

Index - Final Report

1.	Final report	2
1.1	Project details	2
1.2	Executive summary	3
1.3	Project results	7
1.3.1	Introduction	7
1.3.2	Work Done at DTU Department of Chemistry (DTU-KI)	10
1.3.3	Work Done at DTU Department of Physics (DTU-FYS)	16
1.3.4	Work Done at Southern University of Denmark (SDU)	23
1.3.5	Work Done at Aalborg University (AAU)	28
1.3.6	Work Done at Danish Power Systems (DPS)	33
1.3.7	Work Done at IRD A/S (IRD)	37
1.4	Utilization of project results	49
1.5	Project conclusion and perspective	52

1. Final report

1.1 Project details

Project title	HIGH PERFORMANCE MEAS
Project identification	2008-1-10076
Name of the programme which has funded the project (ForskVE, ForskNG or ForskEL)	ForskEL
Name and address of the enterprises/institution responsible for the project	IRD A/S
CVR (central business register)	14689605
Date for submission	July 4, 2012

1.2 Executive summary

The Danish Fuel Cell R&D efforts within materials, components, and stack design for both the LT PEM FC and HT-PEM technology are mandatory in order to achieve acceptable market cost. This project addressed the challenging MEA key target values related to the cost, performance and lifetime as outlined in the national Danish PEM Road Map.

To fulfill the next target goals of MEA performance, amount (mass) of platinum used, cost and lifetime defined in the national Danish strategy on PEM FC, it is of up most importance, to develop higher performing and more stable materials that will contribute significantly towards achieving the MEA power density targets. The aim of the present project is through modeling, material and process development to obtain significantly better MEA performance and to attain the technology necessary to fabricate stable catalyst materials thereby providing a viable alternative to current industry standard.

This project primarily focused on the development and characterization of novel catalyst materials for the use in high temperature (HT) and low temperature (LT) proton-exchange membrane fuel cells (PEMFC). New catalysts are needed in order to improve fuel cell performance and reduce the cost of fuel cell systems. Additional tasks were the development of new, durable sealing materials to be used in PEMFC as well as the computational modeling of heat and mass transfer processes, predominantly in LT PEMFC, in order to improve fundamental understanding of the multi-phase flow issues and liquid water management in fuel cells. An improved fundamental understanding of these processes will lead to improved fuel cell performance and hence will also result in a reduced catalyst loading to achieve the same performance.

Project partners were:

- IRD A/S, responsible for the following:
 - Project coordination
 - Development of durable seals
 - MEA development, benchmarking and FC test (LT-PEM & DMFC)
- DTU Chemical Institute (DTU-KI), responsible for:
 - Development of carbon support materials
 - Synthesis of supported catalyst
 - Characterization of supported catalyst
- DTU Physical Institute (DTU-FYS), responsible for:
 - Catalyst materials development
 - Development of characterization and test methods of catalysts

- SDU, responsible for:
 - Catalyst Synthesis by wet routes
 - Catalyst characterization and test
- ET-AAU, responsible for:
 - Modelling Tools and validation
 - Modelling CO poisoning
 - Modelling of electrode microstructure
- DPS, responsible for:
 - Benchmarking and Pilot Fabrication of Catalyst
 - FC performance concerning HT-PEM

The consortium have obtained significant research results and progress for new catalyst materials and substrates with promising enhanced performance and fabrication of the materials using novel methods. However, the new materials and synthesis methods explored are still in the early research and development phase. The project has contributed to improved MEA performance using less precious metal and has been demonstrated for both LT-PEM, DMFC and HT-PEM applications. New novel approach and progress of the modelling activities has been extremely satisfactory with numerous conference and journal publications along with two potential inventions concerning the catalyst layer.

Research Highlights were:

1. **DTU-KI** has investigated the effect of the pre-treatment temperature of the carbon support for the Pt catalyst. It was shown that heat treatment of the carbon black significantly improves the carbon stability, however, at expense of the specific surface area. Commercial samples were used for this study.
2. **DTU-KI** has evaluated carbon nanotubes (CNTs) as alternative catalyst supports. Techniques for the surface activation and modification were developed by oxidative pretreatment in mixtures of hot acids, which were found to be able to effectively activate the CNT surface and facilitate the loading and dispersion of the platinum nanoparticles.
3. **DTU-KI** developed a method for the preparation of supported catalysts yielding a very good particle dispersion with platinum particle size of around 2-5 nm.
4. **DTU-KI** found that compared the untreated carbon black as support, graphitized carbon and CNTs exhibited excellent chemical and electrochemical stability. The supported catalysts showed significantly improved long term durability.

5. **DTU-FYS** conducted experiments using identical location transmission electron microscopy (IL-TEM) to study the Pt/C catalyst degradation and developed a novel experimental design and protocol for that purpose.
6. **DTU-FYS** provided the first direct, microscopic proof that the degradation in performance of Pt/C catalysts is primarily due to Pt dissolution. Hence, future catalyst design and synthesis should be tailored towards strategies to prevent Pt dissolution.
7. **DTU-FYS** attempted to prevent Pt dissolution by stabilizing Pt/C by alloying with Au, W and Nb. However, such alloys could not be stabilized.
8. **DTU-FYS** has demonstrated that the specific activity of the ORR over Pt nanoparticles decreases with particle size, with a maximum in mass activity for 3 nm particles.
9. **DTU-FYS** also tested Pt_xY nanoparticles as alternative catalyst. Initial measurements indicate that the Pt₃Y nanoparticles show ~4 fold improvement in surface specific oxygen reduction activity over Pt nanoparticles of a similar size. Overall, a 10-fold improvement of the state of the art pure Pt/C catalysts used in a fuel cell was found initially.
10. **SDU - Department of Chemical Engineering, Biotechnology and Environmental Technology (KBM)** investigated the synthesis of catalyst by wet routes and attempted to synthesize platinum black electrodes by decomposition of platinum complexes with metastable ligands. The advantage is that such synthesis can be carried out at moderate temperature (280 C). However, the materials were found to be insoluble in all common solvents tested.
11. **SDU-KBM** also investigated metal organic frameworks (MOF) containing platinum as catalyst. Results are promising but this technique is still at a very early stage.
12. The surface physics group at the **SDU Department of Physics and Chemistry** is working on transformation of carbons into silicon carbide. In a separate project ("Catbooster") they succeeded to produce electrodes which show similar activities as Vulcan based electrodes, and these were made available for this project.
13. **ET-AAU** developed two computational fluid dynamics models, a LT PEMFC model based on CFX-4 and a DMFC model based on CFX-13. Both models have unique and world leading capabilities.
14. **ET-AAU** invented the "water uptake layer". A minor modification to the current catalyst layer structure at virtually no additional cost may prevent anode side dehydration, caused by the electro-osmotic drag, and it may allow for fuel cell operation without the need of external humidification of the inlet gases. This would

substantially reduce the cost and complexity of fuel cell systems and improve fuel cell performance, hence reducing the required amount of catalyst.

15. **ET-AAU** also investigated the effect of the CL morphology on the heat and mass transport inside the CL. A suggestion was to increase the pore-size distribution (PSD) inside the CL to improve liquid water transport. It was proposed to try and increase the grain size distribution of the carbon support particles in order to obtain a wider PSD. At the current state it is unknown whether this is feasible and will have the desired effect.
16. Modeling work at **ET-AAU** has also shown that the use of the interdigitated flow field has advantages over the commonly used straight channel or serpentine flow fields in that it allows for low stoichiometry operation, which again increases system efficiency (less compression power) and thereby reduces cost. A stoichiometric flow ratio as low as 1.2 at the cathode side has been demonstrated numerically.
17. **DPS** has worked on benchmarking and pilot fabrication of catalyst.
18. **DPS** demonstrated improved electrode manufacturing process and higher MEA performance in HT-PEM application.
19. Durable seals bound in a polymer and integrated with the membrane electrode assembly was developed and demonstrated by **IRD**.
20. **IRD** established process routes leading to increase in precious metal utilization for LT-PEM and DMFC application.
21. **IRD** demonstrated 50% reduction in precious metal content in DMFC MEAs without compromising the performance
22. Overall, more than 8 papers published in leading international journals with high impact factors and additional 5 papers and 1 patent are submitted

1.3 Project results

1.3.1 Introduction

1.3.1.1 Preface

The original three-year project application was submitted to the ordinary PSO 2007 call in September 2007. The project started on the 1-Feb-2008. The entire project was originally planned for 36 months. The consortium requested to prolong the activities into ultimo 2011, mainly due to lack of personnel allocation. November 2010 Energinet approved the project end date to be 31. December 2011. The project partners have thereby been able to address and fulfill all the milestones and deliverables defined in the project workplan.

1.3.1.2 Project Objectives

The Danish Fuel Cell R&D sector has in the recent years obtained significant improvement within materials R&D, components, and stack design for both the LT PEM FC and HT-PEM technology. Additionally, the R&D efforts have contributed to significant cost reductions that are mandatory in order to achieve acceptable market cost.

To fulfill the next target goals of MEA performance, amount (mass) of platinum used, cost and lifetime defined in the national Danish strategy on PEM FC, it is of utmost importance to develop material compositions and process technologies that will contribute significantly towards achieving the power targets for PEM and DMFC. This proposal addresses the challenging key target values in the national Danish PEM Road Map as outlined in Table 1 defined at the time of the project application.

The aim of the present project is to combine the results obtained in earlier national and international projects and through modeling and, material and process development to obtain significantly better MEA performance and to attain technology necessary to fabricate catalyst materials thereby providing a viable alternative to current industry standard. The project will focus on development of high-performance, lower cost membrane electrode assemblies (MEAs) that:

- Use less precious metal than current state-of-the-art constructions
- New catalysts made from novel processes amenable to high volume manufacturing
- Optimized with respect to catalyst/support interactions and intrinsic microstructure
- Encapsulated in durable seals for high speed assembly processes
- Meet the demanding target for LT and HT PEMFC performance
- Enhancement and validation of an advanced Computer Fluid Dynamics (CFD) model

1.3.1.3 Project Overview

The project Gannt including WP-leaders is shown in Figure 1. The defined milestones for the project are listed in Table 1.

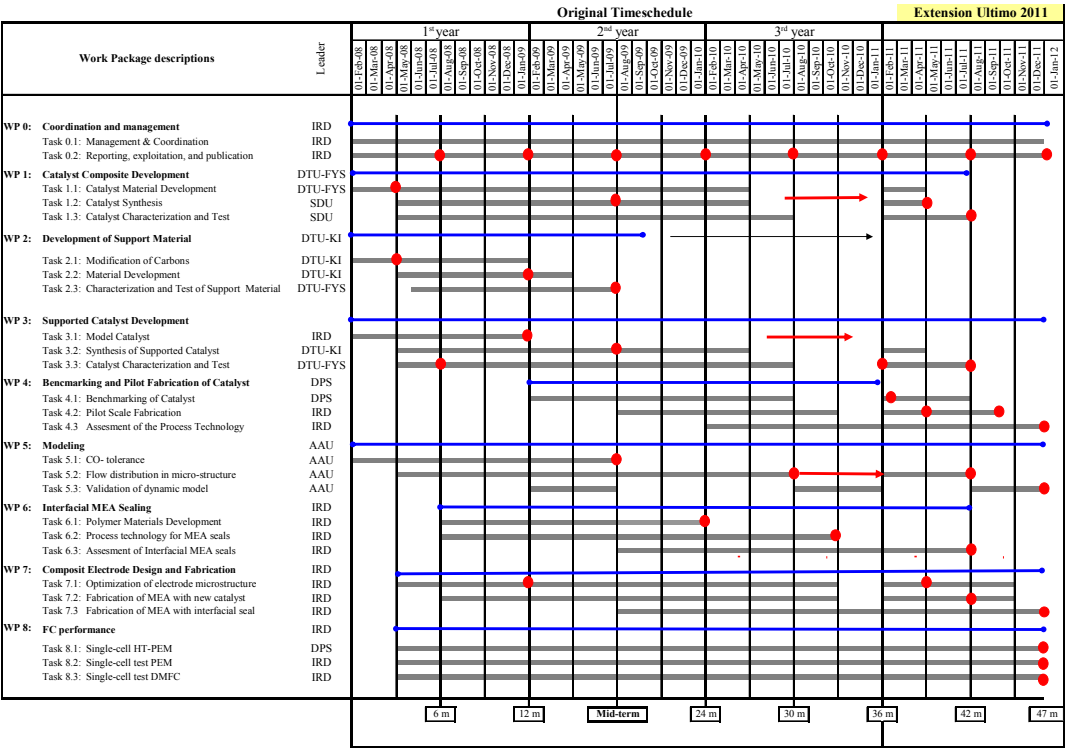


Figure 1 Project Gannt Plan.

Milestone	Title	Elaborated
M1	Report on experimental design and protocol for catalyst testing	Completed
M2	First samples of synthesized platinum group metal (PGM) catalyst	Completed
M3	Evaluate the performance of advanced PGM catalyst formulations	Completed
M4	Report on non-supported catalyst characterisation	Completed
M5	Report on stability test procedures	Completed
M6	First sample of carbon supports and characterization results	Completed
M7	Characterization and evaluation of supports finished	Completed
M8	Model catalyst finalized	Completed
M9	Report on experimental design and technique for kinetic evaluation	Completed
M10	First small batch of new catalyst on modified/alternative support	Completed
M11	Report on corrosion test	Completed
M12	Report on supported catalyst characterization	Completed
M13	Benchmarking supports and catalyst selected	Completed
M14	Process route for catalyst fabrication defined	Completed
M15	Catalyst pilot fabrication 200 g	Revised 50 g batch completed c.f section 1.3.7.2
M16	Technical evaluation of the catalyst fabrication routes developed	Completed
M17	Report on CFD modelling of CO poisoning	Revised c.f. section 1.3.5
M18	Report on CFD modelling of electrode microstructure	Completed
M19	Validation of the complete CFD modelling	Completed
M20	Identification of durable seal materials completed	Completed
M21	Process route for integrated seal finalised	Completed
M22	Integration concept for MEA edge seal evaluated	Completed
M23	Report on electrode morphology	Completed
M24	Evaluate most promising electrode designs in MEAs	Completed
M25	Evaluate most promising electrode designs with new catalyst in MEAs	Completed
M26	Evaluate optimised MEAs with interfacial seals	Completed
M27	Demonstration of HT-PEM MEA cell units completed	Completed
M28	Demonstration of LT-PEM MEA cell units completed	Completed
M29	Demonstration of DMFC MEA cell units completed	Completed
M30	4 papers with peer review published (or patents filed)	Completed c.f. section 1.4

Table 1 List of Milestones

1.3.2 Work Done at DTU Department of Chemistry (DTU-KI)

The present section summarizes the activities and most important findings for the work performed at Department of Chemistry, Technical University of Denmark. Many of the experimental results were presented and compiled in separate milestone reports.

Carbon modification

The DTU-KI research started with preparation of carbon support materials. Two types of commercially used carbon blacks are selected as benchmark materials for comparison: The typical examples of the used carbon blacks: Vulcan XC-72R (Cabot) with a surface area of 250 m²/g and Ketjen EC300J (Ketjen Black) with a surface area of 840 m²/g. In close collaboration with a carbon producer Timcal, a series of carbon black samples has been prepared by post heat-treatment at temperatures of up to 3000°C, covering a BET surface area range from 60 to 790 m²/g. Corrosion evaluation of these materials is under the way. A milestone report (M5: Report on stability test procedures) was delivered with proposed protocols for carbon corrosion and catalyst stability evaluations.

Modification of carbon support materials was started with Vulcan XC-72R (Cabot) carbon black and first thermally treated at 2800°C. After the treatment, graphitization was verified by the Raman bands at 1582, 1333 cm⁻¹ and 2659 cm⁻¹. Significant reduction in the specific surface area was observed, from more than 200 to 60 m²/g. Another series of carbon black supports (Ensaco 350G, Timcal) were also prepared covering a BET surface area range from 60 to 790 m²/g. BET, XRD, TGA and corrosion tests for the material evaluation have been performed (M6 Milestone Report on First Sample of Carbon Supports and Characterization Results). Further evaluations were made based on the supported catalysts with platinum loading of 40-60 wt% , including gas phase oxidation, TEM, as well as TGA and fuel cell performance and durability tests (M10 Milestone Report on First Small Batch of New Catalysts on Modified/alternative Supports).

The materials were further characterized with stability by corrosion test under conditions similar to HT-PEMFC, i.e. in 85% H₃PO₄ at 150°C. Significant improvement in the oxidative stability was observed in the studied potential range from 1.0 to 1.6 V versus the reversible hydrogen electrode (RHE). By holding the potential at 1.2 V versus reversible hydrogen electrode, the corrosion current was recorded in a period of 3 hours. The corrosion current was expressed as a specific current for a unit mass of the carbon black samples, mA/g-C and plotted against the heat treatment temperature, as shown in Figure 2 (M11 Milestone Report on Results of Carbon Corrosion Test). Heat treatment of the carbon black significantly improves the carbon stability, however, at expense of the specific surface area.

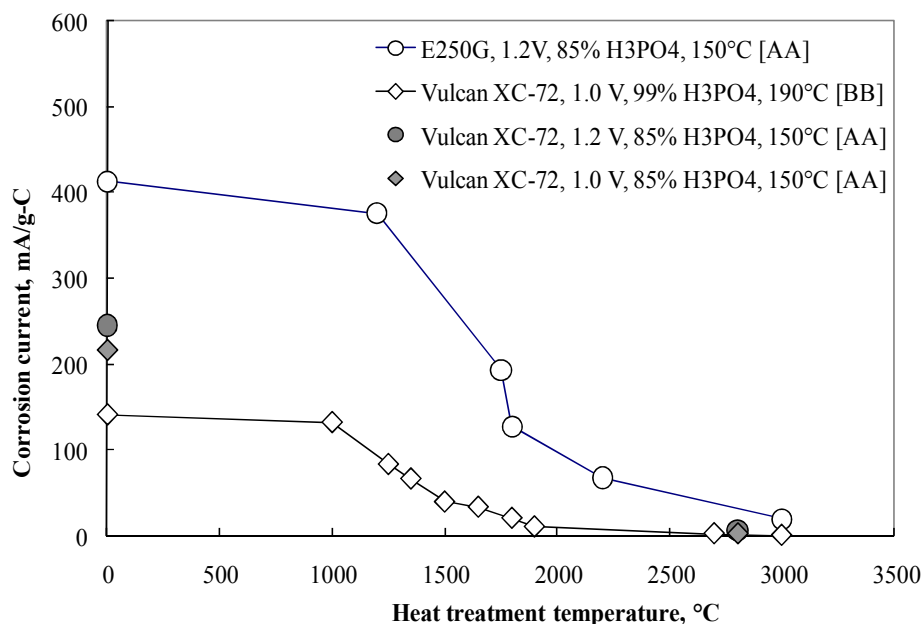


Figure 2. Corrosion current of Vulcan XC-72 and E350G carbon 85% phosphoric acid at different temperatures and potentials. [AA] from the present project. [BB] From literature [Landsman DA and Luczak FJ, in *Handbook of Fuel Cells*, Vielstich W, Lamm A and Gasteiger HA (eds), vol 4, pp811-831, John Wiley (2003)].

Nanostructured carbon supports

Identification and development of tailored nanostructure carbon materials with sufficient conductivity and thermal and chemical stability were done have been started. Carbon nanotubes (CNTs) have been evaluated as alternative catalyst supports. Both single wall carbon nanotubes (SWCNT) and multi wall carbon nanotubes (MWCNTs), with various types of functional surface groups such as $-OH$ and $-COOH$, have been explored as possible catalyst supports. Techniques for the surface activation and modification were first developed by oxidative pretreatment in mixtures of hot acids, which were found to be able to effectively activate the CNT surface and facilitate the loading and dispersion of the platinum nanoparticles.

Preparation of supported catalysts

An issue of utilizing alternative catalyst support is the development of new methods for preparation of the noble metal catalysts. At DTU-KI, carbon black supported Pt catalysts were prepared by a colloidal adsorption method, where platinum salt is first reduced and adsorbed on carbon supports. For modified carbon supports with reduced BET areas, efforts were made to activate the carbon surface activation by acidic oxidation. The graphitized carbon black and CNTs, in general, have inert surface orientations, which limit the catalyst

metal location, dispersion and adherence during the consequent catalyst loading. Chemical activation, typically by acid oxidation, facilitates to create surface functional groups, such as carboxyl (-COOH), carbonyl (-C=O) and hydroxyl (-OH) groups as well as surface defects, which improve the dispersion and immobilization of catalyst particles. The acid oxidation, however, reduces the corrosion resistance of the carbon materials. Another way to activate the carbon surface is to impregnate carbon with functional polymers such as polybenzimidazole (PBI) which contains nitrogen sites for the catalyst loading. The polyol method was also explored by dispersing Pt particles in e.g. polyethylene glycol medium and then transferred to the supports. The last method proves to be less demanding for the carbon surface area and has been used for preparation of catalysts with various types of supports. Good dispersion was achieved with platinum particle size of around 2-5 nm.

Fabrication of gas diffusion electrodes and membrane-electrode-assemblies

For the catalyst evaluation, gas diffusion electrodes were fabricated from different batches of catalysts. The electrodes were fabricated with polybenzimidazole (PBI) as the binder, which after acid doping serves as ionomer in the catalysts layer. The electrodes were tested in HT-PEMFC for both activity and stability evaluations using phosphoric acid doped PBI membrane.

HT-PEM fuel cell tests with emphasis on durability

Based on selected carbon supports, platinum catalysts were prepared for characterizations and fuel cell tests. These samples are listed in Table 2 below.

Table 2. Summary of carbon supports and catalysts prepared with the supports.

Carbon support samples	Catalysts	Notes
E350G	Yes	Timical commercial
E350G HT1800	No	Heat treated at 1800°C
E350G HT2200	No	Heat treated at 2200°C
RE-159 HT-3000	No	Heat treated at ca. 3000°C
VXC-72R	Yes	Cobat commercial
G-VXC-72R HT-2800	Yes	Heat treated at 2800°C
Ketjen EC300J	Yes	JM Commercial
MWCNTs	Yes	Commercial
MWCNTs-OH	Yes	Commercial
MWCNTs-COOH	Yes	Commercial

The catalysts supported on graphitized carbon black and various CNTs were evaluated in an accelerated aging test with the potential cycling between 0.9 and 1.2 V in fuel cells (M5 Milestone Report on Stability Test Procedures). OCV and ASR measurements were carried out during the cycling tests, showing little degradation of membranes. As a result, the observed performance degradation during the test was attributable to the catalyst. Compared with the untreated carbon black as support, graphitized carbon and CNTs exhibited excellent chemical and electrochemical stability. The supported catalysts showed significantly improved long

term durability. Detailed results were presented in M27 report (Demonstration of HT-PEM fuel cell units).

For the electrochemical active area determination, the fuel cell cathode was switched from operation with air to argon. Voltammograms recorded at a sweep rate of 20 mV/s during the cathode switch are shown in Figure 3. Before the switch the fuel cell OCV was about 0.94 V, from which the voltammetry started, followed by cycling between potentials of 0.45 V and 0.05 V with the hydrogen anode as the reference. As the oxygen was depleted, the reduction current was gradually decreased while the hydrogen adsorption and desorption peaks appeared. From such a voltammogram (Fig.3) the total charge for the hydrogen adsorption was obtained by integrating in the potential range from 0.05 to 0.4 V (for voltammograms at a sweep rate of 20 mV/s). Assuming the charge of $210 \mu\text{C}/\text{cm}^2$ for adsorption of a monolayer of hydrogen atoms, the electrochemical active area of the electrode and its variation during the potential cycling was calculated.

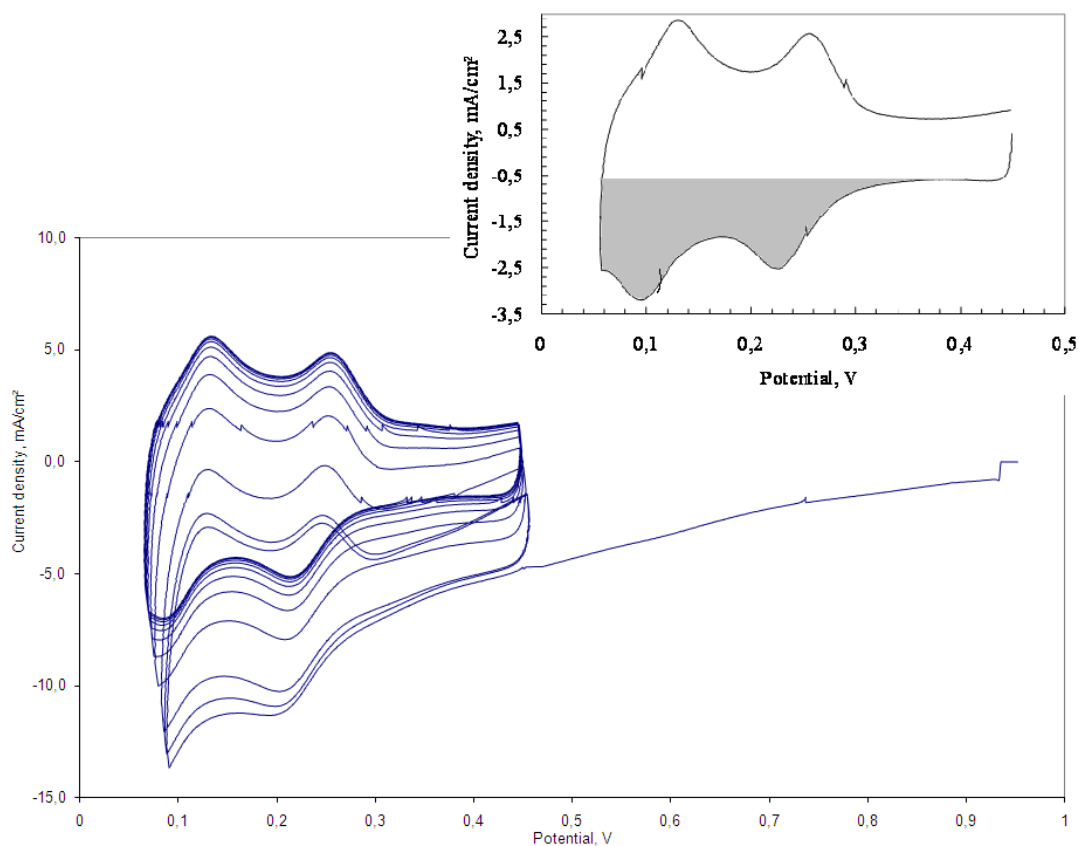


Figure 3. Voltammograms of a PBI based fuel cell operating at room temperature. The cathodic catalyst was 40 wt% Pt supported on Vulcan XC-72R. (A) when the cathode gas was switched from air to argon; (B) Voltammogram for the electro chemical active area determination of the cathode catalyst. The sweep rate was 20 mV/s.

A set of typical polarization curves of HT-PEMFC fuel cells during the accelerated potential cycling between 0.9 and 1.2 V were shown in Figure 4. The electrodes prepared from catalysts based on graphitized carbon black and the potential cycling numbers are indicated in the figure. A steady degradation was observed but with a very much improved stability.

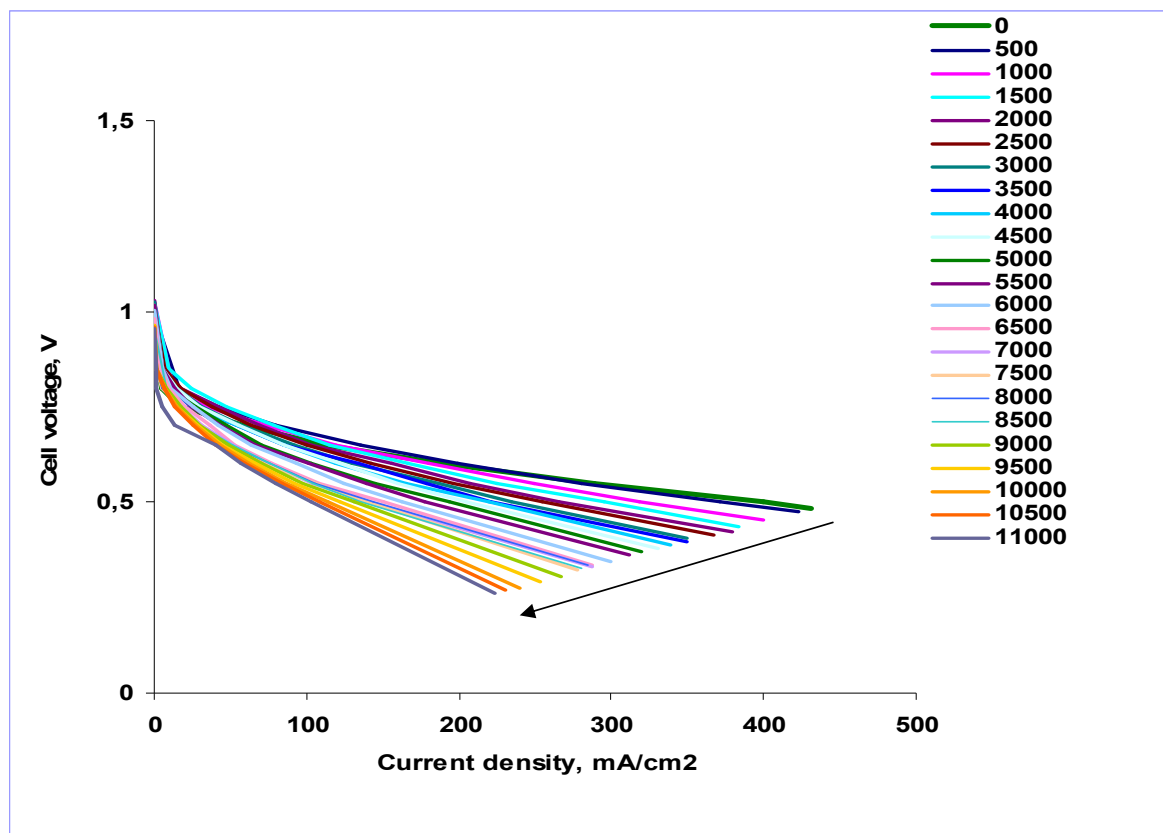


Figure 4. Polarization curves of a PBI fuel cell after different number of potential cycling (1 cycle = 2 min between 0.9 and 1.2 V). Platinum loading of the electrode was $0.7 \text{ mg Pt cm}^{-2}$ and the active area of the electrode was 25 cm^2 . Hydrogen and oxygen flow rates were 100 ml min^{-1} and the air flow rate was 200 ml min^{-1} .

Figure 5 summarizes the fuel cell performance degradation results during the potential cycling tests with catalysts supported on carbon materials. The performance losses were calculated as the relative current density (in percentage) at a cell voltage of 0.5 V with the initial performance as the reference. For each catalyst, two parallel cell tests were performed, showing reasonably good reproducibility. A strong dependence of the performance loss on the catalyst supports was observed. The as received VXC carbon blacks exhibited the fastest performance loss under the potential cycling test conditions at 150°C in the presence of phosphoric acid in PBI cells. Heat treatment of the carbon black improves the carbon stability and therefore the catalyst durability. CNTs as catalyst support showed further improvement in the fuel cell durability. The cycling potential range between 0.7 and 1.0 V, instead of routine test between 0.9 and 1.2 V, gave much less performance loss, as showing in the figure.

However, no systematic investigation was made on the performance dependence on the accelerated potential cycling range in the present study.

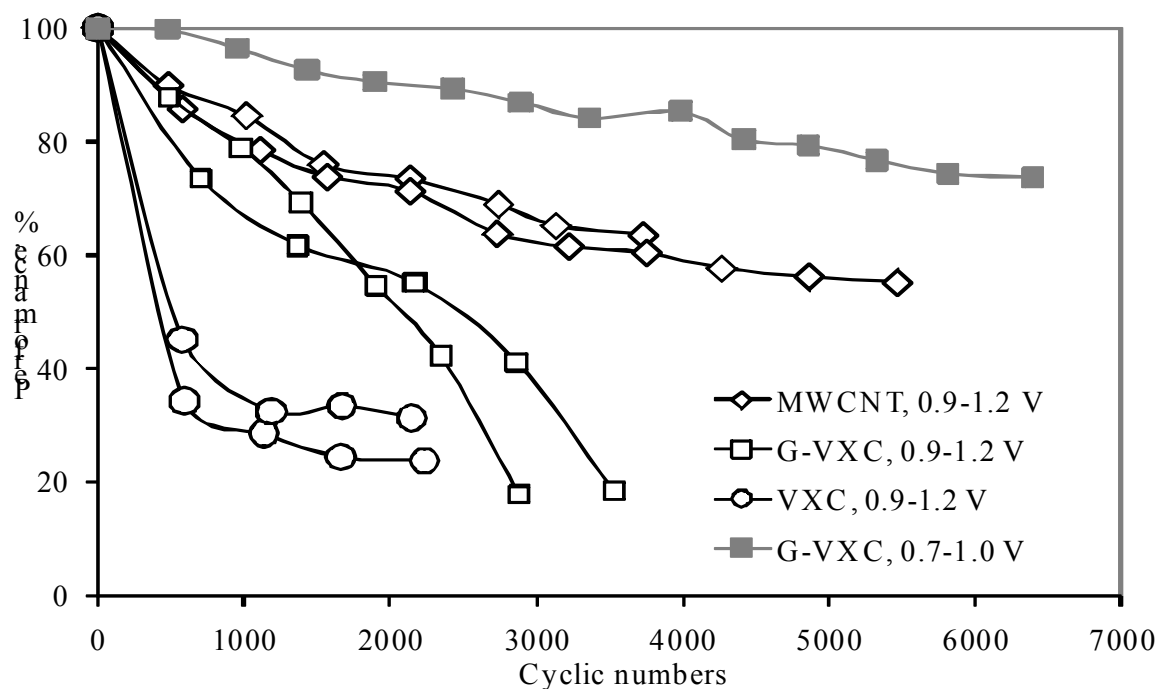


Figure 5. Fuel cell performance degradation (relative current density at 0.5V) during the potential cycling tests between 0.9 and 1.2 V (open symbols) or between 0.7 and 1.0 V (solid symbols) at 150°C.

Conclusions

Different types of carbon support materials have been selected and prepared. Platinum catalysts were synthesized using these carbon supports. Systematical characterizations of these materials were carried out through this project. Emphasis was placed on electrochemical characterizations especially HT-PEMFC performance and durability tests. With respects to the long term stability by means of accelerated potential cycling tests, significant improvement was achieved by using modified or alternative carbon supports, i.e. the graphitized carbon black or nanostructured carbon nanotubes without or with various functional groups.

1.3.3 Work Done at DTU Department of Physics (DTU-FYS)

At Department of Physics, Technical University of Denmark we have taken several approaches towards developing catalyst materials for the oxygen reduction reaction (ORR): (a) identical location transmission electron microscopy (IL-TEM) studies of Pt/C catalyst degradation (b) stabilising Pt/C by alloying with Au, W and Nb (c) model studies of size-selected Pt and Pt_xY nanoparticles. These are explained in detail below.

(a) Identical location transmission electron microscopy (IL-TEM) studies of Pt/C catalyst degradation¹

Catalyst stability is also of critical importance for PEMFC applications.² Pt/C catalysts tend to corrode with time, manifested as an increased overpotential, due to an effective loss of catalyst surface area. It is particularly pronounced when the cathode is exposed to high potentials, either during shut down/start up cycles or through inadvertent 'cell reversal'.

In order to study the stability of these particles under oxygen reduction conditions and study the effect of reaction conditions on nanoparticle stability we have utilized Identical Location TEM (ILTEM).¹ We performed this on Pt//C catalysts that we synthesized using an inverse-micelle method. The experiments allowed us to gain insight into how the nanoparticles look before and after activity measurements, and to understand the cause of catalyst degradation in PEMFC's. On the basis of earlier studies developed by other groups, we developed our own experimental design and protocol for this purpose (MS1 and MS12 Milestone reports). Figure 6 shows the configuration we have used whereby a Au TEM grid is placed inside a holder adapted for the rotating disk electrode measurement configuration. Prior to measurement, TEM is performed on several noted areas of the grid. The grid is then placed in the rotating disk set-up, ORR is performed and the sample is then taken out again in order to perform TEM post-activity measurement. By using the appropriate coordinates, the same area on the TEM can be located.

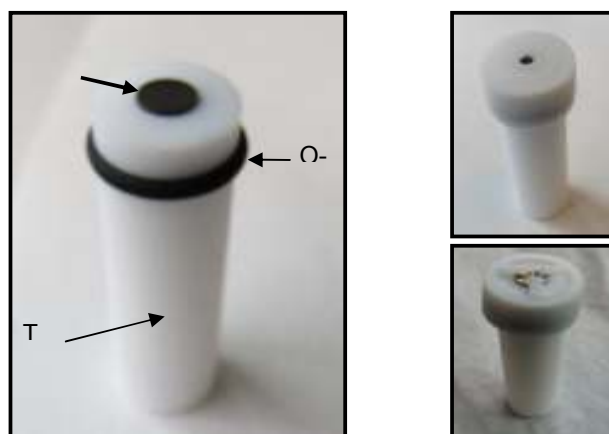


Figure 6. IL-TEM setup. a. Without teflon cover b. Previous configuration, with teflon cover. c. New configuration, with teflon cover, and Au TEM grid in place.

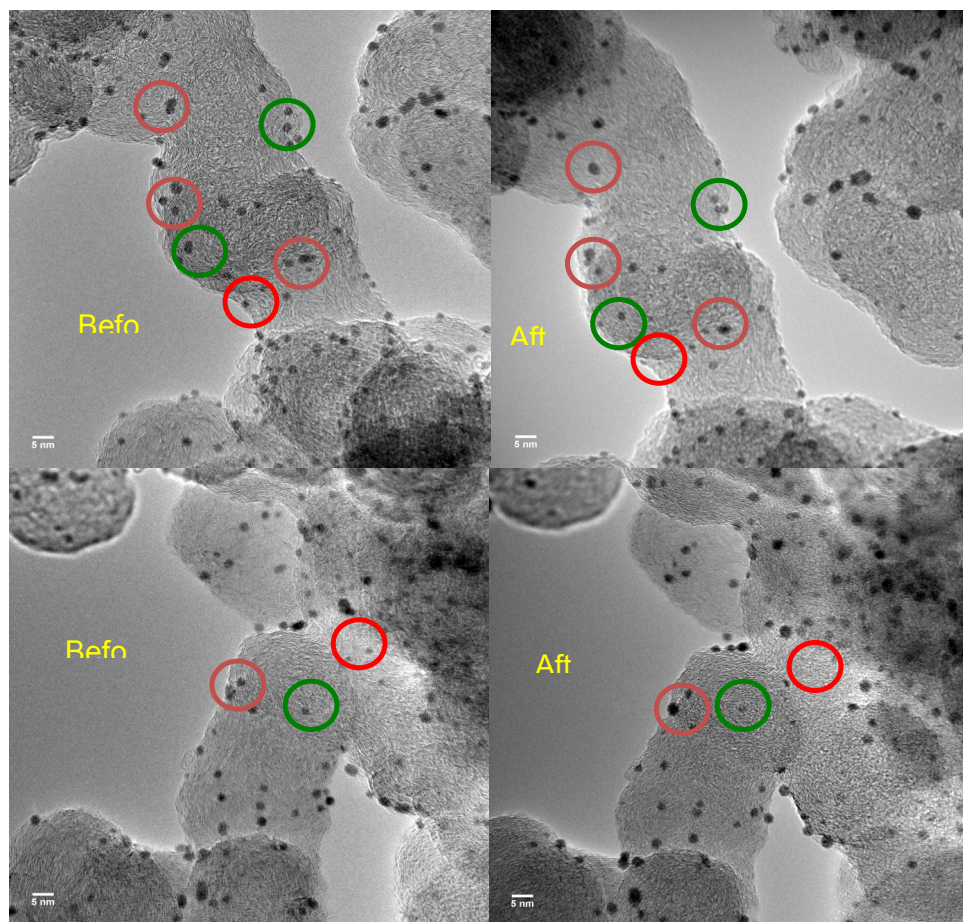


Figure 7. IL-TEM images taken before and after accelerated corrosion test (sample was subjected to 30,000 cycles between 0.6 and 1.1 V at 200 mV s⁻¹ in 0.1 M HClO₄)

Figure 7 displays the set of TEM images, before and after the accelerated corrosion test under these conditions. According to the images, there is some reduction in particle size (green circles), nanoparticle disappearance (red circles) and mild sintering (blue circles). The size distribution graph, shown in Figure 8a, confirms this trend: there are a higher number of large particles and there is an appreciable increase in the number of small nanoparticles. The total volume and the area of Pt present in the IL images have been calculated before and after the ORR experiment, as shown in Figure 8b. A decrease of around 30 % in Pt volume was observed after the ORR corrosion experiment. These results explain the deactivation of 35 mV $\square E_{1/2}$ in ORR activity measured before and after aging, as shown in Figure 8c. We observed a similar trend when the catalyst was cycled 3,000 times between 0.6 and 1.2 V, although the degradation was more pronounced; this suggests that increasing the upper potential limit accelerates the catalyst corrosion.

Our results constitute the first direct, microscopic results that the degradation in performance of Pt/C catalysts is primarily due to Pt dissolution. We anticipate that similar degradation of Pt would occur during the start up and shut down cycles of a fuel cell. As such, future catalyst design and synthesis should be tailored towards strategies to prevent Pt dissolution.

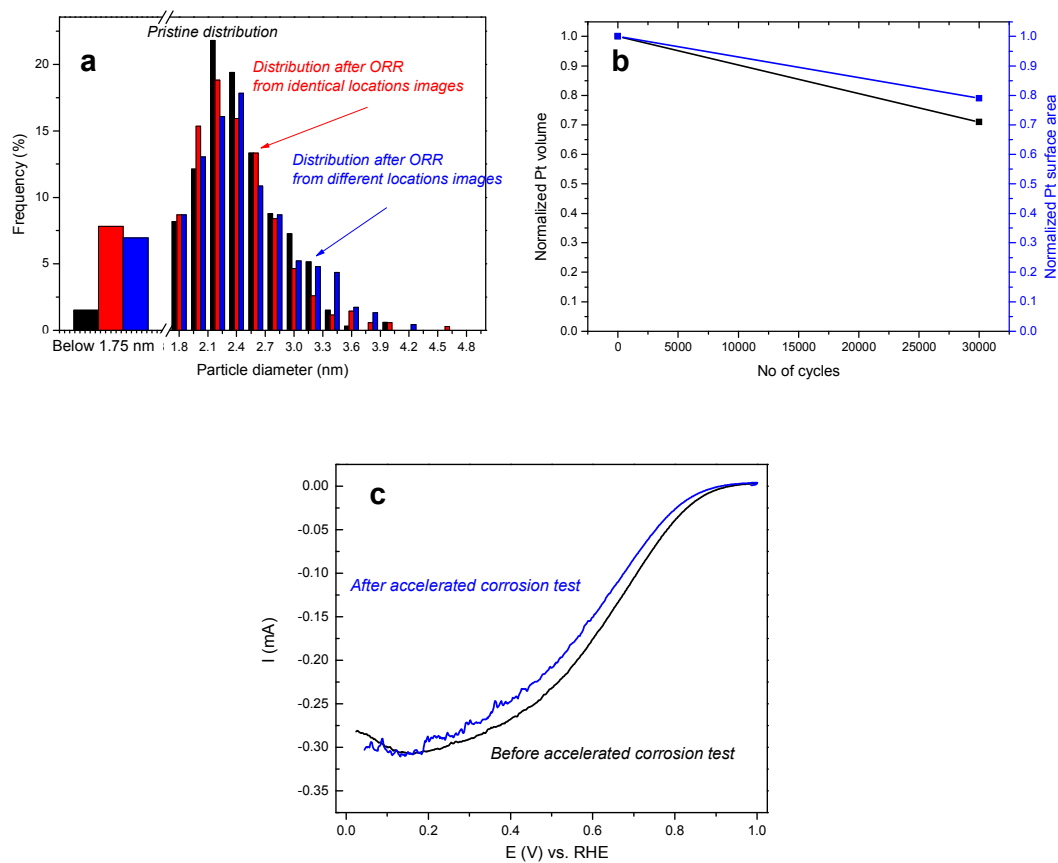


Figure 8. a. Nanoparticle size distribution graphs of sample subjected to 30,000 cycles between 0.6 and 1.1 V, scan rate = 200 mVs^{-1} (black histogram: distribution from pristine sample (303 particles), red histograms: distribution after accelerated corrosion test from identical locations (233 particles), blue histograms: distribution after accelerated corrosion test from different locations (230 particles); b. Normalized amount and surface area of Pt calculated before and after accelerated corrosion test from identical locations images c. ORR curve of sample before (black line) and after (blue line) accelerated corrosion test

(b) Stabilising Pt/C by alloying with Au, W and Nb

On the basis of the IL-TEM studies described above, we aimed to develop strategies to prevent the dissolution of Pt/C catalysts by alloying the Pt with Au, W and Nb (MS1 and MS12 Milestone reports). This work was inspired by experiments by Adzic and co-workers.³ They showed that the electrochemical deposition of submonolayer amounts of Au onto Pt/C stabilized the catalyst upon extensive cycling between 0.6 V and 1.1 V. The increased stability of these catalysts can be understood on the basis that the presence of these elements could protect the atoms on the catalyst most prone to dissolution, the undercoordinated sites.⁴ These sites are the most reactive sites on the catalyst; as such we would expect that there would be a driving force for metals such as Au or metal oxides such as WO_x or NbO_x to occupy them and hence prevent the dissolution of the underlying Pt.

We synthesized these Pt alloy/C nanoparticles using the inverse micelle method used for the IL-TEM studies described above. Our first attempt was based on AuPt/C nanoparticles, similar to those of Adzic and co-workers.³ We anticipated that this synthesis method could afford a greater deal of control over the properties of the particles than the electrochemical method used by Adzic and co-workers. Moreover, it could be simpler to implement these catalysts in a real fuel cell.

Unfortunately, we found that for our catalysts, Au did not prevent the loss of Pt surface area when cycling up to 1.2 V (RHE). However, it might be the case that they would exhibit enhanced stability over pure Pt when cycled to 1.1 V, corresponding to the original conditions of Adzic and co-workers.

We also tried other, similar approaches, but incorporating W and Nb into the particles. Although alloying the Pt with W resulted in modest improvements to the electrocatalytic activity, we were still unable to stabilize the particles.

(c) Model studies of size-selected Pt and Pt_xY nanoparticles.^{5, 6}

We developed an experimental design and technique to evaluate the kinetics of the ORR upon Pt and Pt alloy nanoparticles under carefully controlled, well designed conditions (MS1 and MS9 Milestone reports). To this end, we have been studying the properties of Pt nanoparticles synthesized using a mass selected cluster source. This is a physical vapour deposition method, which allows size selected Pt and Pt_3Y nanoparticles to be deposited on a glassy carbon disc. The primary aim is to verify whether it is possible to reproduce the high activity of bulk, polycrystalline Pt_3Y , which we reported in an earlier investigation⁷, albeit in the more technologically relevant nanoparticulate form.

We are able to characterize the materials ex-situ using a large number of different techniques to ascertain the bulk and surface composition as well as morphology. These techniques include temperature programmed desorption (TPD), scanning electron microscopy

(SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS) and X-ray photoelectron spectroscopy (XPS). Following the ex-situ characterization, we tested the catalysts for oxygen reduction using a rotating disk electrode (RDE) assembly in a liquid three electrode cell containing 0.1 M HClO_4 .

The first step was to test the activity of size selected pure Pt nanoparticles. Improvements to the reaction kinetics require an understanding of the fundamental factors that control the ORR activity of Pt, in particular the dependence of the ORR rate as a function of particle size. This has been the topic of numerous studies in the last few decades⁸(and references therein). However, most earlier experiments are performed on catalysts supported on high surface area catalysts, which are synthesized using chemical techniques. By supporting the catalysts on planar surfaces, we avoid the need to correct for capacitive currents. By using mass selected particles, we avoid effects due to surfactant molecules that would be present on particles produced using chemical synthesis methods.

Figure 9 shows the CO temperature programmed desorption spectra obtained from four different samples, in comparison to the particle size histograms and representative transmission electron microscopy (TEM) micrographs. The CO desorption spectra serve as a means of determining the orientation of the surface facets of the nanoparticles. The hatched areas on the spectra, relative to the total area, provide us with an estimate of the fraction of terraces. Evidently the proportion of terraces increases with an increase in particle size.

The ORR specific activity and mass activity for the different catalysts studied is plotted in Figure 10. Our results agree well with earlier theoretical predictions; in particular (a) extended Pt surfaces exhibit the same activity as 11 nm nanoparticles, and (b) there is a four-fold increase in ORR activity going from 2 nm Pt particles to extended surfaces^{9, 10}. Moreover, we confirm that the Pt mass activity for the ORR shows a maximum for a particle size of 3nm.^{10, 11} The electrochemical experiments are also supported by the CO-TPD results: the ORR activity approximately scales with the proportion of terraces, as demonstrated by Figure 10. In summary, we have demonstrated that the specific activity of the oxygen reduction reaction over Pt nanoparticles decreases with particle size, with a maximum in mass activity for 3nm particles. The ORR activity roughly correlates with the proportion of terraces. We conclude that the active sites for the ORR are only located on the terraces of the nanoparticles, in agreement with earlier theoretical predictions^{9, 10}.

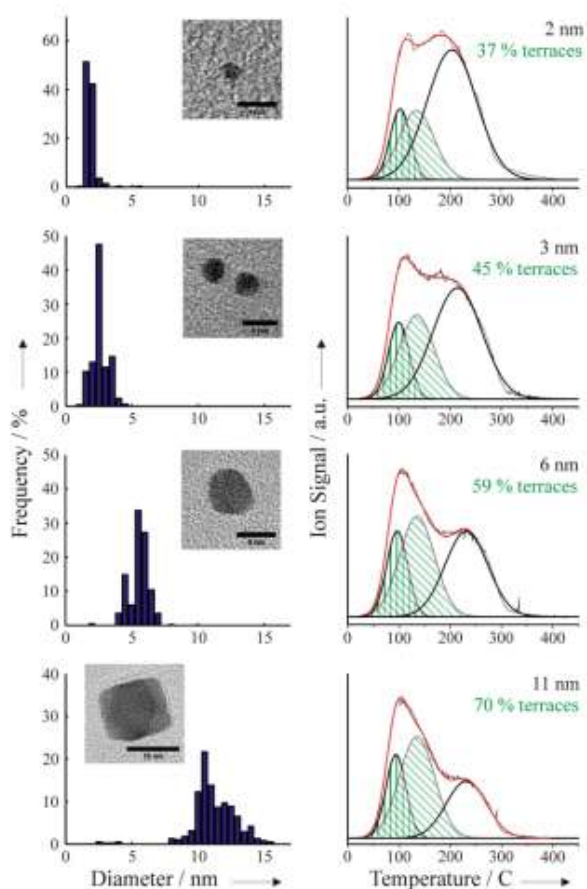


Figure 9. Nanoparticle size distributions and the associated CO desorption profiles of Pt/SiO₂ samples for particle sizes of 2 nm, 3 nm, 6 nm and 11 nm. Included with each TPD profile are the integrated proportions of terraced particle surface area.

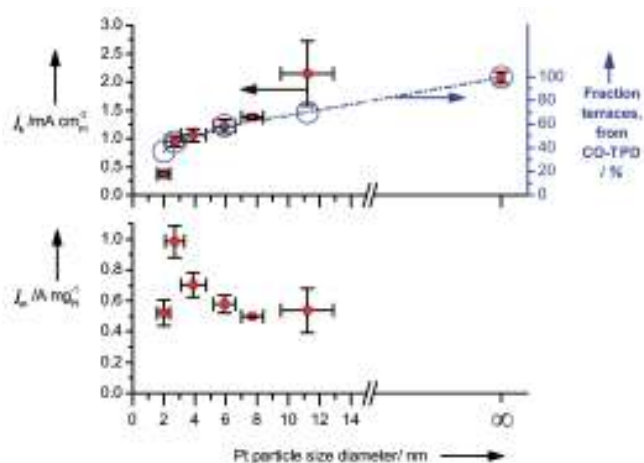


Figure 10. ORR kinetic current densities (above) and mass activities (below) at 0.9 V (RHE) of different particle sizes, from CV's in O₂-saturated 0.1 M HClO₄, sweep rate= 50 mVs⁻¹, 1600 rpm at 23 °C. The blue circles in the above plot represent proportions of terraced particle surface area calculated from CO TPD profiles.

Having developed the methodology for pure Pt nanoparticles, we then went on to test Pt_xY nanoparticles. According to our initial measurements, the Pt₃Y nanoparticles shown ~4 fold improvement in surface specific oxygen reduction activity over Pt nanoparticles of a similar size, and a mass activity of 1.6 A mg⁻¹, i.e. a 10-fold improvement of the state of the art pure Pt/C catalysts used in a fuel cell.¹¹

1.3.4 Work Done at Southern University of Denmark (SDU)

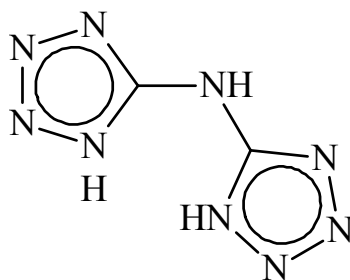
The work at Department of Chemical Engineering, Biotechnology and Environmental Technology (KBM) as well as on Institute of Physics and Chemistry (IFK) at Southern University of Denmark has focused on two work packages: WP1 Catalyst Synthesis by wet routes (task 1.2.1) and WP1 Catalyst characterization and test (task 1.3). Incidentally, a small contribution was made late in the project to WP2: Development of support materials as SiC material made at the Department of Physics and Chemistry was made available to the project.

In the project a post doc was employed at the two institutes. It was found practical that the same person was responsible for catalyst synthesis as well as catalyst characterization in order to avoid that "waiting time" became an issue. In the beginning of the project the majority of the time was used on catalyst synthesis under the guidance of Professor Hans Toftlund. After Professor Hans Toftlunds unfortunate death in November 2009 the post.doc. Pia Nielsen concluded the work on the catalyst synthesis and the work focused on catalyst characterization for the remaining period. Late in the project a new type of catalyst supports based on SiC and developed at the surface physics group at IFK became available. A method to make the otherwise electronically insulating SiC substrates conductive was successfully developed and some initial tests which confirmed "proof of concept" were performed just before the end of the project.

Catalyst Synthesis by Wet Routes

Explosive ligands:

In the synthetic part of this project platinum black electrodes were sought synthesised by decomposition of platinum complexes with metastable ligands as H₃bta (*N*-(1*H*-tetrazol-5-yl)-1*H*-tetrazol-5-amine),



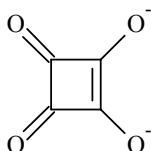
The idea behind is to exploit the fact that this ligand is potentially explosive and therefore easy to remove by controlled conversion of the ligand into N₂ (for instance by heating) if used in complexes, thus leaving only the central Platinum atom.

Heated on a Kofler bench the platinum complex exploded at approximately 280 °C – indicating that it should be possible to coat suitable substrates using this technique even at not so elevated temperatures. Unfortunately the materials showed to be insoluble in all common solvents tested. X-ray powder diffractometry on the material formed by decomposition of the

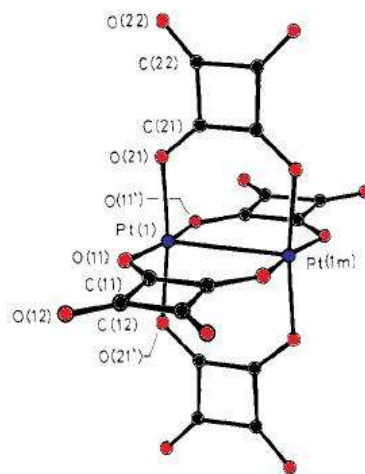
complex showed it to be platinum, but with a particle size of approx. 20 nm, which is larger than optimal for fuel cell electrodes. Due to this and to the lack of a suitable impregnation method for the complex due to its insolubility it was decided to stop further development and focus on some metal organic frameworks.

Metal Organic Frameworks MOFs:

Some Metal Organic Frameworks (MOFs) was found to produce platinum containing electrode materials with good catalytic properties.



The squa²⁻ anion.



Crystal structure of the [Pt₂(squa)₄]⁴⁻ anion.

Especially one of the MOFs, the Pt-Pt MOF, which has the chemical composition [Pt(NH₃)₄]_x[Pt₂(squa)₄]_y showed some very good results. The initial catalytic experiments revealed a compound with catalytic properties comparable to those of the well-known HighSpec 1000 catalyst.

All the MOFs were synthesised by titrating solutions of [Pt(NH₃)₄]^{2+/3+} in water with solutions of Na_x[Pt₂(squa)₄] (also in water).

The Pt-Pt MOF was boiled in order to convert it to platinum black (PB). Although powder-XRD did not confirm that platinum black was formed, the formed materials possess catalytic abilities comparable to commercially available catalysts and they did show cyclic voltammograms with typical platinum features. There may be two reasons for this discrepancy. Either the amount formed were below the detection limit of the X-ray diffractometer or the platinum was formed as an amorphous phase.

One problem, from a commercial point of view, was that one of the essential precursors was a byproduct from another synthesis and there were no instructions on how to synthesize it. Information about the compound was also very scarce; only one article concerning the anion existed. It dealt with the X-ray structure of the barium salt, Ba₂[Pt₂(squa)₄]. Hence efforts were made to try and develop a synthetic route for Na_x[Pt₂(squa)₄]. First choice was to employ a better starting material than *cis*-platinum. The tetraaquaplatinum(II) complex,

$[\text{Pt}(\text{OH}_2)_4]^{2+}$ was chosen as experience has proven that it was necessary in order to make suitable platinum materials. Testing the compound by reacting it with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ gave the desired green gel-like compound similar to the one seen in the Pt-Pt synthesis. The green gel was subsequently proven to be the same as the previous synthesized Pt-Pt MOF. Unfortunately there still exists one drawback; so far it has not yet been possible to control the amount of $\text{Na}_x[\text{Pt}_2(\text{squa})_4]$.

Catalyst characterization and test

The catalyst materials were characterized by cyclic voltammetry (CV). The measurements were performed by covering one side of a gold electrode with a suspension of the MOF in question. All CV measurements were done with the impregnated gold electrode as working electrode, calomel as the reference electrode, and a platinum blank electrode as counter electrode with 1 M H_2SO_4 as the electrolyte.

The most intriguing part of the CV is the presence of a fairly large middle peak in the hydrogen desorption area. When compared to data recorded on HighSpec 1000 (HS1000) the three peaks are not the same for the Pt-Pt MOF as they are for HS1000.

This may be significant because the different peaks are known to be caused by different platinum crystal faces with different catalytic properties. Initial catalytic experiments were therefore performed with the same setup except for the electrolyte. Instead of 1 M H_2SO_4 these measurements were done using an 0.5 M H_2SO_4 + 0.5 M CH_3OH solution. Some of the data are depicted in the figure. While HS1000 seems to have the best catalytic properties the properties of the Pt-Pt MOF still seem significant – especially since Pt-Pt seems to catalyze the oxidation of methanol already at 0,396 V whereas HS1000 does not do so until 0,495 V (values relative to calomel).

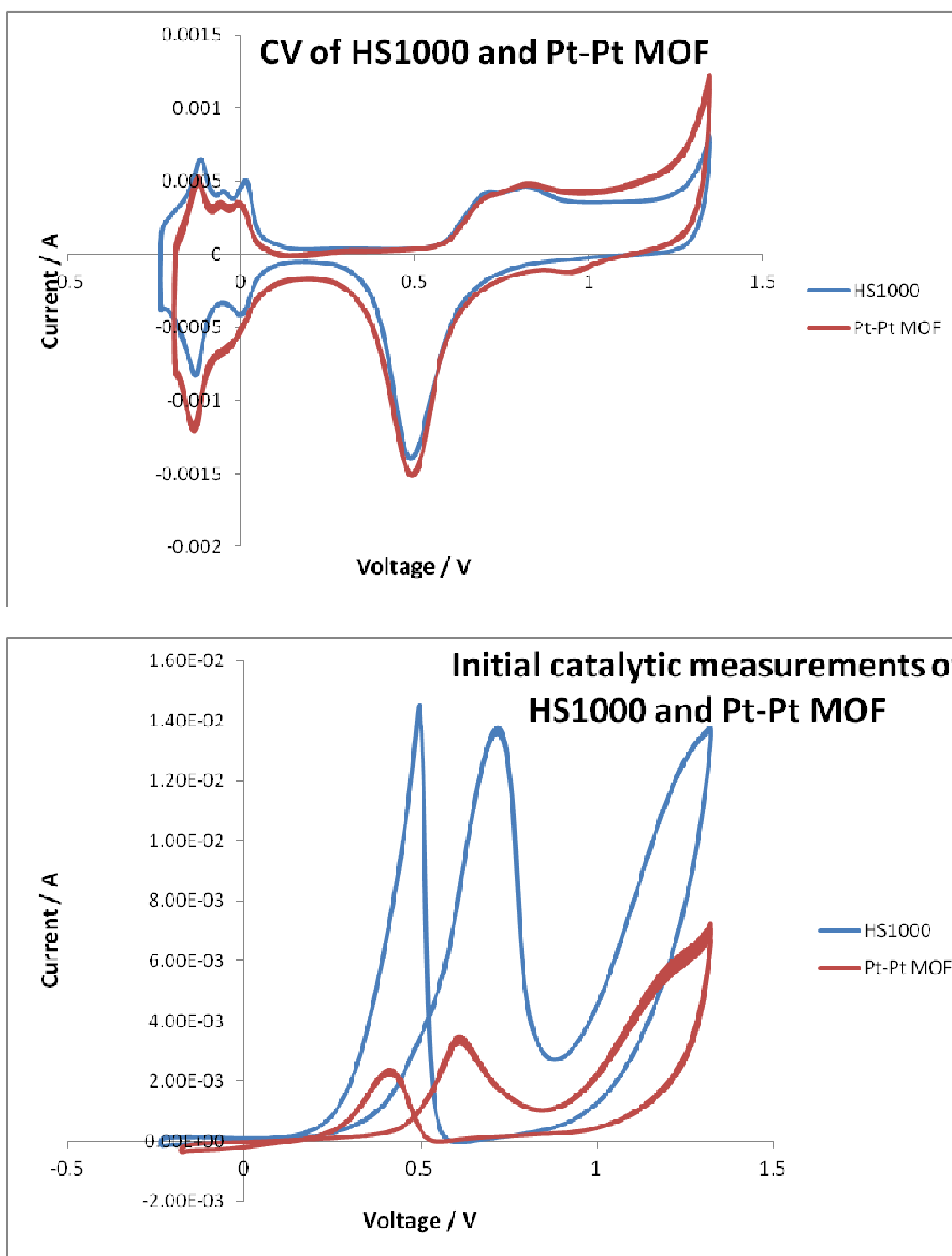


Figure 11.

Modification of carbons

At the surface physics group at the Department of Physics and Chemistry at SDU ongoing work on transformation of carbons into silicon carbide came to our attention and it was decided to try to modify Vulcan carbon supports by the method they had developed. The modi-

fication was successful, but the material was an insulator. It was then decided to try similar activation procedures for the SiC substrate as those developed in the N-INNER "NanoDuraMea" project for activation of nano- carbon tubes and -fibers. The method was successful and a preliminary characterization using cyclic voltammetry (CV) was made. In the figure the results of different treated SiC substrates platinized using the polyol method has been compared to a Vulcan based catalyst. Although the activity is smaller than for the Vulcan based material the characteristic peaks of platinum is evident. It should also be noted that the CV baseline is horizontal proving that the SiC material has been made electronically conductive. The work has been continued in the Catbooster project and we are now able to produce electrodes which show similar activities as Vulcan based electrodes.

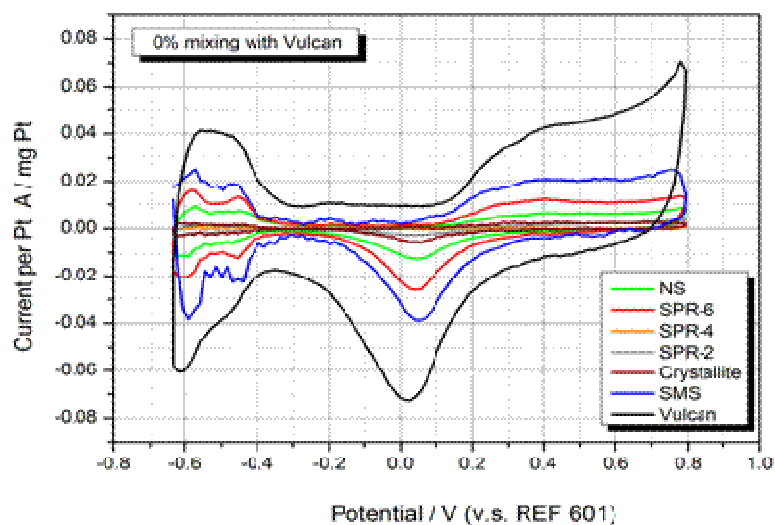


Figure 12.

Conclusion

Platinum containing Metal Organic Framework precursors have been successfully prepared. Although platinum could not be detected by X-ray analysis the materials showed unmistakably platinum catalytic activity and the oxidation of methanol was found to take place at lower potentials than on a standard platinum fuel cell catalyst. Unfortunately no satisfactory preparation method for the precursor was found. Different catalytic activities for the methanol oxidation reaction has also been found on other substrates using more ordinary platinum catalyst and the interplay between substrate and catalyst is investigated further in the Catbooster project. Vulcan carbon substrates have successfully been converted into silicon carbon substrates which have been proven useful as catalyst substrates.

1.3.5 Work Done at Aalborg University (AAU)

Department of Energy Technology at Aalborg University was actively involved in Modelling (WP5). The present section summarizes the overall work and accomplished results.

Summary

The overall progress of the modelling activities at AAU has been extremely satisfactory with numerous conference and journal publications along with two potential inventions concerning the catalyst layer that will be described below. Moreover, a potential patent application resulted indirectly out of this project.

Part of the project was also the education of one PhD student on the side of AAU, Anders Christian Olesen. His task was to develop a PEMFC/DMFC model based on the state-of-the-art commercial software package CFX-13 (ANSYS Inc.), and the idea was to transfer parts of the physical model developed by T. Berning and S. Kær into a more up-to-date computer package. Progress has been excellent, and several publications are in preparation.

In detail the capabilities of both computer models as of 2011 are:

PEMFC model based on CFX-4 (T. Berning, S. K. Kær)

- The computational domain includes anode and cathode bipolar plates (for heat transfer), gas diffusion layers, micro-porous layers and catalyst layers, as well as the polymer electrolyte membrane.
- Temperature distribution, oxygen and hydrogen distribution, water vapour and liquid water distribution by accounting for the key material properties of the porous media, determination of limiting current density, membrane water content, water balance.
- World-leading description of liquid water transport in porous media by use of the "multi-fluid approach" available in CFX-4 (not available in Fluent 6).
- An important contribution has been the formulation and implementation of a boundary condition for the liquid phase at the interface between the GDL and the flow channel. This part was never treated in a physically correct manner, and our proposed boundary condition is believed to be the best to date.
- State-of the-art description of water transport through the polymer electrolyte membrane. We were able to show that nearly all previous publications on water transport in proton exchange membranes during the passage of current are flawed because they neglect one important mathematical term.
- A comprehensive numerical study comparing the frequently used parallel channel (or serpentine channel) flow field with the interdigitated flow field revealed that there are significant advantages of the latter compared to the conventional design. These advantages include improved heat and mass transfer and the possibility of operating at low stoichiometric flow ratios. The engineering problems associated with the interdigitated flow field, e.g. the required uniform compression of the porous media, are

believed to be manageable. Altogether, the advantages of using the interdigitated design seem to outweigh the drawbacks. Consequently, we recommend the use of the interdigitated flow field for PEMFC.

PEMFC/DMFC model based on CFX-12 (Ph.D. cand. A. C. Olesen, T. Berning, S. K. Kær)

- The computational domain includes anode and cathode bipolar plates (for heat transfer), gas diffusion layers, micro-porous layers and catalyst layers, as well as the polymer electrolyte membrane.
- State-of-the-art description of multiphase flow in channels and porous media.
- A. Olesen visited the Ansys Inc. development center near London, UK, in order to learn about and improve the implementation of multi-phase flow with great success.
- The model can run in PEMFC mode or DMFC mode, but the focus is on DMFC mode.
- The compression effect of porous media under land has been accounted for and a conference paper and a journal paper were published.
- Methanol cross-over has been studied and a paper is in preparation.
- Validation experiments for the DMFC that have been carried out by A. C. Olesen at IRD A/S during the fall of 2011.

CO poisoning (WP5 Task 5.1)

In contrast to our assumption when starting the project, the AAU fuel cell model based on the commercial software package Fluent 6 (ANSYS Inc.) was not working satisfactorily as of 2007. In addition, the principal researcher, Dr. Torsten Berning, was an expert in using the software package CFX-4 (ANSYS Inc.). Hence it was decided to abandon the Fluent model and start developing a PEMFC model based on CFX-4.

It was primarily due to this reason that the CO-poisoning effect was not investigated. In addition, some potential break-through inventions were made at AAU that required to be investigated in more detail within the scope of the current project; the model that was developed from scratch did not reach a point of development that allowed for the investigation of the CO poisoning effect.

Flow distribution in micro-structures (WP5 Task 5.2)

In terms of flow distribution in microstructures we have made several major contributions that have been published:

- The importance of the pore-size distribution (PSD) on the liquid water level (accumulation) in porous media was found from reasoning: the driving force for capillary transport of liquid water inside the porous media is primarily the derivation of the capillary pressure with saturation (liquid volume fraction): $\partial p_c / \partial s$. The higher this term is the higher is the driving force for liquid water to move through the porous medium. In the literature the dependency of the capillary pressure on saturation is typically given by the co-called Leverett function, which is a cubical dependency. By looking at the so-called Young-Laplace equation that can be used to calculate the capillary pressure in a single pore as function of the pore-diameter, and comparing it to the Leverett equation it emerged that the Leverett equation must be closely related to the PSD of the porous medium, and a wider PSD should yield better liquid water transport. Based on this theory the literature was studied, and it provided an excellent match with qualitative data concerning the "flooding" behaviour and the type of porous media that was employed. Hence, a wider PSD leads to improved liquid water transport. A practical example is that SGL type of diffusion media typically shows better performance under "wet" conditions than Toray paper. For the catalyst layer it was suggested that a wider PSD can conceivably be obtained by varying and mixing the size of the carbon carriers inside the CL, expecting that a wider grain size distribution also leads to a wider PSD. This theory has been communicated to IRD/Cabot.
- The role of the electrolyte loading in the CL's is seen in a different light now, as the specific surface area of electrolyte is critical for the water absorption to the membrane and the overall water balance. A "water uptake layer" was invented that facilitates water absorption at the cathode CL and may allow for dry fuel cell operation. Hence, we were able to shed new light on the role of the CL morphology on the water balance in PEMFC.
- The effect of the compression of the porous media on the liquid saturation level was modelled in a separate study by Olesen et al., and the qualitative effect on the expected current distribution was determined and published.

Milestones

In detail, AAU was responsible for the following milestones:

Milestone M17: Report on CFD modelling of CO poisoning

In research projects AAU has developed and demonstrated a CFD based modelling approach that accounts for CO poisoning. Initially, it was the intention to continue this work under this contract. During the project execution it was decided to change the focus away from this activity and hence a report on the CO poisoning model was not completed. There are two main reasons for this. Firstly, it was decided to rewrite the entire fuel cell model from scratch to take advantage of superior capabilities of another CFD code in a critical area, water transport modelling. Secondly, we realized there were much more significant contributions to be made in the other focus areas of the project i.e. water transport and water management.

Milestone M18: Report on CFD modelling of electrode microstructure

This topic was covered extensively in the bi-annual reports. Two important inventions concerning the micro-structure were the "water uptake layer" and the "catalyst layer with distributed grain size of the carbon carrier to facilitate liquid water transport" and have been described extensively in the bi-annual reports and in several publications.

Milestone M19: Validation of the complete CFD modelling

The model was used in order to define validation experiments. AAU and IRD discussed a set of experiments to verify key modelling findings ("water uptake layer", "catalyst layer with distributed grain size of the carbon carrier to facilitate liquid water transport"). However, due to a lack of time these experiments could not be finished.

Milestone M30: 4 papers with peer review published (or patents filed)

The excellent progress made on the side of AAU is best documented by the list of publications our group has had and is planning in the near future, when Anders C. Olesen finishes his PhD. The overall list includes 10 journal papers, 5 conference papers (probably more), one invited book chapter, and one potential patent. In addition, oral presentations were given at numerous national and international conferences.

Conclusions

The computational models developed at AAU based on CFX-4 (PEMFC; T. Berning, S. Kær) and on CFX-13 (DMFC/PEMFC A. Olesen, T. Berning, S. Kær) are state-of-the-art modelling tools with world leading capabilities to model multi-phase flow in fuel cells. The approach chosen is superior to the more commonly employed multiphase mixture (M^2) model in that it can include the fraction of hydrophilic pores in the porous transport layers, and consequently predict realistic liquid water distributions in fuel cells. Moreover, our model allows for the calculation of flow fields with significant pressure drop such as the interdigitated flow field, and so far this has not been modelled with the M^2 approach.

The PEMFC model also includes a novel membrane model for water transport that is superior to previously published approaches. With the aid of this model it was possible to invent the "water uptake layer", i.e. a layer with a high specific surface area of the electrolyte phase located adjacent to the membrane to facilitate water absorption, which was found to be the limiting step in the overall transport of water across the membrane. Common perception was that the net transport of water is a balance of diffusion and electro-osmotic drag, but our model has led to the fundamental understanding that diffusion is by far the predominant transport mechanisms of water inside the membrane. Moreover, it was found that a water uptake layer allows for membrane operation on completely dry inlet gases without the membrane drying out, a very important step in fuel cell development because it potentially reduces both cost and complexity of fuel cell systems.

In order to further refine the model and make it more robust we conducted extremely challenging simulations of low stoichiometry operation using the interdigitated flow field. It was found that the anode side may operate at a stoichiometric flow ratio as low as 1.05, and even lower, which opens new pathways for anode operation without the commonly used flow shifting or hydrogen recirculation, which may simplify the system and reduce cost. These modelling findings will have to be verified in future work.

Hence, while there was no activity in terms of CO poisoning due to the fact that we needed to develop a model from scratch, we had significant progress and contributions in terms of MEA design and morphology ("water uptake layer", "catalyst layer with increased carbon carrier grain size distribution to facilitate liquid water transport"). Finally, significant contributions were made in terms of fundamental understanding of water transport in fuel cells.

1.3.6 Work Done at Danish Power Systems (DPS)

The work at Danish Power Systems has focused on two work packages: WP4 Benchmarking and Pilot Fabrication of Catalyst and WP8 FC performance concerning HT-PEM (Task 1.1).

The present section summarizes the activities and most important results.

Benchmarking and Pilot Fabrication of Catalyst

Task 4.1 Benchmarking of Catalyst

For the HT-PEM three different catalysts have been investigated:

- The previous DPS reference catalyst supplied by Johnson Matthey (HiSPEC, 50% Pt/ carbon black).
- DTU prepared catalyst (40% Pt/carbon black)
- Current reference catalyst supplied by Johnson Matthey (HiSPEC, 60% Pt/carbon).

The previous reference catalyst was supplied by Johnson Matthey (HiSPEC, 50% Pt loading on carbon black). This catalyst has now been discontinued. DTU has a standard procedure for making a 40% catalyst (40% Pt loading on carbon black). However, the performance of this catalyst is not quite as good as the JM reference (c.f. Figure 13).

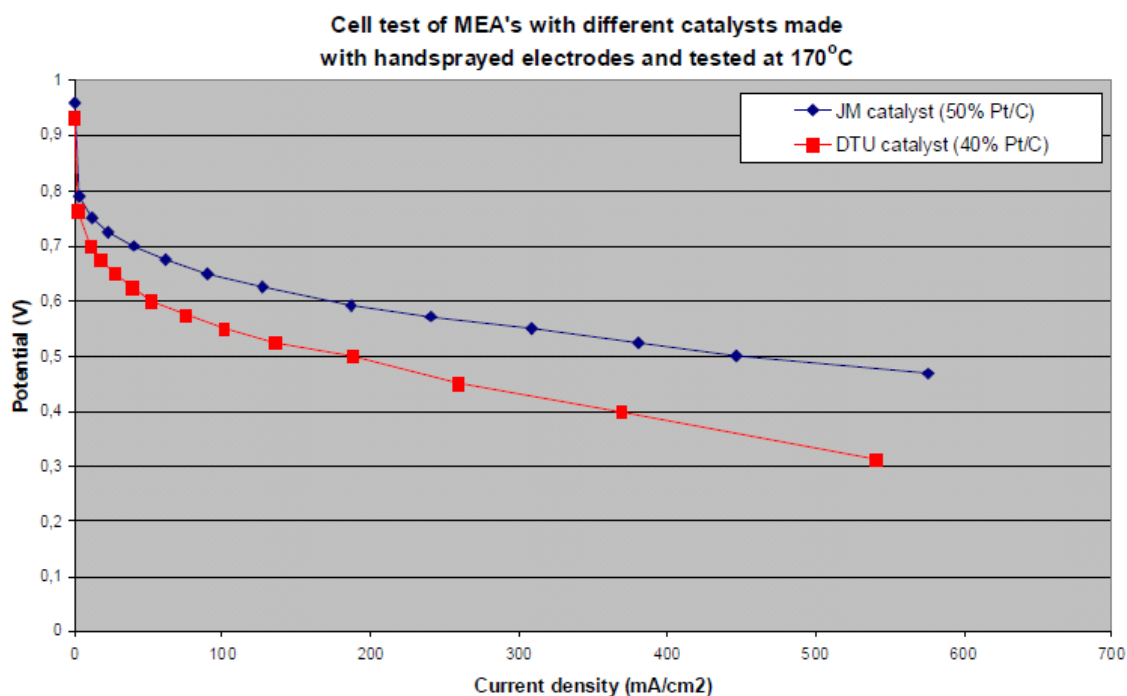


Figure 13. Both MEA's were made with approx. 0,7mg Pt/cm² on both the anode and the cathode side.

The main reason for the difference in performance that the one with the higher Pt/C loading have a thinner catalyst layer giving rise to a lower ohmic resistance of this layer. It is therefore not fair to say that the JM (Johnson Matthey) catalyst is better than the DTU catalyst, but if the focus is on the highest overall performance the JM catalyst should be chosen.

The new catalyst supplied by Johnson Matthey with higher Pt loading (60% Pt/carbon) has a significant better performance (see Task 8.1).

Single-cell test HT-PEM

HT-PEM electrodes with different Pt loadings and catalysts have been produced and tested at DPS. Three different catalysts have been investigated:

- The previous DPS reference catalyst supplied by Johnson Matthey (HiSPEC, 50% Pt/ carbon black).
- DTU prepared catalyst (40% Pt/carbon black) (results shown in Task 4.1).
- Current reference catalyst supplied by Johnson Matthey (HiSPEC, 60% Pt/carbon).

The results for the 50% Pt/C from Johnson Matthey are shown in Figure 14.

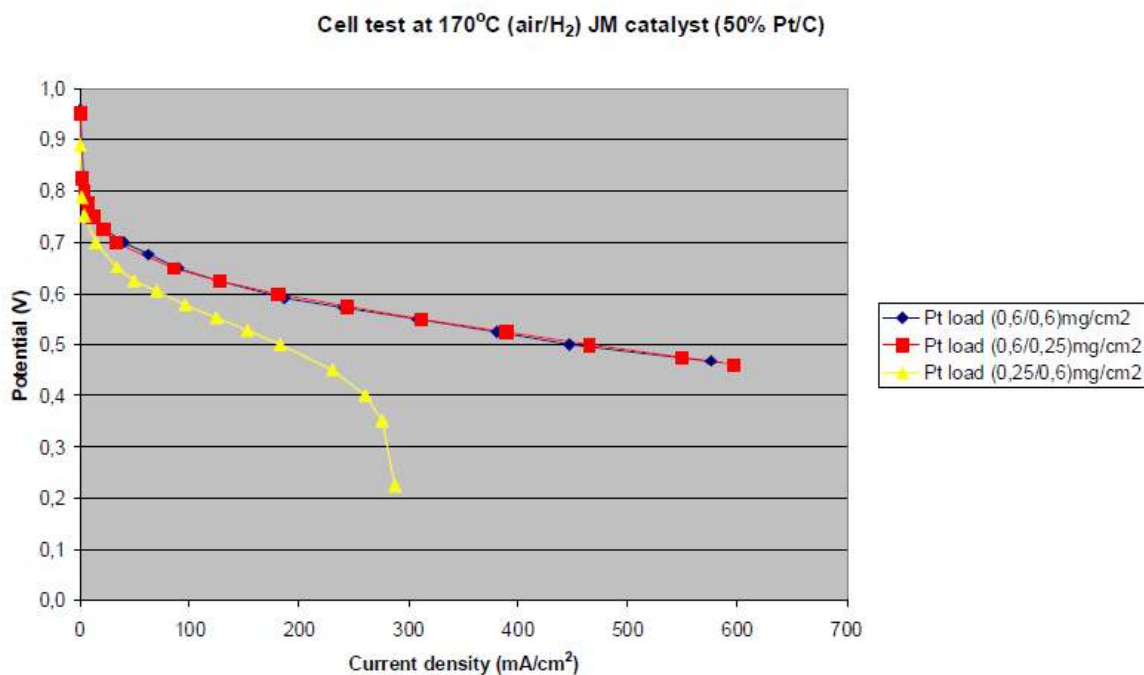


Figure 14. Pt load test showing that the performance of the MEA does not change by lowering the Pt load on the anode side to 0,25mg/cm² (from 0,6mg/cm²).

However, lowering the Pt load on the cathode side largely decreases the MEA performance. The Pt loadings are listed as cathode/anode.

The results show that:

- The Pt-loading on the anode (hydrogen) can be reduced from 0.66 mg/cm² (standard loading) to 0.25 mg/cm² without reducing the performance.
- A large reduction of Pt-loading on the cathode causes an increase in the activation loss.
- An increase in Pt-loading on the cathode does not reduce the activation loss.

The variation in Pt-loading is obtained by spraying different amounts of catalytic ink. A comparison with the published performance of BASF MEA's (<http://www.basf-fuelcell.com/en/projects/celtec-mea/celtec-p-1000-mea.html>) shows that the main reason for the lower performance is due to a higher activation loss in the DPS MEA's (the loss due to ohmic resistance is the same for BASF and DPS MEA's).

It can be concluded that increasing the Pt-loading on the cathode by spraying more ink is not a feasible solution for reducing the activation loss when using the 50% Pt/C catalyst. This is most likely due to a tradeoff between increased amount of Pt and increased thickness of the catalytic layer. The DPS effort was therefore focused on increasing the catalytic activity at the vicinity of the PBI membrane rather than making the catalyst layer thicker.

The investigations of the 60% Pt/C confirmed this approach. The results are shown in Figure 15.

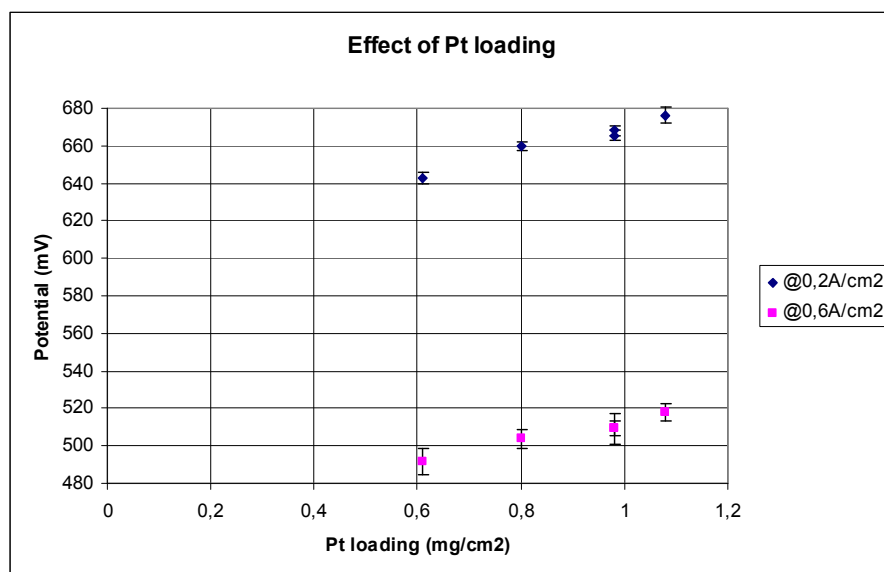


Figure 15. Effect of Pt loading on the cathode when using a 60% Pt/C from Johnson Matthey.

Manufacture:

The electrodes were produced using a hand held spray gun (50% Pt/C and DTU catalyst), potentially resulting in a large electrode to electrode variation. This was changed to a more reproducible electrode manufacturing process (c.f. Figure 16), where the electrode to electrode variation is expected to be significantly reduced.

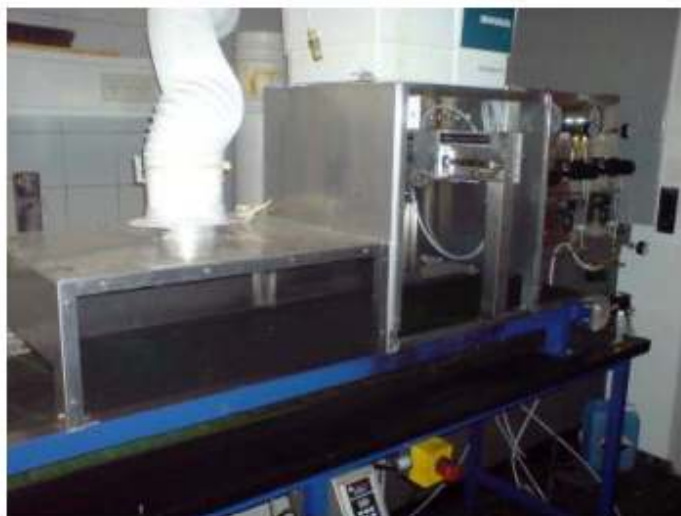


Figure 16. Picture of existing spraying equipment. The equipment was modified in order to enable a more reproducible electrode manufacturing process.

The modifications involved a spray gun /nozzle modification, which enables spraying of a highly well defined area and amount of catalytic ink. The experiences and results from the project has served as a basis for a further optimization of the electrode manufacturing process performed in the HotMEA project (c.f. Figure 17).



Figure 17. Photo of the equipment for the optimized electrode manufacturing process (build as a part of the HotMEA project).

Conclusion:

The DPS MEA's has improved in terms of:

- Improved performance due to the introduction of the new Johnson Matthey catalyst (60% Pt/C).
- Improved electrode manufacturing process

The project has been an important step towards obtaining the HotMEA consortium.

1.3.7 Work Done at IRD A/S (IRD)

The present section summarizes the activities and most important findings for the work performed at IRD. Many of the experimental results were presented and compiled in separate milestone reports. The work at IRD has been concentrated on:

Model Catalyst (WP3)

Benchmarking and Pilot Fabrication of Catalyst (WP4)

Interfacial MEA sealing (WP6)

Composite Electrode Design (WP7)

FC performance focus on LT-PEM & DMFC (WP8)

1.3.7.1 Model Catalyst

The overall project objective has been to develop new catalyst materials and supports with optimized stability and kinetic performance. The work at IRD has included model catalyst synthesized with a well characterized structure and texture for the purpose of understanding and investigating complex phenomena that can not be quantified or explained by working with practical complex catalysts and to develop and introduce techniques for electrochemical testing and screening of catalyst materials. The work was carried out by Signe Sarah Shim industrial Ph.D at the side of IRD in the period from January 2008 to September 2011 under supervision of CINP, DTU Department of Physics by Ib Chorkendoff and IRD.

In the literature there is substantial theoretical and experimental evidence suggesting that the stability of platinum particles is determined by their size. Thus, if the size of the platinum particle is enlarged their stability could be enhanced.

The platinum particles manufactured at DTU-FYS using the inverse micelle synthesis route for making mono-disperse nano-particles have been investigated at IRD as candidate for a model catalyst with precise control of composition and particle size.

The prepared platinum particles using the inverse micelle method resulted in particles of an average diameter around 3 nm (Figure 18). It was relatively difficult to alter the inverse micelle method to obtain larger platinum particles. The electrochemical active surface areas of the platinum synthesized by the inverse micelle method were very low compared to the theoretical calculated surface areas (Figure 19). It is suggested that the surfactant used in

the synthesis of the platinum particles are blocking part of the surface. Thus new synthesis methods were considered and explored.

Platinum particles synthesized using the polyol method also explored by DTU-KI were investigated. In the polyol method a Pt-salt is reduced by oxidized derivatives of ethylene glycol (EG). The different parameters in the synthesis such as pH, water to ethylene glycol ratio, time and temperature can have great influence on the resulting nano particles. The polyol method does appear very simple and does not require a stabilizing agent.

The experiments showed that a narrow gaussian particle size distribution of platinum particles can be achieved is obtained when the carbon dispersion is added after the reduction of platinum particles but the achieved average size of the particles is smaller (2 nm) than desired (5 nm). The model catalysts prepared were used to employ the experimental techniques together with DTU-FY. The techniques mainly focused on two issues, i.e. one is to elucidate the mechanism for platinum corrosion, the other is to establish a corrosion test method in which only the catalyst is tested and not the support of the particles. Using a non-destructive transmission electron microscopy technique enabled the observation of identical location of a catalyst before and after oxygen reduction reaction. The work was summarized and published in *Journal of Power Sources*, 196, 6085, (2011) and in the Ph.D Thesis report "Corrosion Studies of Platinum Nano-Particles for Fuel Cells" by Signe Sarah Shim (January 2012).

1.3.7.2 Benchmarking and Pilot Fabrication of Catalyst

New directions in nano-catalyst materials and supports with promising catalytic properties and stability have been developed by the project partners. In the search for new catalyst materials alternative routes and instructions for synthesizing and fabrication have been investigated as small lab-scale level in the project by DTU-KI, DTU-FY and SDU.

IRD's task has been evaluation of the potential for large-scale production of the developed catalysts based on results of small scale pilot fabrication together with input from partners:

Most of these important advances have focused on characterizing catalysts, discovering new catalysts and find routes for synthesis. The synthesis for these advanced materials are at the early development stage and focus on understanding and improving the scale-up and commercialization of laboratory-scale catalyst discoveries remain subject of vigorous research. According to the public literature, the common method to produce the carbon-supported Pt and PtRu electrocatalyst powders currently used in low temperature fuel cells is by precipitating or impregnating the Pt group metals using chemical reduction techniques in an aqueous slurry of carbon black support. These aqueous precipitation approaches are the typical methods by which many commercial heterogeneous catalyst powders are produced.

The approach and paths to the research and development of new electrocatalyst production methods in the project is summarized below.

Lab-scale synthesis

Dry-routes:

At SDU Platinum containing Metal Organic Framework precursors have been successfully prepared. Although platinum could not be detected by X-ray analysis the materials showed unmistakably platinum catalytic activity and the oxidation of methanol was found to take place at lower potentials than on a standard platinum fuel cell catalyst. Unfortunately no satisfactory preparation method for the precursor was found.

Inverse-micelle method:

At DTU-FY materials development performed for Pt/C catalyst that were synthesized using an inverse-micelle method. The experiments allowed us to gain insight into how the nanoparticles look before and after activity measurements. IRD pursued the method however the electrochemical active surface areas of the platinum synthesized by the inverse micelle method were very low compared to the theoretical calculated surface areas.

Vapour deposition.

The method was used at DTU-FY for model studies of **selected Pt and Pt_xY nanoparticles**. The properties of Pt nanoparticles synthesized using a mass selected cluster source. This is a physical vapour deposition method, which allows size selected Pt and Pt₃Y nanoparticles to be deposited on a glassy carbon disc.

Pilot scale catalyst fabrication:

It was demonstrated the synthesis of noble-metal nanostructures can be achieved method the polyol process. The polyol process is a solution-phase method has the ability for preparing noble-metal nanostructures with well-defined morphologies. Although the exact mechanisms related to the formation of particular morphologies are yet to be fully understood. Both at IRD and DTU-KI the polyol method was explored by dispersing Pt particles in e.g. polyethylene glycol medium and then transferred to the supports. The last method proves to be less demanding for the carbon surface area and has been used for preparation of catalysts with various types of supports. Good dispersion was achieved with platinum particle size of around 2-5 nm.

At DTU-KI a large batch of catalyst synthesis was tried on a scale of totally 50 g of catalysts, consisting of 40 wt%Pt and 60 wt% carbon. It was based on a reduction-adsorption method. Uniform catalysts with good dispersity of platinum nanoparticles on carbon were achieved. Compared with the characterization results of previously prepared catalysts on small scales of up to a few grams, the reproducibility of the catalyst performance seemed acceptable. Anyhow, no efforts were made to fabricate the catalysts on a larger scale, though it is believed to be technically viable from the synthetic point of view.

Assessment and Perspectives of the process routes:

The technical and commercial feasibility of the developed fabrication routes have been analyzed.

Based on input from DTU-KI estimation of the manufacturing cost does not seem possible, at this stage of development however, of the material cost, the platinum salt is absolutely dominating (about 99%) while the cost of other chemicals is relatively negligible when Vulcan XC carbon blacks were used as the support. With nanostructured or functionalized support materials, synthesis was only made on small scales (1-2 g) primarily for characterization and performance test purpose. Graphitization of carbon blacks was made at up to 2800 °C in a furnace accessible by one partner, which is able to treat up to 10 g carbon black each batch. Carbon nanotubes e.g. of multiwalled types, are available commercially at a scale of kilograms. The price is about 5000-10,000 DDK/kg. For functionalized carbon nanotubes (with -OH or -COOH functional groups, for example, which are shown to be essential for both the catalyst dispersion and stabilization), this price would be more or less doubled. As a good estimation, the (functionalized) carbon nanotubes would accounts to up to 5-10 % of the overall material cost in case of the catalysts with carbon nanotubes as supports. In other words, the use of nano-structured carbon supports, preferably with functional groups, is expected to increase, though not decisively, the material cost. It is believed to be technically viable from the synthetic point of view.

At the lab-scale level there has been a steady progress in the ability to control the size, structure and composition of catalyst. From a practical application standpoint design and fabrication of the new novel catalyst particles with the desired surface structures will require additional development as well as methods to better control particle architecture and cost-effective to produce well defined structures. Explore these new synthesis methods and develop improved tools for catalyst scale-up and large -scale manufacturing will be needed to allow fabrication towards commercial application.

1.3.7.3 Interfacial MEA sealing

A polymer seal integrated with the Membrane Electrode Assemblies providing mechanical rigidity and chemical stability has been developed within the present project.

Due to Membrane Electrode Assembly (MEA) handling and durability issues, the most critical and difficult sealing interfaces within a FC stack are those between the MEA and the adjacent flow field/separator plates. There is a need to combine the MEA with an advanced seal that integrates chemical and mechanical integrity of MEA such that the durability and viability in Fuel Cell applications are met. The gas barrier properties of the bipolar arrangement are critical in order to prevent the fuel gas and oxidant gas supplied to the electrodes from leak-

ing out or prevent these two kinds of gases from mixing together, gaskets are arranged on the periphery of the bipolar plate with the MEA inside this gasket and the use of sealing/gasket material has become an important part of the total stack design. Both the materials used and the design employed can have a significant influence on performance.

The identification and characterization of the seal materials and development of processes for their fabrication within the present project has been completed as a joint effort between IRD and a sub supplier to IRD. Two materials were found to have acceptable properties to form a gasket. Two different approaches for processing of seals are being investigated in this project. Seal bound on the GDL or directly bound onto the polymer membrane edge on the MEA, Figure 20.

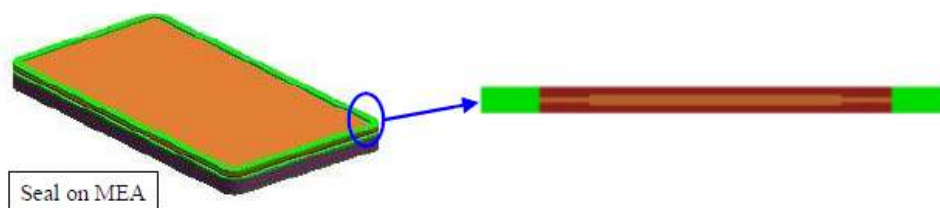


Figure 20. Interfacial MEA seal.

Since each cell in a fuel cell stack requires one or more seals and each stack contains up to hundreds of cells, it is necessary to develop a high-volume manufacturing process to make this feasible. This requires significant development of a molding process and new tooling to attain the required high precision molded seals. Together with a sub-supplier IRD has designed and generate pre-formed gaskets on a carrier frame at their manufacturing facility that could be subsequently applied to the MEA for validation of the edge seal and gaskets. Other seal designs such as flat/profiled gaskets were evaluated in the on-going EFP project on "Low Cost MEA Laminate and Bipolar Plate Fabrication Processes" (EFP- 63011-0068).

Design and Finite Element Analysis (FEA) of edge seal performed were conducted in order to fit into the IRD LT-PEM standard flow plates and stack design. As these flow plates presently have gasket channels, it is slightly different from the optimal solution with flat sealing, but it will allow testing of the edge seal concept in a well proven fuel cell stack design. Future use of the edge seal with flat sealing alone will need a redesign of the flow plates and the mould tools. This could provide a better and simpler solution, however these steps are to be considered after evaluation and validation of the concept.

In total two batches of seals were manufactured. Initial a batch of 50 seals were produced for evaluation in single-cells and verification in a small 10-cell prototype PEM FC stack. In the second batch a total of 200 prototype interfacial seals were produced.

Short stack evaluation

A Short stack assembly and test to evaluate the design and edge-seal concept prior to full scale demonstration was conducted. The results were first of all: Stack assembly with the new edge seal bound directly onto the GDL is a little more requiring than the state-of-the-art IRD MEAs. This is mainly due to the adhesion of the MEA to the gasket, in a way that the MEA has to be correctly placed in the first attempt. However, the adhesion has also some beneficial advantages in the long term as the MEA is totally fixed. The test includes 10 cells with edge-seals as well as 10 cells with state-of-the-art IRD MEAs. The test can be considered as an accelerated test, as the operational pattern is 4 hours on continuous load followed by a stop and one (1) hours stand-by to cool down. Furthermore, the stack has been tested in a dead-end pure hydrogen fuel circuit to simulate the operational parameters of IRDs μ CHP-unit. The test was conducted for 215 operational hours. The initial performance of the two set of MEAs are shown in Figure 21. The cells equipped with the edge-seals shown a slightly lower performance than the SoA (State-of-the-Art) IRD MEAs. This is most likely due to the stack compression set that is optimized to the standard IRD sealants and narrow design tolerances, inducing a difference in MEA compression for the 10-cells equipped with edge-sealant compared to the 10-cells with state-of-the-art seals. However, the observed degradation of the two sets of MEAs are equivalent, as can be seen in Figure 22.

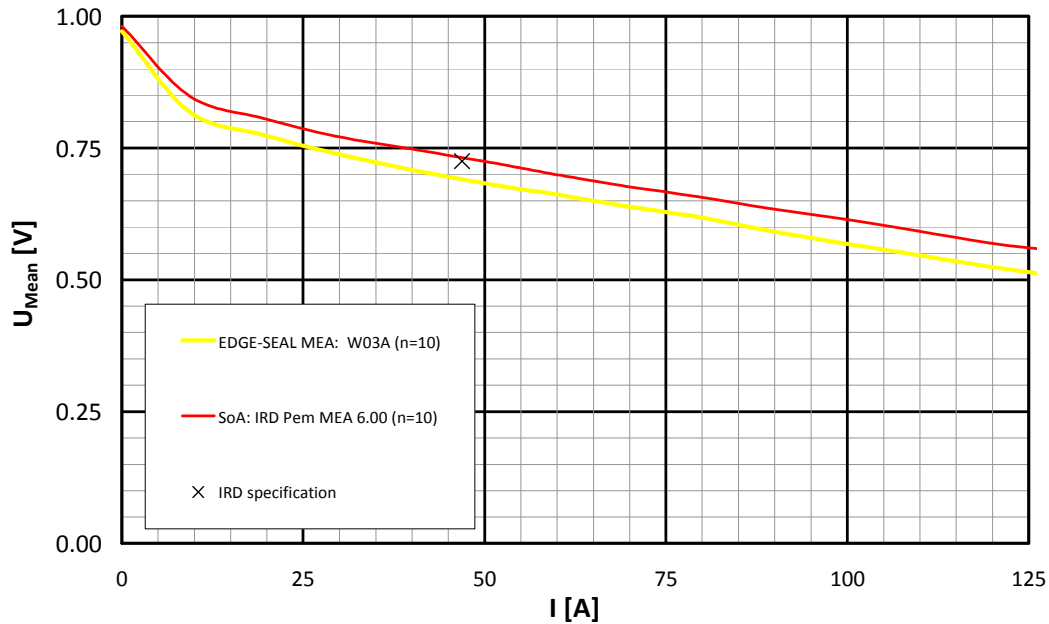


Figure 21. IV curves recorded at BoL operation.

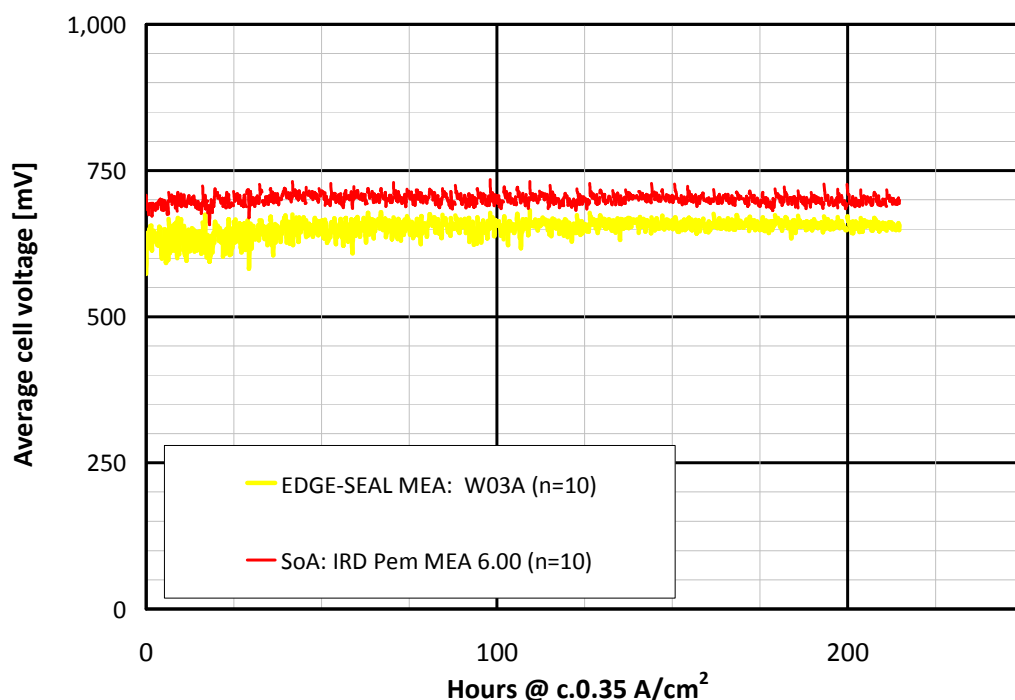


Figure 22. Test has been conducted for 215 operational hours in LT-PEM

Design modifications of the standard IRD PEM flow plate were necessary i.e. dimensional change of the seal recess in the bipolar plate.

The tools in the present project were constructed for prototype manufacture only in the quantity of ~1000 pieces. The simple set-up and construction allowing the use of “normal” steel plates and only limited features like vacuum venting and alignment.

Scale up for series production (~100.000 pc. +) require additional investment in prototype molds in hardened steel and implementation of various features for inserting, de-molding and flash-free molding. In addition investment in redesign of the flow plates and the required mould for the bipolar plate production could provide a better and simpler solution.

Based on these results a full-size LT-PEM stack was constructed and demonstrated for 900 operational hours, refer to section 1.3.7.5

The Danish national road-map target lifetimes for LT PEM stacks are 50000 hours in year 2012. This lifetime test has not been the objective of the present project and has to be demonstrated in another context.

1.3.7.4 Composite Electrode Design

The overall objective was to design and develop MEA's with improved power density and reduced catalyst loading. The MEA typically consists of an ion-conducting polymer membrane sandwiched between the anode and cathode; each contain a macroporous diffu-

sion backing and active catalyst layer. The pore size distribution of printed primer and catalyst layers is largely dictated by the pore size distribution of the powders used to make the printing ink; the printing process (using a small scale wet serigraphic printing) itself does not introduce any characteristic pore sizes. Another aspect of the electrode development is layer structure and its interface with the membrane. Even a catalyst with the best possible dispersion and intrinsic activity can demonstrate poor performance in a MEA if the electrode structure is not optimized to allow maximum extraction of catalyst performance (example illustrated in Figure 24).

Catalyst composite electrodes fabricated using catalyst powders with significant different morphology compared to traditional solution precipitation/impregnation methods were investigated and compared. Traditional commercial Pt/Ru carbon-supported catalyst powders (Taneka and Johnson Matthey) and catalyst powders supported on different modified carbon supports Ketjenblack (KB EC600), produced in collaboration with CABOT by a spray based method were used for the electrode development. The electrode surfaces were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in order to characterize the microscopic features of Pt/Ru nanoparticles on the carbon support material. The spray-based process results in formation of unique spherical, micron-sized aggregates consisting of sub-micron electrocatalyst particles where the nanometer sized active phases (Pt and PtRu) are highly dispersed on the surface of carbon supports (Figure 23).

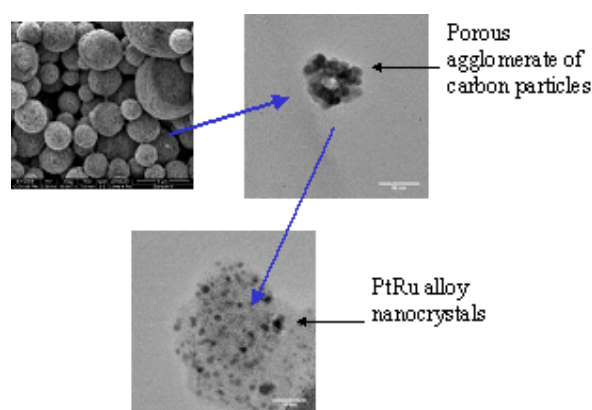


Figure 23 Hierarchical structure of the spray based Cabot electrocatalyst.

Electrodes with different Pt-loadings were prepared by IRD for testing in LT-PEM and DMFC single-cell testing with the various catalysts using an ultrasonic spray coating technique. The electrodes consist of a gas diffusion layer (GDL), and coated catalyst layer (CCL). The catalyst suspension was ultrasonic coated onto a gas diffusion layer with subsequent evaporation of the solvent (Process A) or directly onto the membrane (Process B). Many of the experimental results were presented and compiled in periodic reports and separate milestone reports.

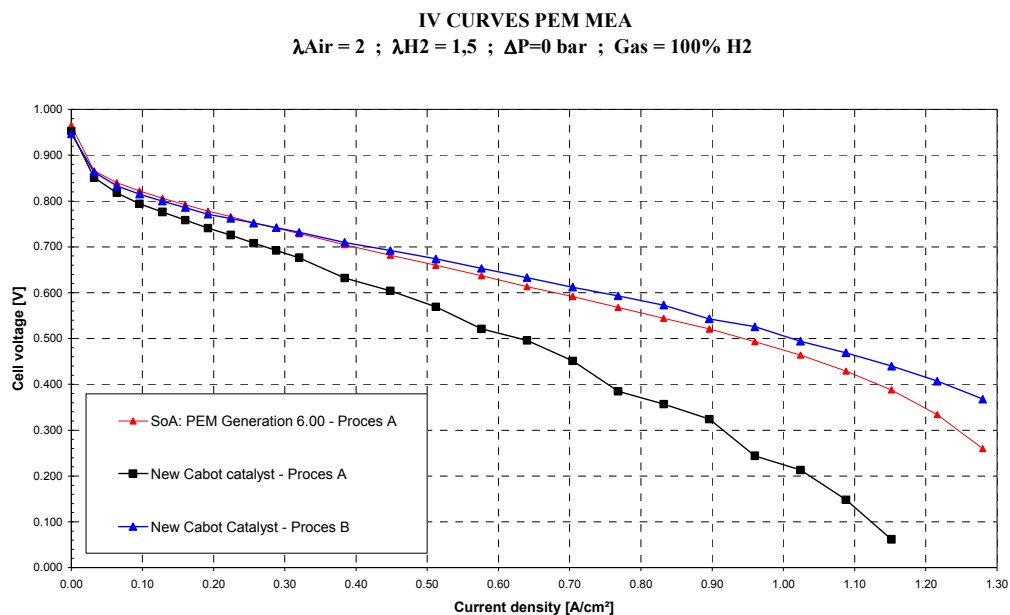


Figure 24. Due to the very different structure of these catalyst compared to traditionally prepared catalyst (Tanaka and Johnson Matthey) an initial screening of the effect on performance with various ionomer content using the IRD standard process method (process A) for coating electrodes was tested. The processing of the electrode was modified (process B) to a level where the performance improved significant, and provide similar or slightly better performance than the state-of-art IRD PEM MEA based on traditional catalyst materials.

Composite electrode structures for DMFC applications were optimized significant by reducing the Pt-loading by 50% compared to SoA (Stat-of-the-Art) at project start. Figure 25 show the DMFC MEA 7.00 performance achieved with reduced catalyst loading compared to SoA at project begin referred to as MEA 5.00.

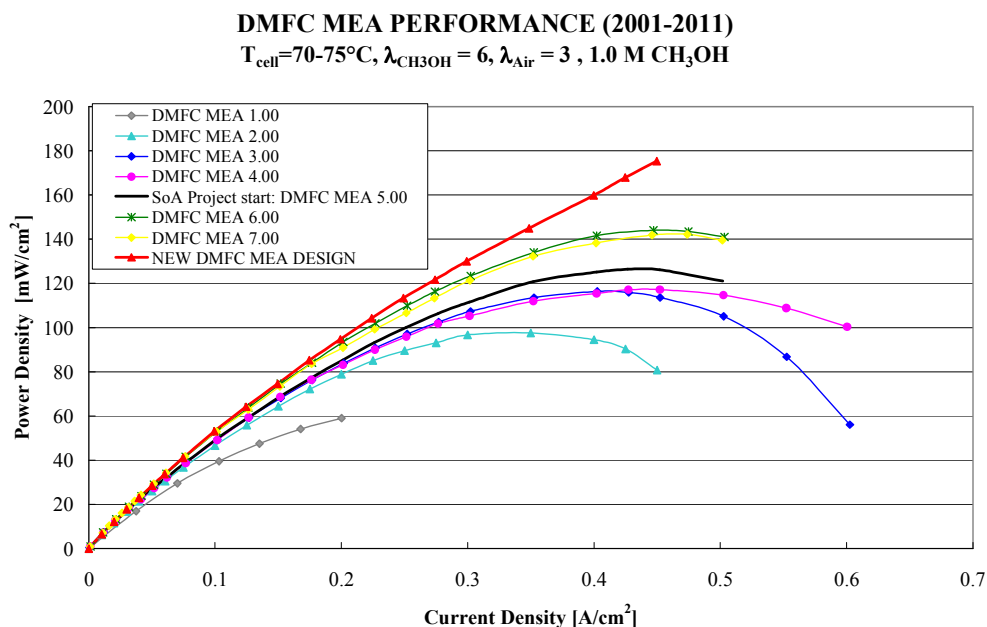


Figure 25. Power density obtained for DMFC MEAs comparing State-of-the-Art at the project start MEA 5.00 to the MEA 7.00 with 50% reduced catalyst content.

The work conducted and experience gained has been very useful and successful for optimizing the Pt-utilization in MEAs and has gained insight how to utilize new catalyst materials as well as commercial materials. The results will be further utilized and continued in the project "Catbooster" (PSO 2011-1-10669) for PEM FC applications.

The results achieved show that:

- The precious metal content in the DMFC MEAs could be lowered by 50% without compromising the performance
- Process route to increase in Pt utilization in LT-PEM without reducing the performance has been established.

1.3.7.5 FC performance focus on LT-PEM & DMFC

The overall Task within this WP is to perform FC single-cell testing to conclude the project outcome of the work performed in WP1-WP7.

LT-PEM - Full size stack demonstration

A 47-cell stack designed for stationary μ -CHP (Combined Heat and Power) applications has in the present project been tested for ~ 1000 hours. The stack was equipped with the optimized IRD PEM MEAs fabricated as CCM's (Catalyst Coated Membrane) and the developed edge-seals based the work obtained in WP6 Interfacial MEA sealing and WP7 Composite Electrode Design.

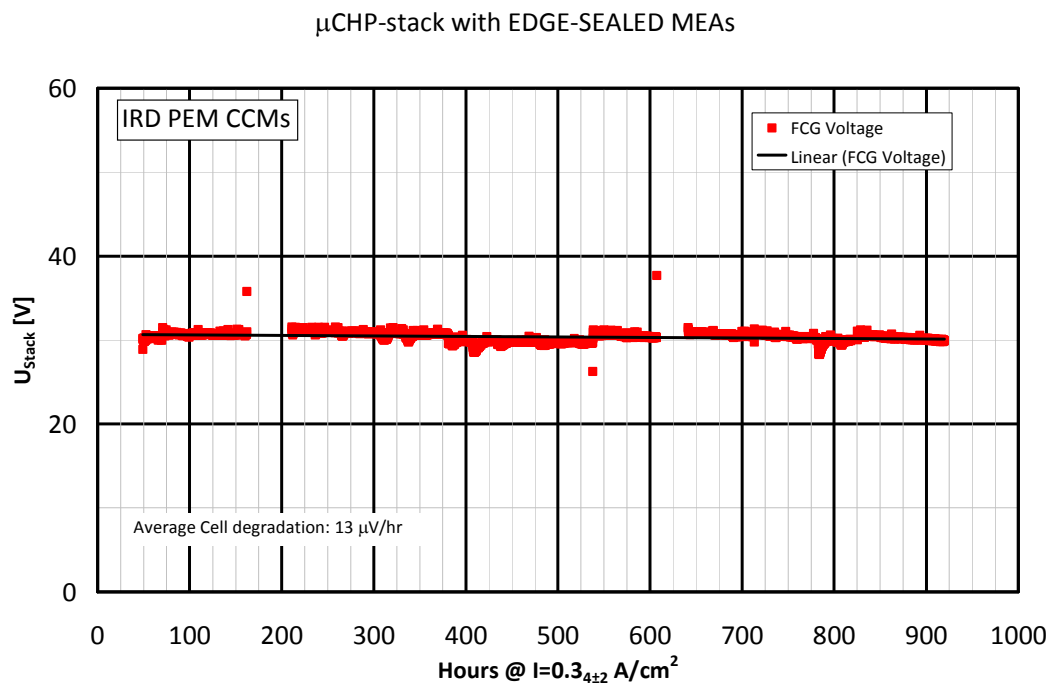


Figure 26. Average cell voltage during constant applied load.

The results look encouraging no degradation or failures has been detected. However to validate the long-term benefit of the edge-seal endurance test beyond 5000 hours is recommended. This has not been the objective of the present project and has to be demonstrated in another context.

The development of optimized MEAs with respect to higher catalyst utilization and using less precious metal loading will continue in the parallel project "Durapem" and Catbooster.

DMFC Performance

Based on the work conducted in the project the MEA performance in DMFC applications was improved significant with respect to lower the Pt-content in the electrode structures, without compromising the performance. Figure 27 show the catalyst utilization improvements.

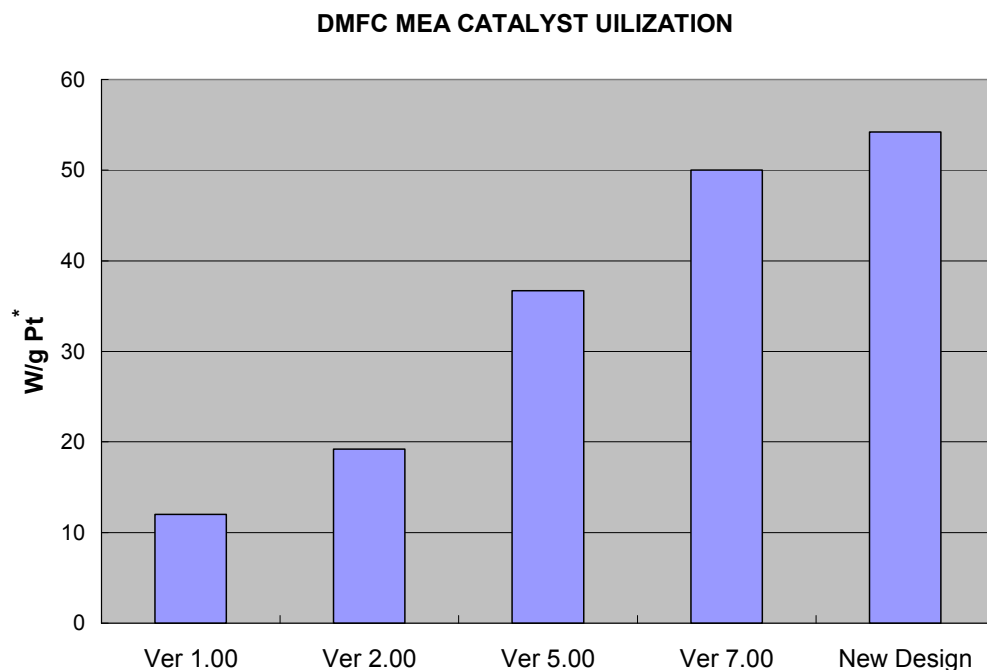


Figure 27. Improved catalyst utilization enabling DMFC MEA using less precious metal.

The stability and lifetime of the MEAs is an important step towards verification and implementation. MEAs based on Cabot catalyst composite electrodes with the same lower precious metal content is therefore tested in the parallel on-going project "DuRaPem" (PSO 2010-1-10505) and 10000 hours has been demonstrated in single-cells for these electrodes.

Conclusion:

- Pilot-scale fabrication of totally 50 g of catalysts demonstrated. It is believed to be technically viable from the synthetic point of view.
- The precious metal content in the DMFC MEAs could be lowered by 50% without compromising the performance
- Process route to increase in Pt utilization in LT-PEM without reducing the performance has been established.
- Durable seals that are bound in a polymer and integrated with the Membrane Electrode Assemblies developed - provide mechanical rigidity and chemical stability.

1.4 Utilization of project results

The project results have been published in a range of occasions including several posters, many oral presentations and in papers. Furthermore the project work has resulted in a patent application by Aalborg University. The patent at project end is not disclosed but all project partners are informed according to the consortium agreement between the project partners.

In this project a lot of important research results have been performed leading to a lot of knowledge on new materials with promising enhanced performance and fabrication of the materials using novel methods. However, the new materials and synthesis methods explored are still in the early research and development phase.

From a practical application standpoint design and fabrication of the new novel catalyst particles with the desired surface structures will require additional development as well as methods to better control particle architecture and cost-effective to produce well defined structures. Explore these new synthesis methods and develop improved tools for catalyst scale-up and large -scale manufacturing will be needed to allow fabrication towards commercial application. The project has contributed to the development of optimized MEAs with reduced precious metal content for both HT- and LT-PEM applications, an important stone for DPS and IRD in bringing fuel cells to market.

Two PhD students have been involved in the present project and contributed with papers and presentations. Anders C. Olesen PhD student at Aalborg University and Pia Nielsen PhD student at SDU. Furthermore 3 post doc's, at DTU-FYS worked within the project; Bille Abrams, Francisco Perez-Alonso and Ifan Stephans.

Published Papers:

- T. Berning, S. K. Kær, "Low stoichiometry operation of a proton exchange membrane fuel cell employing the interdigitated flow field – a modelling study", *Int. J. Hydrogen Energy*, *accepted*, January 2012.
- A. C. Olesen, T. Berning, S. K. Kær, "The effect of inhomogeneous compression on water transport in the cathode of a PEM fuel cell", *Journal of Fuel Cell Science and Technology*, *accepted*, 2012.
- L.N. Cleemann, F. Buazar, Q.F. Li, J. O. Jensen, C. Pan, T. Steenberg, S. Dai and N. J. Bjerrum, Catalyst Degradation in High Temperature Proton Exchange Membrane Fuel Cells Based on Acid Doped Polybenzimidazole Membranes, submitted to *J. Power Sources* (2011)
- T. Berning, M. Odgaard, S. K. Kær, "Water balance simulations of a polymer electrolyte membrane fuel cell using a two-fluid model", *J. Power Sources*, Vol. 196, Issue 15, (2011).
- T. Berning, "On water transport in polymer electrolyte membranes during the passage of current", *Int. J. Hydrogen Energy*, Vol. 36, Issue 15, (2011).

- F. J. Perez-Alonso, C. F. Elkjær, S. S. Shim, B. L. Abrams, I. E. L. Stephens and I. Chorkendorff, *J. Power Sources*, 2011, 196, 6085-6091.
- T. Berning, M. Odgaard, S. K. Kær, "A study of multi-phase flow through the cathode side of an interdigitated flow field using a multi-fluid model", *J. Power Sources*, Vol. 195, Issue 15, (2010).
- T. Berning, M. Odgaard, S. K. Kær, "A computational analysis of multiphase flow through PEMFC cathode porous media using the multifluid approach", *J. Electrochem. Soc.* 156 B1301 (2009).

Submitted Papers:

- T. Berning, "The dew point temperature as a criterion for optimizing the operating conditions of proton exchange membrane fuel cells", *Int. J. Hydrogen Energy*, submitted, January 2012.
- A. C. Olesen, T. Berning, S. K. Kær, "Two-fluid modelling of water and methanol transport in Direct Methanol Fuel Cells", *Int. Journal of Hydrogen Energy*, to be submitted, 2012.
- A. C. Olesen, T. Berning, S. K. Kær, "Two-fluid modelling investigation on the effect of MPL heat and mass transport properties along with dimensions on DMFC performance", *Int. Journal of Hydrogen Energy*, to be submitted, 2012.
- A. C. Olesen, T. Berning, S. K. Kær, "Two-fluid modelling investigation on the effect of MPL heat and mass transport properties along with dimensions on DMFC performance", *Int. Journal of Hydrogen Energy*, to be submitted, 2012.
- A. C. Olesen, T. Berning, S. K. Kær, "Modelling and experimental study of the effect of channel open ratio on DMFC performance", *Int. Journal of Hydrogen Energy*, to be submitted, 2012.
- F. J. Perez-Alonso, D. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen and I. Chorkendorff, 2012, submitted to *Angewandte Chemie International Edition*.

Invited book chapters

- T. Berning, M. Odgaard, S. K. Kær "A multi-fluid model to simulate heat and mass transfer in a PEM fuel cell", in: "Computational Fluid Dynamics Modelling in Development of renewable Energy Applications", *The International Energy and Environment Foundation*, ISBN 13: 978-1-46623-131-3.

Patent applications

- AAU Invention (T. Berning) currently not disclosed at this time, due to potential patent application.

Conference papers and oral presentations

- T. Berning, "A Three-dimensional, two-fluid model of PEM Fuel Cell cathodes", *ECS Trans.* 16 (2), 23 (2008).
- M. Odgaard, "Durability and Performance of the MEAs in the Commercial Fuel Cell Applications", *FUEL CELLS DURABILITY & PERFORMANCE 2009*, Alexandria Dec 2009 (oral).

- T. Berning, M. Odgaard, S. K. Kær, "Water balance simulations of a PEM Fuel Cell using a two-fluid model", *ECS Trans.* 33 (1), 1503 (2010).
- M. Odgaard, "Novel MEA designs", 12th Small Fuel Cells Conference 2010, Cambridge April 2010 (oral).
- F. J. Perez-Alonso, C. F. Elkjær, S. S. Shim, B. L. Abrams, I. E. L. Stephens and I. Chorkendorff, presented in part at the 61st Annual Meeting of the International Society of Electrochemistry, Nice, France, September, 2010.
- F. J. Perez-Alonso, C. F. Elkjær, S. S. Shim, B. L. Abrams, I. E. L. Stephens and I. Chorkendorff, presented in part at the Nordic Symposium on Catalysis, Helsingør, Denmark, August, 2010.
- T. Berning, S. K. Kær, "Modelling multiphase flow inside the porous media of a polymer electrolyte membrane fuel cell", *WIT Transactions on Engineering Sciences*, Vol. 70, 2011.
- T. Berning, M. Odgaard, S. K. Kær, "Low stoichiometry operation of a polymer electrolyte membrane fuel cell employing the interdigitated flow field design", *ECS Trans.* 41 (1), 1897 (2011).
- A. C. Olesen, T. Berning, S. K. Kær, "The effect of inhomogeneous compression on water transport in the cathode of a PEM fuel cell", *Proceedings of ASME*, 2011.
- Q. Li, D. Aili, J. O. Jensen, L. N. Cleemann, H.C. Rudbeck, T. Steenberg, H.A. Hjuler and N. N. Bjerrum. Oral presentation at Hydrogen + Fuel Cells 2011: Recent progress in material development and durability evaluation. International Conference and Exhibition, Convention Centre in Vancouver, May 15-18, 2011.
- H. A. Hjuler, T. Steenberg, H. C. Rudbeck, L.N. Cleemann, Q. Li J. O. Jensen and N. J. Bjerrum. Performance and durability of high performance MEAs for high temperature PBI fuel cells. Oral presentation at Hydrogen + Fuel Cells 2011: International Conference and Exhibition, Convention Centre in Vancouver, May 15-18, 2011.
- A. A. Permyakova, Q. Li, J.O. Jensen and N. J. Bjerrum, Development and characterisation of active and durable electrocatalysts for HT-PEM fuel cells. Poster presentation at Hydrogen + Fuel Cells 2011: International Conference and Exhibition, Convention Centre in Vancouver, May 15-18, 2011. (poster)
- J. O. Jensen, Q. Li, A. Vassiliev, L. N. Cleemann, C. Pan, A. Permyakova, and N. J. Bjerrum. HT-PEMFC in Denmark. PROCON Summer school, Changchun Institute of Applied Chemistry (CIAC) Chinese Academy of Sciences, Changchun, August 16-17. 2011 (oral)
- L.N. Cleemann, Durability issues and recent progress of PBI based HT-PEMFCs, PROCON Summer school, Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences, Changchun, August 16-17. 2011 (oral)
- A. A. Permyakova, Q. Li, J. O. Jensen, and N. J. Bjerrum. Development and characterisation of active and durable electrocatalysts for HT-PEM fuel cells. Advanced studies of polymer electrolyte fuel cells. 4th. International Summer School. Yokohama National University, Japan, September 5-9. 2011. (abstract, poster)
- H. A. Hjuler, T. Steenberg, C. Terkelsen, J. O. Jensen, L. N. Cleemann, Q. Li, N. J. Bjerrum, S. J. Andreasen and S. K. Kær. High Temperature Polymer Fuel Cells: From laboratory towards commercialization. The 45th Power Sources Conference. Las Vegas, USA, June 11-14, 2012.

1.5 Project conclusion and perspective

The overall project achievement is as follows:

- New directions in catalyst materials with promising catalytic properties have been developed
- In the search for new catalyst materials alternative routes and instructions for synthesizing and fabrication have been investigated.
- Stable support materials based on graphitized carbon and Carbon Nano Tubes for fuel cell catalyst developed with excellent chemical and electrochemical stability. The supported catalysts showed significantly improved long term durability.
- Pilot-scale fabrication of totally 50 g of catalysts demonstrated
- Durable seals that are bound in a polymer and integrated with the Membrane Electrode Assemblies developed - provide mechanical rigidity and chemical stability.
- Water balance simulations of a PEMFC using a multi-fluid model. The work implemented a novel approach and has been published in several publications
- More than 8 papers published and additional 5 papers and 1 patent submitted

This project we have made three major breakthroughs in relation to the stability and activity of Pt cathode catalysts for fuel cells:

- (a) Using identical location transmission electron microscopy (IL-TEM), we elucidated the conditions under which Pt may corrode under fuel operating conditions.¹ We found that the degradation in catalyst performance could be accounted for the surface area loss as a result of Pt dissolution. To be the best of our knowledge, this is the first direct, microscopic evidence that a major cause of the performance degradation in fuel cells could be attributed to the dissolution of Pt. Future strategies are needed to prevent Pt dissolution on supported Pt-based catalysts.
- (b) We studied the oxygen reduction activity on well defined, size selected Pt and Pt_xY nanoparticles. On pure Pt nanoparticles, we confirmed the notion that the surface specific activity decreases with the particle size and that the activity scales with the proportion of terraces. This is in agreement with earlier theoretical predictions,⁶ confirming their validity in describing the electrocatalytic functionality of nanoparticulate surfaces.
- (c) Pt₃Y nanoparticles have shown ~4 fold improvement in surface specific oxygen reduction activity over Pt nanoparticles of a similar size, and a mass activity of 1.6 A/mg-1, i.e. a 10-fold improvement of the state of the art pure Pt/C catalysts used in a fuel cell.¹¹ With funding from other ongoing projects, we will continue our studies of these highly active catalysts. We are trying to gain further insight into their structure, and to use this knowledge to obtain even higher activity and stability.

- (d) Different types of carbon support materials have been selected and prepared. Platinum catalysts were synthesized using these carbon supports. Systematical characterizations of these materials were carried out through this project. Emphasis was placed on electrochemical characterizations especially HT-PEMFC performance and durability tests. Durability of PEMFC based on acid doped PBI membranes has been the subject of recent study because the higher operational temperatures impose more challenges for both membranes and the catalysts. The degradation of catalysts supported on different carbon materials was investigated under the accelerated potential cycling tests at 150 °C. As the major mechanism of the fuel cell performance degradation, the electrochemical active area of the cathodic catalysts was monitored by voltammetry, showing a steady reduction in electrochemical active area, which was confirmed by the post TEM and XRD analysis. The fuel cell performance degradation under the accelerated potential cycling test showed strong dependence on the catalyst supports. Heat treatment of the carbon black improves the stability and therefore the catalyst durability though at the expense of a significant decrease in the specific surface area. Multiwalled carbon nanotubes as catalyst support showed further significant improvement in the catalyst and fuel cell durability.
- (e) Platinum containing Metal Organic Framework precursors have been successfully prepared. Although platinum could not be detected by X-ray analysis the materials showed unmistakably platinum catalytic activity and the oxidation of methanol was found to take place at lower potentials than on a standard platinum fuel cell catalyst. Unfortunately no satisfactory preparation method for the precursor was found. Different catalytic activities for the methanol oxidation reaction has also been found on other substrates using more ordinary platinum catalyst and the interplay between substrate and catalyst is investigated further in the Catbooster project. Vulcan carbon substrates have successfully been converted into silicon carbon substrates which have been proven useful as catalyst substrates.

The computational fuel cell models developed at Aalborg University within the framework of this project are among the world-leading fuel cell research tools. They were employed to shed new understanding in terms of liquid water transport through the various layers of a fuel cell, and numerous publications were made. Moreover, the models were used to make at least two inventions. The water-uptake layer, a layer of high specific surface area of the electrolyte phase inside the catalyst layers adjacent to the membrane, was devised to facilitate water absorption to the membrane and allow for fuel cell operation on completely dry inlet gases, according to our modelling results. Varying and mixing the grain size of carbon particles inside the catalyst layer is believed to result in a wider pore-size distribution, and this in turn is believed to lead to improved liquid water transport inside the catalyst layers. Shortly after the project ended a final, patentable invention was made which can not be disclosed at the current time.

The DPS MEA's for HT-PEM application has improved in terms of: a) Improved performance due to the introduction of the new Johnson Matthey catalyst (60% Pt/C) and b) Improved electrode manufacturing process. The project has been an important step towards obtaining the HotMEA consortium.

The precious metal content in the DMFC MEAs could be lowered by 50% without compromising the performance and process route to increase in Pt utilization in LT-PEM without reduc-

ing the performance has been established within this project. The work and experience gained will be utilized for development of the next generation MEAs and continue within the project "Catbooster" (PSO 2011-1-10669) for PEM FC applications.

References

1. F. J. Perez-Alonso, C. F. Elkjær, S. S. Shim, B. L. Abrams, I. E. L. Stephens and I. Chorkendorff, *J. Power Sources*, 2011, **196**, 6085-6091.
2. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. I. Kimijima and N. Iwashita, *Chem. Rev.*, 2007, **107**, 3904-3951.
3. J. Zhang, K. Sasaki, E. Sutter and R. R. Adzic, *Science*, 2007, **315**, 220-222.
4. J. Greeley, *Electrochim. Acta*, 2010, **55**, 5545-5550.
5. D. McCarthy, P. Fernandez-Hernandez, A. Nierhoff, C. Strebel, I. E. L. Stephens, F. J. Pérez-Alonso, J. H. Nielsen and I. Chorkendorff, 2012, **in preparation**.
6. F. J. Perez-Alonso, D. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen and I. Chorkendorff, 2012, **submitted**.
7. J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff and J. K. Nørskov, *Nat. Chem.*, 2009, **1**, 552-556.
8. M. Nesselberger, S. Ashton, J. C. Meier, I. Katsounaros, K. J. J. Mayrhofer and M. Arenz, *J. Amer. Chem. Soc.*, in press, DOI: **10.1021/ja207016u**.
9. J. Greeley, J. Rossmeisl, A. Hellman and J. K. Nørskov, 2007, **221**, 1209-1220.
10. G. A. Tritsarlis, J. Greeley, J. Rossmeisl and J. K. Nørskov, 2011, **141**, 909-913.
11. H. A. Gasteiger, S. S. Kocha, B. Sompalli and F. T. Wagner, *Appl. Catal. B-Environ.*, 2005, **56**, 9-35.