 December 2014**

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

HYGEAR which provided support letter during the formulation of this project is also continuing collaboration with another Horizon 2020 project on Gasifier SOFC systems (invited for signing grant agreement) which further delves into fuel cell performance for different fuel mixtures (with a the goal of developing a gasifier-SOFC integrated system). Both TU Delft and HyGear are partners and are supposed to work together in the project. The results obtained in this ADEM project can be directly used in selecting a suitable SOFC for such a system (together with the results from additional experiments).

**All output from 2014**

1. Paper submitted to *Applied Energy* “Oxidation of H₂, CO and syngas mixtures on ceria and nickel pattern anodes” HC Patel, AN Tabish, F Comelli, PV Aravind

**Other**

-
Introduction

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

YSZ Thin Films

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

Synthesis of Y-doped Barium Zirconate

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

Research results from 1 January until 31 December 2014

Rapid Densification YSZ Thin Films
A method for the density determination of sol-gel derived thin films[3] was used to study the effect of the substrate and temperature on the final thin film density. Since the YSZ is used as an electrolyte material in SOFCs, a sufficiently high density is necessary to separate the oxidant from the fuel.

![Graph showing densification behaviour of YSZ films on Al2O3 (0001) and SiO2/Si (001) substrates at 650 °C (black), 850 °C (red), and 1000 °C (blue), respectively. The absolute measurement error is ~1 %.](image)

Figure 5: Densification behaviour of 8YSZ films on (a) Al2O3 (0001) and (b) SiO2/Si (001) substrates at 650 °C (black), 850 °C (red), and 1000 °C (blue), respectively. The absolute measurement error is ~1 %.

Synthesis of Y-doped Barium Zirconate
Nano-crystalline (10-20 nm) phase-pure BZY has been prepared at temperatures < 150 °C via a sol-gel alkoxide-hydroxide precipitation method. Dilatometry measurements show that the nano-sized grains are highly sinteractive, and densities > 95% have been obtained at 1350 °C. Also, thermogravimetric analysis (TGA) showed hydration behaviour (i.e. incorporation of OH-defects, necessary for proton conduction). The main advantage of a sol-gel approach for the synthesis of this material is the incorporation of OH-defects, inherent to the sol-gel reaction. This normally considered negative effect, might lead to an enhanced performance. A microscopy study showed that, although the grain boundary region is almost defect-free, a subtle yttrium enrichment was found (see Figure 2). In combination with the small grain sizes after sintering, the total conductivity was determined mainly by the grain boundary contribution.
Figure 2: (a) HR-TEM image of grain boundary region after sintering for 24 h at 1350 °C in N₂. (b) The Y concentration in the ellipsoid-shaped areas in (a) measured with EDX. The dotted line indicate the average Y concentration at the GB and grain interior, respectively, measured from at least five regions. (c) EDX spectra obtained from the GB (red line) and grain interior (black line), respectively.

Kinetics of Barium Titanate Nanocrystal Formation
Time-resolved small angle X-ray scattering and X-ray diffraction were successfully employed to elucidate the reaction mechanism of barium titanate nanocrystal formation in benzyl alcohol below 78 °C. The amorphous-to-crystalline transformation is predominantly determined by the total amount of water released from the barium hydroxide octahydrate precursor, and different rate-limiting regimes were found (see Figure 3). Sufficiently high water concentrations enabled rapid succession of nucleation, crystallization, and growth events, and the formation rate was only limited by the dehydration rate of the Ba precursor. Water lean conditions resulted in impeded gel formation, and only gradual nucleation, crystallization, and growth process was observed.

Figure 3: Overview of rate-limiting regimes for reactions performed under (a)-(b) stoichiometric, and (c)-(d) off-stoichiometric precursor conditions. The red, blue, and green areas represent the regimes in which the gel formation rate, water concentration, and a combination of both are the rate-limiting conditions, respectively. The red circles indicate reactions performed with adjusted water conditions.
References:

**Industrial collaboration until 31 December 2014**
No industrial collaboration. Collaborating with Dr. A. George (Rice University, TX, USA), Dr. T.M. Stawski (University of Leeds, Leeds, UK), and Dr. S. Guillemet-Fritsch (Paul Sabatier University, Toulouse, France).

**All output from 2014**

**PhD Thesis:**

**Articles:**

**Oral Presentation:**

**Other**
-
Today, Li-ion batteries provide the highest energy density of all existing systems. Although used in many electronic devices and cars, most manufacturers agree that the Li-ion technology is still not satisfactory for long distance EV use. Higher energy density, reduced costs and improved safety are needed. After some discussion at the last ADEM conference, the Program board therefore decided to include in the ADEM projects research to (I) develop new generations Li-ion batteries delivering roughly twice the energy density and to satisfy the safety requirements of today's systems, and (II) step in new or relatively unexplored areas if we are to significantly increase energy storage beyond Li-ion, such as e.g. solid-state, Lithium-sulfur, or Lithium-air batteries. These decisions were established in close collaboration with the industries involved.

ADEM projects

Within the ADEM Battery theme, seven projects have been accepted and five of them started in 2014. A start has been made to figure out whether certain projects within the Fuel Cell theme could have an overlap with this Battery theme so as to identify their mutual interest of the industrial contribution. It is foreseen that project TUE-P06 will start soon. The last open project, initially allocated to a Bolivian PhD student as part of the 'in-return' of a potential investment of the Bolivian state mine company Comibol-GNRE, is still under discussion. Since the theme only started to become active recently, not many scientific results have been achieved yet. The achievements so far are described under each of the ongoing individual projects.

Industrial involvement

Valorisation of, and industrial involvement in, the proposed work are two of the major tasks concerning the use of the results. In that regard, the interdisciplinary research is characterized by four important features (Note that the interested industries are mentioned between brackets, while those underlined already delivered an official contribution):

- fundamental science (NXP)
- modelling (NXP, Philips)
- materials development and fabrication (Euro Support, Tata Steel, Norit, Süd-Chemie, Roth&Rau, Tempress, Oxford Instruments, Sabic, RGS)
- system testing and evaluation (Comibol, IMEC, HTAS).

In total, an amount of k€ 350 has been obtained already to cover the industrial contribution.
Planning

The last two projects will start in 2015. It is foreseen that there will be an integration of projects and industrial contribution of the Battery and Fuel cell theme. Further extension of industrial contribution is in progress – hence, various discussions are being undertaken. The financial contribution of the projects will be arranged theme-wise (plus the Fuel cell theme) rather than project-wise. A workshop on STM-AFM-SECM for ADEM PhD students is in preparation with an equipment supplier and can also be considered as industrial contribution.

Theme Coordinator

Dr. Erik M. Kelder
Delft University of Technology, section Fundamental Aspects of Materials and Energy, RST
Introduction

Today, Li-ion batteries provide the highest energy density of all existing systems. However due to society’s increasing use of portable electronics, the need to balance the fluctuating output of renewable energy sources, and the rise of electric vehicles, higher energy density Li-ion batteries are needed. Therefore the aim of this research is to identify and (electrochemically) characterize new materials for Li-ion batteries. The focus will be on high capacity electrode materials for conventional Li-ion batteries, as well as on materials for new-concept batteries, such as solid electrolytes.

Research results from 1 January until 31 December 2014

Electrochemical cycling measurements were conducted on silicon nitride thin films with varying Si to N ratios (SiNx). Preliminary results indicate that SiN0.7 is a suitable, high capacity, anode material for Li-ion batteries. Figure 1 shows a typical galvanostatic measurement of a SiN0.7 thin film anode. In the first cycles the film has a reversible specific capacity of around 1400 mAh/g. A specific capacity of over 1000 mAh/g is obtained for the first 70 cycles. The irreversible capacity in the first cycles, associated with solid electrolyte interface formation, is low compared to pure Si electrodes.

Figure 1: Specific capacity of thin film SiN1.7 measured in a Li half-cell setup for different (dis)charge rates. The dashed line indicates the maximum specific capacity of the anode in a commercial Li-ion battery.
Industrial collaboration until 31 December 2014
SiN$_x$ thin films and carbon nanotube samples have been deposited and supplied by Roth&Rau and Tata Steel, respectively

All output from 2014
-

Other
-
**Introduction**

For control and safety purposes temperature measurements of Li-ion batteries (packs) are of major importance and therefore essential information for battery management systems (BMS). For example, high battery temperatures may lead to a reduction in performance and lifespan. Furthermore they can cause unsafe situations like thermal runaway which may result in fire and explosions. On the other hand low temperatures reduce the energy and power performance. In addition lithium plating may occur which leads to permanent loss of cyclable lithium and to possible short circuits. For all these reasons it is important to maintain the battery temperature within a well-defined range with use of a thermal management system. This system uses the battery temperature as an input parameter and therefore it is important to measure temperature as fast and accurate as possible. Battery temperature measurements can be achieved through electrochemical impedance spectroscopy (EIS), which is a relatively new technique to measure temperature. The objective of this study is to find a relationship between battery impedance and temperature in such a way that the impedance (or a part of it) can be used to indicate the battery temperature, which is important for battery powered applications. In the end this technique must be faster, more precise and more practical in comparison to the traditional temperature measurement such as e.g. surface mounted or intrusive temperature sensors. Furthermore fundamental research on battery impedance in relation to temperature will be done to understand its phenomena.

**Research results from 1 January until 31 December 2014**

A theoretical analysis on a simplified equivalent circuit (EQC) model, which can be used to simulate battery impedance, revealed that the intercept frequency ($f_0$) decreases exponentially with increasing temperatures. The intercept frequency is the frequency at which the impedance intercepts with the real axis of the complex plane, i.e. the imaginary impedance is equal to zero. The theoretical analysis on the EQC was verified with experiments on three battery types: a 7.5 Ah pristine and cycled Li(NCA)O$_2$ cell and a 2.3 Ah LiFePO$_4$ cell. The intercept frequency of the pristine NCA and LiFePO$_4$ cells are shown in *Figure 1* and *Figure 2* as a function of temperature for five different state-of-charge (SoC), respectively. As the theoretical analysis already revealed it can be seen that the intercept frequency indeed decreases exponentially with increasing temperature. Furthermore the experiments show that the intercept frequency is essentially independent of SoC. *Figure 3* shows the impedance of a pristine and cycled NCA cell at a temperature of 10°C. It can be seen that the impedance of the cycled cell increased extremely at low frequencies (large semi-circle). However, the high frequency part of the impedance hardly changed, already indicating that the intercept frequency is independent of cycling.
This indication is confirmed in Figure 4 where the intercept frequency is plotted as a function of temperature for a pristine and cycled cell. This figure proves that the intercept frequency did not change as the battery cycles.

The intercept frequency as a function of temperature can be stored in look-up tables. Since the intercept frequency can be measured in a battery power application the battery temperature can be indicated by using this look-up table. From above findings it can be concluded that the proposed temperature indication method is applicable to batteries of different chemistries, dimensions and storage capacities.

In addition to impedance measurements with electrochemical laboratory equipment also impedance measurements with a proof-of-concept printed circuit board (PCB) from NXP Research are conducted. This PCB is specially developed to measure battery impedance in mobile battery powered applications. A user interface is designed to interact with the PCB. Therefore it is possible to control and operate the PCB while it simultaneously feeds back information and saves measurement data. EIS measurements with the PCB are conducted in order to verify the accuracy with respect to measurements with laboratory equipment. The impedance measurements of the PCB revealed similar behaviour as the measurements conducted with the laboratory equipment. Therefore it can be concluded that NXP’s PCB is suitable to measure impedance in e.g. mobile battery powered applications.

**Figure 1:** Intercept frequency as a function of temperature for a pristine NCA battery [1].

**Figure 2:** Intercept frequency as a function of temperature for a pristine LiFePO₄ battery [1].

**Figure 3:** Impedance spectra of a pristine and cycled NCA battery at SoC = 60% and T = 10°C [1].

**Figure 4:** Measured intercept frequency as a function of temperature for a pristine and cycled NCA battery at SoC = 60% [1].
Industrial collaboration until 31 December 2014

This work is done in collaboration with NXP Research in Eindhoven. NXP provides proof-of-concept printed circuit boards to measure battery parameters and provides useful theoretical background information about electronics. NXP uses the output which is found at the university to improve their product and for presentations to customers and conferences.

All output from 2014


Introduction
The expansion of portable electronic applications as well as the emerging electrical vehicle (EV) and static battery market demand effective and efficient energy storage. Li ion batteries are increasingly dominating the rechargeable battery market. Materials research for cathodes and anodes of Li ion batteries is intensive worldwide. For the anodes Si shows large promise due to its high specific capacity, its low (de)lithiation voltage, abundance and low cost. However, the practical application of silicon is largely hindered by a large volume change during charge and discharge, which results in severe fracturing and pulverization of the electrode particles, which leads to the loss of active Si. Meanwhile, the formation of solid electrolyte interfaces (SEI) caused by decomposition of liquid electrolyte and reaction with Si results in further loss of active material. The main challenges for developing Si anodes for Li ion batteries is the control of volume expansions, and SEI formation. Although Si has been studied extensively the often sophisticated techniques and novel sample processing are still not viable on commercial scale. Therefore the main objectives of this project are to apply cost-effective and scalable methods to prepare Si nanoparticles and electrodes for high energy density Li ion batteries. These methods include Si nanoparticle deposition on structured, porous, current collectors, and also production of continuous but nano porous Si layers on commercial, flat current collectors. Also the templating of the electrodes which enables higher amounts of active material in the battery will be studied. The Li ion diffusion and electronic conduction in the electrodes will be studied throughout the research, the role of electrolyte will be investigated as well.

Research results from 1 January until 31 December 2014
In collaboration with ADEM partner Roth & Rau (Eindhoven) Si nanoparticles produced by Plasma Enhanced Chemical Vapour Deposition (PECVD) are deposited onto porous conductive carbon fibres or on massive Cu foil (Goodfellow) directly. Carbon fibre sheets before and after Si deposition are characterized using SEM (Figure 1(a)-(d)). The carbon fibers are interconnected and produce an extremely porous carbon morphology allowing for Si deposition both on top and inside the carbon current collector. It is observed that most Si nanoparticles adhered to the surface of individual carbon fibers and the average thickness of Si nanoparticles deposition layer amounts to approximately 15 μm. Si nanoparticles penetration in deeper layers of the carbon sheet also occurs. The total thickness of the layer of Si nanoparticles (together with carbon fibres) reaches about 50 μm. As for the Si nanoparticle deposition on Cu foil, the SEM cross sectional image (Figure 1(e)) illustrates its layer-by-layer, porous, Si particle deposition morphology, with each layer having around 10 μm thickness. The electrochemical properties of Si-C/Cu sheets are tested within battery cells with Li metal as counter electrode, and galvanostatic charge and discharge between 0.01 V and 2.0 V. The initial lithiation in the Si-C sheets reports large amounts of > 4000 mAh/g Li inserted in the initial lithiation while the first delithiation can reach ~ 1900 mAh/g. The difference mainly attributes to the irreversible
SEI formation. The capacity retention after 50 cycles dis-/charge achieves about 1000 mAh/g, which is considered as a commercially relevant capacity level. The first Li ion insertion and extraction of Si nanoparticles on Cu reaches a capacity > 4600 mAh/g and > 2900 mAh/g, respectively. The capacity retention after 40 cycles dis-/charge achieves ~ 1500 mAh/g, as is shown in Figure 2. These results shows that the scalable electrode synthesis method of direct deposition of Si nanoparticles on the indicated substrates shows promising Li ion insertion capacities. Apart from direct depositions the carbon sheet is also used as current collector for slurry-based electrodes to improve the overall capacity of the entire electrode. Preliminary promising results indicate that at high Si loading the porous carbon sheet provides a rigid template and network to accommodate the volume expansion, and to avoid the electrical conduction losses.

Figure 1: SEM images of (a) carbon sheet; (b) cross-section of carbon sheet; (c) Si deposition on carbon sheet; (d) cross-section of Si nanoparticles deposition on carbon sheet; (e) cross-section of direct Si nanoparticle deposition on Cu foil.

Figure 2: Charge/discharge performance at 100 mA/g of direct Si deposition on (a) carbon sheet based electrode for Li ion battery; (b) Cu based electrode for Li ion battery.
**Industrial collaboration until 31 December 2014**

Roth & Rau (Eindhoven) is producing Si nanoparticles and performing the direct deposition of Si on substrates for the experiments in a collaborative effort. The conditions of sample production are being optimized according to the experimental research results; and Roth & Rau is taking efforts to bring the scalable sample preparation method/equipment to commercialization. For the carbon based current collectors we collaborate with Norit/Cabot, and for carbon coated steel current collectors with Tata Steel. In both cases preliminary experiments using Norit or Tata materials have been performed.

**All output from 2014**

In preparation:

1. Scalable direct deposition synthesis of Si nanoparticles for Li ion battery anodes.
2. Si nanoparticles integrated in porous carbon networks as Li ion battery anode.

**Other**

-
### Facilities ECN

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<th>Owner and Location</th>
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<td>Setaram High Pressure (HP) Differential Scanning Calorimetry (DSC) Thermogravimetry (TG) + OmniStar Mass Spectrometer</td>
<td>2013</td>
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<td>2010</td>
<td>Klaas Bakker</td>
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<td>2012</td>
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<td>DryEtcher/StandaloneLoader</td>
<td>2012</td>
<td>Peter Venema</td>
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<td>Ion implanter and anneal/oxidation oven</td>
<td>2014</td>
<td>Peter Venema</td>
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Setaram High Pressure (HP) Differential Scanning Calorimetry (DSC) Thermogravimetry (TG) and OmniStar Mass Spectrometer ECN-I02

Contact: Gertjan Herder, herder@ecn.nl
ECN Environment & Energy Engineering, eee@ecn.nl

Application

• Thermal storage and release
• Investigation of Phase Changing Materials
• Melting points under pressure
• Thermal effects of chemical reactions of solids with gases under pressure

Differential Scanning Calorimetry under Pressure

• Measurement of thermal events (endo- exotherm) such as melting, crystallization, T_m, chemical reaction enthalpy, C_p, etc.
• Elevated pressures (up to 100 bar) and reactive atmospheres, such as NH_3
• Simultaneous Thermogravimetry (TG) and DSC possible at atmospheric pressure
• Coupling with Mass Spectrometer for gas analysis

Mass Spectrometer

• Mobile instrument, for coupling to virtually any gas source
• Analysis of components up to 100 Amu
• Qualitative and quantitative gas analysis
• Operating temperature: up to 200°C
• Low detection limit (< 1 ppm)
• Stainless steel and quartz capillary
UltraShort pulse laser Pharos with R2R option and Q-sys 4-axis motion control
ECN I08

Application
- Layer removal by ablation
- Surface modification like hydrophobic texturing
- Machining ‘without’ heat effects

A versatile platform for ultra short pulse laser process investigation:
- Fully integrated workstation
- Ultra short pulses in continuous adjustable range of 250 fs to 10 ps
- Three wavelengths: 1030, 515 and 340 nm

Technical features

Laser
- Light Conversion, Pharos
- Diode pumped oscillator/regenerative amplifier
- Pulse width: tunable
- Pulse length: 200 fs to 10 ps
- Wave length: 1030 nm, 515 nm, 340 nm
- Average power: 10 W at 1030 nm
- Beam Quality: m² = 1.2

Workstation details
- Scanner optics, 3 wave lengths, multiple lenses available
- 4 degrees of freedom: X-Y-Z translation and rotation
  (limited to 100 x 100 mm)
- R2R setup available
- Maximum speed: 2500 mm/s

Q-sys XYZ system:
- X/Y stage: linear motor
- XYZ stroke: 1500x1000x300 mm
- Accuracy: 1.5 µm (X/Y), 5 µm (Z)
- Straightness: 3 µm (X/Y), 10 µm (Z)
- Rotary axes: two, direct drive

Specialties
- X-Y-Z with galvo integration
- On the fly marking
- Vision with smart camera integrated
- Galvo stage integration
- Continuous adjustable pulse length

Contact:
M.A. de Keijzer, dekeijzer@ecn.nl
ECN Environment & Energy Engineering, eee@ecn.nl
Hitachi SU70
Analytical Scanning Electron Microscope
ECN I09

Application
- High resolution microscopy, 0.9 nm at 30 kV
- Crystallographic characterisation
- Surface characterisation of metals and non-conductive materials (e.g. ceramics, plastics) using low acceleration voltages down to 0.1 kV with nm resolution
- Element analyses down to Boron and 0.05wt% accuracy

Contact:
E.W. Schuring, schuring@ecn.nl
ECN Environment & Energy Engineering, eee@ecn.nl

Technical features
- Oxford AzTec and INCA analyses tools for simultaneous EDX-WDX and EBSD-EDX
- Large area X-ray mapping
- Upper and lower SE detectors, using upper detector specific energies can be filtered out for optimised imaging
- 5 segment retractable back scatter detector (BSE)
- Sample tilt up to 70° (for EBSD, Electron Beam Scattering Diffraction)
- Large samples: Ø150 mm to 25 mm height
Application
The IM4000 ion miller allows for:

- Deformation and defect free preparation of cross sections of thin layers and sections
- Post polishing, flat milling, of samples to remove final distortions introduced during standard preparation of areas up to 5 mm in diameter. This is especially important for crystallographic characterisation

Technical features
The advantage with respect to other similar preparation techniques like FIB (Focused Ion Beam):

- Off line sample preparation, the SEM is available for other work
- Large area cross sections of 1-2 mm in width and 0.5 mm depth in 1-2 hours of preparation
- Cross sections can be made with a precision of 1 μm
- Cross sectional milling and flat milling is obtained using an Argon ion beam, either perpendicular to the surface (cross sectioning) or at a low angle (flat milling)
- Maximum sample temperature can reach 80°C, intermittent milling can prevent overheating
Hitachi S3700 SEM with large chamber and element analysis (EDX)
ECN I10

Application
- Microscopy with resolutions up to 10 nm attainable, magnification starting at 5x up to 100,000x
- Full size examination of sample up to 200 mm in diameter and 110 mm in height due to the large vacuum chamber
- In situ testing of real not cleaned components in situ testing of tensile and heat treatmens
- Typical for failure analyses

Materials
- Metals, conductive materials
- Non conductive materials like alumina, glass fibre reinforced plastics and glass without the application of a conductive layer
- Porous and contaminated samples
- Grease
- Test samples in intermediate stages of testing. Tests can be continued after the examination as the sample has not been altered

Technical features
- A Tungsten filament Scanning Electron Microscope operation under high vacuum or variable pressure (VP) up to 270 Pa.
- The S3700 is equipped with an Oxford AZTec EDX analyses system, using a 50 mm diameter silicon detector for fast analyses and allows for:
  • Point and selected area analyses
  • Automated analyses (using INCA software)
  • Line scans, counts, true line and quant line
  • X-ray mapping, also over large stitched areas
- Sample height to 110 mm and 300 mm diameter
- Sample weight till 5 kg
E-beam evaporation system Cryofox Discovery 500 EB from Polyteknik A.S.

Examples for research and applications
- Thin film metallization for crystalline silicon wafer based solar cells (blanket or masked)
- Patterned electrodes for test structures
- Optical layers
- Barrier layers
- Seed layers for plating

Tool features
- Carrousel with 6 large pockets (40 cm³) to allow deposition of thick layers (up to several μm)
- Electron beam evaporation source enabling deposition of wide range of materials
- Substrate size up to 156 x 156 mm, and IR lamp heating up to 500°C
- Substrate holder and line-of-sight process compatible with shadow masks
- Reactive processing possible (O, connected to system, flow and pressure controlled)
- Computer control for fully automated process sequence
  - Pumpdown
  - Heating of substrate
  - Melting of material and evaporation to desired thickness, including multi layers based on recipe database
  - Gas flow and pressure for reactive processes
  - Controlled cooling and venting

Contact:
ECN Solar Energy,
Benjamin Kikkert, kikkert@ecn.nl
Quantachrome
Autosorb iQ-C

Contact:
G. Herder, herder@ecn.nl
ECN Environment & Energy Engineering, eee@ecn.nl

Application
- Catalytic activity
- Purity of surfaces and/or composition of residues
- Specific surface area
- Binding of gases to solids
- Porosity measurements

Physisorption
- Adsorption isotherms
- Porosity
- Surface area
- Pore volume

Chemisorption
- Catalysis
- Corrosion studies
- Metal dispersion
- TPD/TPR

Gas analysis
- TCD
- Mass Spectrometer

Technical features
- Chemisorption: max. temperature 1100°C
- Pore size region: 0.35 nm – 0.4 μm
- Low surface area by krypton adsorption
- Vapor generator
- Gases: H₂, N₂, Ar, Kr, NH₃, CO₂, He
Automated Pyrolysis/Thermal Desorption combined with GCMS Analysis

Contact:
B.F. van Egmond, b.vanegmond@ecn.nl
ECN Environment & Energy Engineering, eee@ecn.nl

Application
- Determination of composition of organic substances

Aim
- Get structural information of macromolecules by analyzing their thermal decomposition products. E.g. synthetic polymers, biopolymers, biomass and, biomass-derived products
- Research the thermal decomposition behaviour of biomass as a function of temperature, heating rate, residence time etc.

Application

Pyrolysis-GCMS analysis of a lignine sample

Technical features
- Pyrolysis temp. from 350°C to 1000°C adjustable
- Pulsed (flash) pyrolysis or programmable up to 100°/sec
- Pyrolysis products are cryo-focussed prior to GCMS analysis
- Completely heated sample pathway - avoids carry over

TDU Pyrolysis - Operation Modes
- Flash pyrolysis or temperature programmed
- Solvent vent option
- Simulation of TGA (Thermogravimetric analysis)
Linear VHF plasma source for dynamic thin film silicon deposition

Plasma source
Incorporated in a roll-to-roll PECVD system for the dynamic deposition of intrinsic thin film silicon.

Flow rates:
- Silane (SiH₄): 0-500 sccm
- Hydrogen (H₂): 0-2000 sccm
- Argon (Ar): 0-1000 sccm

Process pressure: 0-10 mbar
Electrode dimensions: 15 x 40 cm
Web speed: 0 - 100 cm/min

VHF generator
Frequency: 60 MHz
0 to 1000 W continuous forward power
Accuracy: ± 3% of setpoint from 10% to 100% max output
Rise time <100 ms
Frequency stability ± 0.005%
Harmonic signals: less than ~30dB

Microcrystalline Si:H
Deposition rate: 0.625 nm/s
Photo conductivity: 6.76 x 10⁶ S/cm
Dark conductivity: 7.4 x 10⁻³ S/cm
Microstructure factor R° (FTIR): 0.438
Crystalline ratio R_c: 52%

Amorphous Si:H
Deposition rate: 0.82 nm/s
Bandgap: 1.8 eV
Photo conductivity: 3.75 x 10⁶ S/cm
Dark conductivity: 5.22 x 10⁻¹² S/cm
Activation energy: 1.01 eV
Microstructure factor R° (FTIR): 0.263
Urbach energy E_u: 53 meV

Uniformity
The uniformity in material flow along the length of the VHF electrode is excellent. As an example, the crystalline ratio, normalized to the average over the length of the electrode, is plotted against the lateral position. The variation in crystalline ratio is < ± 3%
Spectral Response Setup

Contact:
Klaas Bakker
High Tech Campus 21
5656 AE Eindhoven
The Netherlands
n.j.bakker@ecn.nl
+31 6 2333 7228

Specifications

- Monochromator: 3 gratings: UV VIS and NIR
- Si and Ge photodiodes as calibrated reference and monitor cells
- Spectral range from 200 till 1700nm
- Spot size minimum diameter 1mm max 2cm. Local measurement, makes it perfect for small size research cells
- Filtered Halogen and or LED background illumination for multi-junction cells
- Lock in technique to measure modulated signal
- Bias Voltage -3.5 till +3.5 Volt

EQE and SR

- External Quantum Efficiency (EQE) => number of electrons as a percentage of the number of incident photons
- Spectral Response (SR) => ratio of current generated to the power incident on the solar cell in A/W

Measurements of Tandem Cells

- Wide range of bias illumination options with LEDs and filtered halogen makes it possible to measure virtually all multi-junction cells.
- Possibility to apply bias voltage makes the measured sub cell operate at local short circuit condition

Optical layout of Setup

- Monochromator
- 2nd order filters
  And chopper wheel
- 2x beam splitter with Si and Ge monitor cell
- LED Bias illumination

Aperture, measurement spot is image of this aperture, used to set the spot size.
**Infrastructure**

**Solar ECN**

Contact:
Leon Laas, laas@ecn.nl

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**Tempress Reactor FANCY**

4-stack process furnace

**Characteristics**

**FANCY system**
- Direct plasma silicon nitride (SiN)
- Anti-reflection coating process
  - Batch size: 238 wafers
  - Wafer size: 232 slots 156 mm, 6 slots 4” round
- Low pressure POCl3 diffusion process
  - Batch size: 1000 wafers
  - Wafer size: up to 156 mm square
- High temperature anneal process
  - Batch size: 500 wafers
  - Wafer size: up to 156 mm square

**HF dry etcher**
- HF etching of P-glass on diffused wafers.
- HF gas cleaning of system components
  - Batch size: 250 wafers
  - Wafer size: up to 156 mm square

**Sherescan**
- 2D-mapping of wafer sheet resistance
- Selective emitter profile mapping

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**Lescheo**

**Tempress HF Dry Etcher**

**Characteristics**

**Sherescan**

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**Levitech Levitrack Thermal ALD Reactor**

**Characteristics**

**Levitrack system**
- Thermal atomic layer deposition (ALD) of aluminium oxide (Al2O3) nano-layers for surface passivation of solar cells
  - Film thickness: 1-10 nm
  - Throughput >3000 wafer/ hours
  - Wafer size: 156x156 mm2
  - Atmospheric ALD process
  - Wafer floats on gas bearing
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<td>NMR upgrade 200 MHz</td>
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<td>Brahim Mezari</td>
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ALD SiO2/Al2O3 stacks for the excellent chemical passivation of diffused silicon solar cells

1. Introduction
- In silicon solar cells, the loss of charge carriers at front and rear surfaces decreases the energy conversion efficiency significantly.
- Thin “passivation” films (0.1-10 nm) on these surfaces can improve the cell efficiency by 1-2% absolute.
- In 2006, aluminium oxide (Al2O3) was introduced as a new passivation material for solar cells.

2. The Challenge
- Goal of this work: optimize passivation for p-type and n-type diffused surfaces. Preliminary, one passivation scheme each for both surfaces.
- For n-type diffused cells, the aim is to passivate the rear surface of the cell by applying thin films (0.1-10 nm) of Al2O3.

3. ALD SiO2/Al2O3 Stacks
- SiO2 becomes stable after Al2O3 or SiN3 capping
- SiO2 controls the charge in the Al2O3

4. Results: Lab-scale
- SiO2/Al2O3 stacks are produced by plasma-enhanced ALD in the classroom
- SiO2/Al2O3 stacks show improved passivation on n-type surfaces compared to single layer Al2O3
- Corona charge experiments show influence of field-effect passivation & reveal the limits of the emitter

5. Industry: Batch ALD Platform
- ASM Loadstar: high throughput ALD batch platform for the solar industry
- Throughput of 4600 wafers/hour for 3 nm Al2O3, with competitive CO2
- Also suitable for synthesis of passivation stacks, annealing, etc.
- Systems installed at various solar cell manufacturers in Asia

6. Conclusions
- ALD Al2O3 is an industrially viable technique which provides superior passivation on p-type silicon surfaces, enabling high efficiency solar cells
- It is currently being extended to ALD SiO2/Al2O3 to enable n- and p-type passivation
- First results are demonstrated

Contact:
B.W.H. van de Loo, H.C.M. Knoops, G. Dingemans, D.S. Saynova, I.Romijn, W.M.M. Kessels
Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
SOLID-STATE NMR FACILITY

Brucker avance 500MHz
Solid-State MAS NMR Facility

The Laboratory of Inorganic Materials Chemistry is equipped with two magnets and a set of variable temperature (VT) Magic Angle Spinning (MAS) probes. In our solid-state NMR lab we are able to perform a variety of NMR experiments e.g. a single pulse, heterocontacts, solid-echo, high-power decoupling, CP/MAS, DQ/MAS and different exchange and correlation experiments.

Using a home-built vacuum setup, we are able to adsorb gases or dissolve in deuterated materials and to freeze to sub-zero temperatures of variable temperature.

Brucker DRX 200MHz

Electrochemical Deuteration of Metastable MgTi Alloys For Hydrogen Storage Applications

Introduction

Mg is interesting for hydrogen storage. Mg suffers from slow rate of (de) hydrogenation and high over-temperatures thermodynamically. The Mg alloy wth transition metals such as Ti, Zr, V, Cr, Fe, Co, Ni, and Cu is good candidates for the storage of hydrogen. In addition, the Mg alloy has an autothermal reaction that releases heat during hydrogenation and allows to use the Mg alloy to store hydrogen (as a solid fuel).

NMR approach

The NMR measurements were conducted in solution using a Bruker 500 MHz spectrometer. The 1H and 13C NMR spectra of Mg-Ti alloy were recorded at ambient temperature, 40, 60, 80, and 100 kHz MAS. The MAS experiments were carried out using a Bruker 500 MHz spectrometer. The 2D exchange and 2D exchange experiments were performed using a Bruker 500 MHz spectrometer.

Conclusion

The results obtained in this work show the potential of the Mg-Ti alloy for hydrogen storage applications. The Mg-Ti alloy exhibits a high hydrogenation capacity and a high rate of hydrogenation. The 2D exchange experiments confirm the sluggish exchange and the presence of a slow exchange process. The 2D exchange experiments confirm the presence of a slow exchange process.

Synergy between extra-framework aluminum species and Brønsted acid sites in faujasites: in situ NMR H/D-exchange study

Introduction

Zeolite Y has unique framework topology containing small and large cages and is widely used as an acid catalyst for hydroprocessing reactions in oil refining. The additional zeolite Y (H3A) prepared by strong extraction, leads to a new framework structure with new Brønsted acid sites. These species are expected to strongly influence the acidity and reactivity of the zeolite.

NMR approach

The high magnetic field NMR study of the H/D exchange reaction between benzene and Brønsted sites was carried out using a high magnetic field NMR spectrometer. The benzene was dissolved in D2O, and the resulting solution was used as a catalyst for the reaction. The reaction was monitored by the change in the chemical shift of the benzene peak. The results show a significant decrease in the chemical shift of the benzene peak, indicating the exchange of the hydrogen atom with deuterium.

Conclusion

The results show that the H/D exchange reaction is highly efficient in zeolite Y. The exchange reaction occurs at a faster rate in the presence of Brønsted acid sites. The exchange reaction is highly efficient in the presence of Brønsted acid sites. The exchange reaction is highly efficient in the presence of Brønsted acid sites.
K-Alpha XPS System

Contact:
Tiny Verhoeven

Principle of XPS

Set-up

Example

XPS Depth-Profiling of a for hydrogen-storage used layered sample

XPS survey scan of Olivine (Mg,Fe)SiO_2

Fully automated workflow from sample entry to report generation
### Facilities TU Delft

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</table>
Rubotherm Magnetic Suspension Balance

Contact:
Name: Prof. Thijs Vlugt
Email: t.j.h.vlugt@tudelft.nl
University: Delft University of Technology
Department: Process & Energy
Faculty: 3ME
Address: Leeghwaterstraat 39
Postal code: 2628 CB
City: Delft

Specifications:
Pressure: vacuum - 350 bar
Temperature: RT - 200 °C
Resolution: 10 μg
Sample weight: 0 - 25 g
Sinker weight: 20 g

Applications:
- Vapor-liquid equilibrium measurements
- Solubility of gases in liquids
- Adsorption isotherm measurements
- Adsorption of gases/vapors on solids
- Density measurements
Deposition techniques

- **RF/VHF-PECVD** (radio frequency / very high frequency plasma-enhanced chemical vapor deposition)
- **RF-sputtering**

PECVD materials

- p-, i-, n-type hydrogenated
- Amorphous silicon (a-Si:H)
- Nanocrystalline silicon (nc-Si:H)
- Silicon carbide (a-SiC:H)
- Silicon nitride (a-SiN:H)
- Silicon oxide (a-SiOx:H / nc-SiOx:H)

RF-sputtering materials

- Aluminum doped zinc oxide (ZnO:Al)
- Intrinsic zinc oxide (ZnO)

Features

- 6 UHV (ultra high vacuum) processing chambers + Load lock
- All chambers connected to a UHV transport chamber
- Capable of handling 5 substrates in sequence
- Fully programmable
- Available process gases: SiH4, B2H6, PH3, CH4, CO2, H2, GeH4, NH3, N2O, Ar, Ar/O2
- Maximum sample size: 10x10 cm²
- Capable of producing thin films and solar cells

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## Facilities University of Twente

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# Financial Report 2014

Financial report 2014  
Status per 31-12-14

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**TU Eindhoven**

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**Universiteit Twente**

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**Programmbureau**

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**Totale kosten realisatie ADEM programma**

| 30.000.000 | 17.070.541 | 57% |
ADEM Organization

ADEM Program Council

- Herman Kuipers, Shell Global Solutions (chair)
- Bert de Vries, Ministry of Economic Affairs
- Tim van der Hagen, TU Delft
- Dave Blank, University of Twente
- Paul Compagne, BioMCN
- Leo Warmerdam, NXP Semiconductors
- Ernst Granneman, Levitech
- Kees van der Klauw, Philips
- Albert Hasper, Tempress Systems

ADEM Theme Coordinators 2014

- Fuel Cells: Stephen Picken, Delft University of Technology
- Wind: Rinze Benedictus, Delft University of Technology
- Catalysis, Membranes and Separations: Louis Winnubst, University of Twente
- Heat: Theo van der Meer, University of Twente
- Solar: Miro Zeman, Delft University of Technology
- Batteries: Erik Kelder, Delft University of Technology

ADEM Steering Committee

- Paul Korting, ECN (chair)
- Paulien Herder, Delft University of Technology
- Hans Kuipers, Eindhoven University of Technology
- Leon Lefferts, University of Twente

ADEM PhD student Committee

- Michiel Aerts, Delft University of Technology
- Shilpa Agarwal, University of Twente
- Emanuelea Negro, Delft University of Technology
- Taha Jibril Taha, University of Twente
- Tim Westphal, Knowledge Centre WMC
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<th>Projectcode</th>
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<tr>
<td>TUD-P11</td>
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<td>Dr. Ir. M. Wagemaker, Dr. E.M. Kelder, Prof. Dr. F.M. Mulder</td>
<td>TU Delft</td>
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<tr>
<td>TUD-P13</td>
<td>Thema Batterijen: TUD-P13/Stable high capacity battery anodes</td>
<td>Dr. Ir. M. Wagemaker, Dr. E.M. Kelder, Prof. Dr. F.M. Mulder</td>
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<td>TU Delft</td>
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<td>Prof.dr.ir. W.M.M. Kessels, Prof.dr.ir. P.H.L. Notten</td>
<td>TU Eindhoven</td>
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<td>TUE-P06</td>
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<td>Dr. E.M. Kelder</td>
<td>TU Delft</td>
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<td>Prof. Dr. F.M. Mulder</td>
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<td>TUD-P09</td>
<td>TUD-P09/Design of stable metal membranes for hydrogen separation from gas mixtures</td>
<td>Dr. Ir. W.G. Sloof, Dr. A.J. Böttger</td>
<td>TU Delft</td>
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<td>UT-P06</td>
<td>UT-P06/Catalysts for sustainable fuels production in hot compressed water: H2 production from aqueous biomass streams</td>
<td>Prof. S.R.A. Kersten, D.W.F. Brilman, Prof. K. SooHan, Prof. L. Lefferts</td>
<td>UT Twente</td>
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<td>UT-P10</td>
<td>UT-P10/Determination of the degradation mechanism of hybrid and organically modified silica membranes</td>
<td>Prof. dr. ir. Andre ten Eshof</td>
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<td>Dr. Ir. Pel, Dr. Ir. H.P. Huisink, Prof. Dr. ir. D.M.J. Smetsiders</td>
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<td>Prof Jurnna Schmitz, Alexey Yu Kovaligl</td>
<td>UT Twente</td>
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<td>Prof. L.K. Nannev, W. Sinke (ECN), Dr. R. Neber (Tempress Systems), Prof. E. Charo</td>
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<td>Prof. Dr. F.M. Mulder, Dr. Jan-Marc Luckies (Tempress Systems), Prof. Dr. M. Zeman</td>
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<td>Prof. Dr. ir. A.A. van Steenhouwen</td>
<td>TU Delft</td>
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<td>Thema Batterijen: TUD-107/Thin film positron annihilation lifetime spectrometer PDSH-PALS for advanced characterization of defects and nanostructure of thin film solar cell layers</td>
<td>Prof. Dr. ir. A.A. van Steenhouwen</td>
<td>TU Delft</td>
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<td>TUE-106</td>
<td>Thema Batterijen: TUE-106/Thin film positron annihilation lifetime spectrometer PDSH-PALS for advanced characterization of defects and nanostructure of thin film solar cell layers</td>
<td>Prof. Dr. ir. A.A. van Steenhouwen</td>
<td>TU Delft</td>
<td>€ 199,500</td>
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