



Self Assembled Nanostructured Electrode for the PEM Fuel Cell (SANEPEMFC)

EOSLT 02025

Final report

Coordinator: Energieonderzoek Centrum Nederland

Co-appliant: TU Delft

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Acknowledgement/Preface

This final report describes activities and results of the project “Self Assembled Nanostructured Electrode for the PEM Fuel Cell” (SANEPEMFC), EOSLT 02025 carried out by ECN-HSF-PEMFC (coordinator) and TU Delft- Chemical Engineering. The project was funded by the Ministry of Economic Affairs in the Netherlands within the framework “Energieonderzoek Subsidies Lange Termijn” implemented by AgentschapNL. The project duration was from 1-11-2005 to 31-08-2010.

Contents

List of tables	4
List of figures	4
Summary	5
1. Scientific report	7
1.1 Introduction	7
1.2 Aim of the project	7
1.3 Approach	7
1.4 Results	8
1.4.1 Template methods	8
1.4.2 Bicontinuous microemulsions	12
1.4.3 Polymerizable surfactant	14
1.5 Discussion	18
1.6 Conclusions	19
2. Implementation of the project	20
2.1 Problems and solutions	20
2.2 Modifications of the work plan	20
2.3 Budget and cost	20
3. Contribution to the EOS LT objectives	21
3.1 Contribution to Sustainable Energy Targets	21
3.1.1 Contributions to PEMFC targets	21
3.1.2 Contribution to a technological break-through	21
3.1.3 Implementation of the results and continuation of research	22
3.2 Improvement of knowledge position of the Netherlands	23
3.2.1 Contribution to knowledge, skills and research facilities	23
3.2.2 Dissemination	24
4. Outcome-indicatoren	27
4.1 Projectresultaten algemeen	27
4.2 Technologische innovatie	28
4.3 Kennis en kennisoverdracht	29
4.4 Samenwerking	30
4.5 Opmerkingen/verbeterpunten	30

List of tables

Table 1 <i>Summary of budget and cost of the project.</i>	20
Table 2 <i>PEMFC projects at TU Delft.</i>	23

List of figures

Figure 1 <i>Synthesis of ordered mesoporous carbons with a controllable pore size</i>	9
Figure 2 <i>TEM images of Pt on CMK3 (left) and OMC-B8 (right). TEM analysis was carried out at the JRC –IE, Petten, The Netherlands</i>	9
Figure 3 <i>V-J characteristics showing the performance of MEAs with state-of-the-art (CB) versus OMC supports (CMK-3 and OMC-B8). The V-j characteristics were recorded at 65°C, ambient pressure. Air at the cathode was either water saturated (100%) or dry (0%).Pt loadings at the cathode were in the order 0.3 mg cm⁻².</i>	10
Figure 4 <i>TEM mages of Pt nanowires synthesized using the hard (left) and soft (right) template method. TEM analysis was carried out at the JRC –IE, Petten, The Netherlands</i>	11
Figure 5 <i>Concept of a fuel cell having a self-assembled electrode based on bicontinuous microemulsion.</i>	13
Figure 6 <i>TEM mages of water/1-hexanol/Fluorocarbon based BμE (left) with ingrown Pt nanoparticles (right)</i>	13
Figure 7 <i>MEA made with self-assembled BμE based electrodes (left) and the performance curve of the MEAs (right)</i>	14
Figure 8 <i>Fluorinated model compounds and surfactants</i>	14
Figure 9 <i>Ionic conductance and surface tension study of surfactant 2 in water at dilute concentrations at 20 °C.</i>	16
Figure 10 <i>Optical microscopy pictures of the 2 and water binary mixtures under crossed polarized light.</i>	16
Figure 11 <i>SAXS spectra for binary mixture of 2 and water at various concentrations and depiction of interdigitated/tilted arrangement of surfactant molecules.</i>	17
Figure 12 <i>FFEM picture of fluorosurfactant 2 and water binary mixtures showing supramolecular rods (a) lamellar sheets (b)</i>	17
Figure 13 <i>Road map for MEA development at ECN, 2010.</i>	22

Summary

The aim of the SANEPFC project was to manufacture a Self-Assembled Nanostructured Electrode for Proton Exchange-Membrane Fuel Cells (PEMFC). By using self-assembly methods well controlled nanostructures can be obtained that allow for further tailoring towards increased utilization of the catalyst as well as decreased transport losses in the electrodes. Improved utilization and reduction of transport losses are required to minimize the cathode overpotential, thus bringing the cost and performance targets of the PEMFC into reach.

This report describes the investigation at ECN and TU Delft of various self-assembly methods for manufacturing (components) of PEMFC electrodes. Valuable new insights into structure-performance relations have been obtained, especially using the unique properties of synthesized ordered mesoporous carbon supports. Electrodes based on mesoporous supports were shown to have superior performance at reduced humidity conditions compared to state-of-the-art electrodes. The originally envisaged electrode based on immobilized bicontinuous microemulsions has not been achieved. However, in the process new synthesis methods have been identified that can result in more robust and efficient electrodes. More specifically:

- Supportless catalysts, i.e. extended Pt nanostructures
- Electrodes with interconnected carbon nanotubes
- Tailored fluorinated (block) copolymers with high sulfonic acid group content for use as proton conducting phase in electrodes as well as membranes.

The research on this subject will be continued in several projects at TU Delft. Although fuel cells are emerging on the market it is also clear that there are still substantial scientific challenges with respect to performance and especially durability to be met, which go beyond incremental improvement. The project results listed above have initiated research at TU Delft on novel materials as well as novel concepts that have the potential of contributing significantly in the required break-through.

1. Scientific report

1.1 Introduction

Commercialisation of fuel cell technology for automotive applications requires a substantial reduction of cost. The cost of a fuel cell system is to a large extent determined by the amount of noble metal, in particular platinum required as a catalyst¹. In 2005 the state-of-the-art technology required 100 g per vehicle or 1.2 g kW⁻¹. To comply with cost targets, and moreover to comply with availability of Pt, the amount should be reduced to 0.2 g kW⁻¹. This is comparable to the amount of Pt present in current exhaust catalysts used in vehicles.

Such a drastic reduction in platinum requires a much more efficient use of the platinum. A major part of the platinum is required to facilitate the reaction at the cathode of the proton-exchange-membrane fuel cell (PEMFC), i.e. the oxygen reduction reaction (ORR). It has been abundantly shown that the platinum in the cathode is both poorly utilized and that the transport losses associated with the ORR are large. Both these phenomena can be related to a non-optimal nanostructure of the electrode.

In state-of-the art fuel cells the electrode structure consists of platinum particles supported on carbon mixed with a polymeric phase of proton conducting material (ionomer). The structure of the electrode is mainly determined by the carbon support of the platinum catalyst. The pore structure of conventional materials is poorly controllable with structures having the high surface area required for highly-dispersed platinum particles often showing a pore structure that inhibits access of reactants to the catalyst sites. An improved electrode structure would have a high surface area, good electronic conduction, good proton conduction and good access of reactant gases

New technology is required that enables accurate control of the organization of these structures on various length scales: the nanoscale at which the electrochemistry takes place, the micrometer scale that applies to the transport processes and the macroscale that is relevant for thermal and mechanical stability. Self-assembly, i.e. the organization of molecules in nanostructured units covering larger length has potential applications in this field. Research in this area indicates the possibility to generate new structures that promise higher catalyst utilization as well as improved access of reactants.

1.2 Aim of the project

The aim of this project was to manufacture a new cathode for the PEMFC that improves the efficiency of the PEM fuel cell by reducing the cathode overpotential while concurrently reducing the Pt content of the cathode. The new cathode will be formed using a self-assembly process resulting in a well controlled nanostructure. The nanostructure should be tailored towards increased utilization of platinum as well as decreased transport losses.

1.3 Approach

Two different approaches were considered in parallel.

- 1) Electrodes synthesized by a template method. This approach was pursued by ECN. Templates (of e.g. silica) are formed in a self-assembly process. Such templates have

¹ W. D. Ernst, C. Stone, and D. Wheeler, Fuel Cell System Cost for Transportation-2008 Cost Estimate, *NREL/BK-6A1-45457* (2009).

therefore a very well defined, nanostructured porous structure. By filling these pores with e.g. carbon or catalyst material and subsequently removing the template a well defined carbon or catalyst structure remains. Materials thus obtained were then used to manufacture Membrane-Electrode-Assemblies (MEAs), which were tested under real fuel cell conditions. It is clear that template methods are cumbersome and expensive as they require additional material and handling. The main purpose of this task was to obtain knowledge on the role of the pore size structure on the catalyst utilization and mass transport in a fuel cell. At the time the project started, the synthesis of some nanostructured carbon materials by template method carbons had been reported in the literature, but applications in fuel cells were still scarce.

- 2) Electrodes synthesized using bicontinuous microemulsions. This is a completely new approach where electrodes are made from a self-assembling bicontinuous microemulsion. The discontinuity of the structure enables the combination of a catalyst supporting phase and a phase for transport of gases with a high surface area interface. By letting this interface be proton conducting a complete electrode structure may be achieved. The concept of bicontinuous emulsions requires the interface to be a surfactant. Proton conducting polymers are usually perfluorinated sulfonic acids containing both acidic, hydrophilic groups and hydrophobic groups, and can act as surfactant. In this project it was envisaged to use polymerizable, fluorinated sulfonic acid molecules as surfactant. After self-assembly of the bicontinuous mixture the structure can then be immobilized by polymerizing the surfactant. The tasks of forming suitable bicontinuous emulsions and of synthesizing a suitable polymerizable surfactant were subject of two PhD studies at TU Delft, Delft Chemical Engineering.

1.4 Results

1.4.1 Template methods

Initial Design

At ECN the method of synthesising so-called ordered mesoporous carbons (OMC) from templates was implemented. These OMCs are then used as supports for the catalysts particles. By making electrodes from these supported catalysts, the electrode structure can be better tuned than when standard carbon black is being used as a support.

Synthesis

Typically this involves first the synthesis of an ordered nanostructured template by a self-assembly method. Based on a literature study the so called SBA-15 structure was selected. This is a well-defined mesoporous material, with a hexagonal symmetry and pore sizes in the order of 6 nm and silica walls of about 4 nm. Synthesis² proceeds by mixing well defined quantities of a surfactant (Pluronic 123), water, hydrochloric acid and the silica precursor tetraethoxysilane (TEOS). After stirring for a specific time the resulting suspension is filtered and dried and after a calcination step at 550°C the SBA15 structure is obtained. The synthesis of the carbon then proceeds by filling pores of the SBA15 with a solution of a carbon precursor, such as sucrose, and some sulphuric acid. After a heat treatment and subsequent carbonization at 900°C a carbon/silica composite is obtained, with carbon in what were previously the pores of the template. By etching away the silica with e.g. hydrofluoride a carbon structure is obtained that is an inverse replica of the silica template, i.e. in this case a hexagonally ordered structure of carbon rods with thickness order 6 nm and pores order 4 nm. This structure is generally referred to as CMK-3. In a later stage a modification of this synthesis was used which allowed for larger pores size of the carbon, while using the same template. The modification implies filling the pores of the template with sucrose and boric acid. During heat treatment the boric acid separates from the carbon and covers the silica walls with borate and silicaborate, which are also etched

² N. P. Lebedeva, A. S. Booiij, and G. J. M. Janssen, Cathodes for Proton-Exchange-Membrane Fuel Cells based on Ordered Mesoporous Carbon Supports, *ECS Transactions*, **16**, 2083-2092 (2008).

away by hydrofluoride. Figure 1 gives an overview of the procedure. With 8 w% boric acid added to the sucrose, the pore size of the resulting OMC-B8 was increased to 6 nm.

Platinum nanoparticles were subsequently deposited on the carbon support by impregnation with a platinum salt followed by reduction by hydrogen. It was possible to deposit up to 40 and 60 wt% Pt nanoparticles onto the OMC. Such high loadings are required to keep the electrodes sufficiently thin. Electrodes were manufactured using standard recipes used at ECN to screen-print electrodes on a suitable substrate.

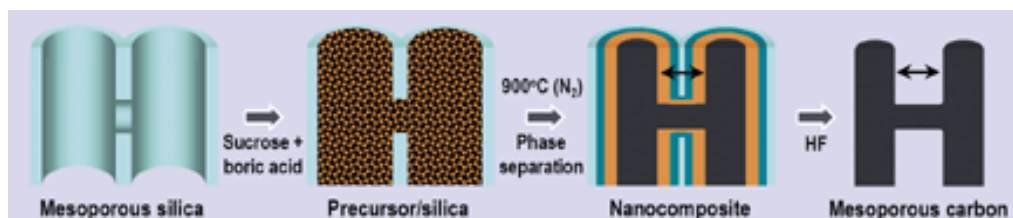


Figure 1 *Synthesis of ordered mesoporous carbons with a controllable pore size*³

Characterization

Ex situ characterization of the synthesized carbon supports (XRD, N₂ porosimetry, TEM) confirmed that materials with well defined pore sizes had indeed been synthesized with a high pore volume. The CMK-3 materials were still ordered, in the case of OMC-B8 the ordering had been lost but a well defined pore size remained. In this respect the materials were very different from the conventional carbon black materials. XRD and TEM showed that the Pt particles were well dispersed on the carbon, with particle sizes in the order of 2 nm being obtained, smaller than found for Pt on carbon blacks at similar platinum loadings (Figure 2).

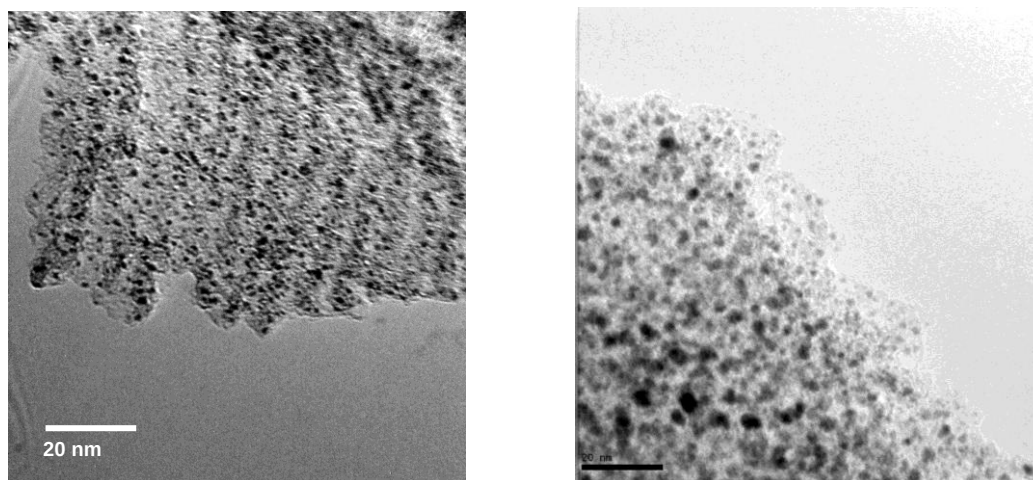


Figure 2 *TEM images of Pt on CMK3 (left) and OMC-B8 (right). TEM analysis was carried out at the JRC –IE, Petten, The Netherlands*

The carbon supports were only tested at the cathode side of an MEA to avoid confounding of anode and cathode effects. For the anode standard electrodes based on carbon blacks were being used with relatively high Pt content. It is well known that such anodes contribute minimally to the fuel cell losses. Also other components of the MEA (membrane, gas diffusion layers) were standard components. This allowed a good comparison of the synthesized and commercial materials for their use in the cathode, i.e. the electrode responsible for the major part of the fuel cell

³ H.-I. Lee, J.-H. Kim, D. J. You, J. E. Lee, Kim J.M., W. S. Ahn, C. Pak, S. H. Joo, H. Chang, and D. Seung, Rational Synthesis Pathway for Ordered Mesoporous Carbon with Controllable 30- to 100-Angstrom Pores, *Advanced Materials*, **20**, 757-762 (2008).

losses. The fuel cell tests took place at a range of realistic conditions (temperature, relative humidity, and fuel and air stoichiometry). Advanced electrochemical techniques such as Electrochemical Impedance Spectroscopy were applied to characterize the main functions of the electrodes: ORR kinetics, proton transport, oxygen transport, water management. In addition to performance characterization, the durability of the materials was evaluated by accelerated stress tests.

Somewhat contrary to expectation it was found that with these ordered mesoporous supports a very high utilization of the platinum surface area was possible, i.e. the electrochemically active surface area was very similar to the total surface area of the Pt particles. Traditionally it was thought that a direct Nafion- Pt contact is required for a Pt site to be electrochemically active. Nafion cannot penetrate into pores with sizes in the order of 4 nm. The findings of these studies therefore corroborate the hypothesis that water is an important medium for proton access in small pores, in addition to Nafion. The overall activity is determined not only by the available surface area, but also by the activity per surface area. Also in this respect the catalysts on OMC performed well. This resulted in a (mass specific) activity 2-3 higher than found for commercial catalysts.

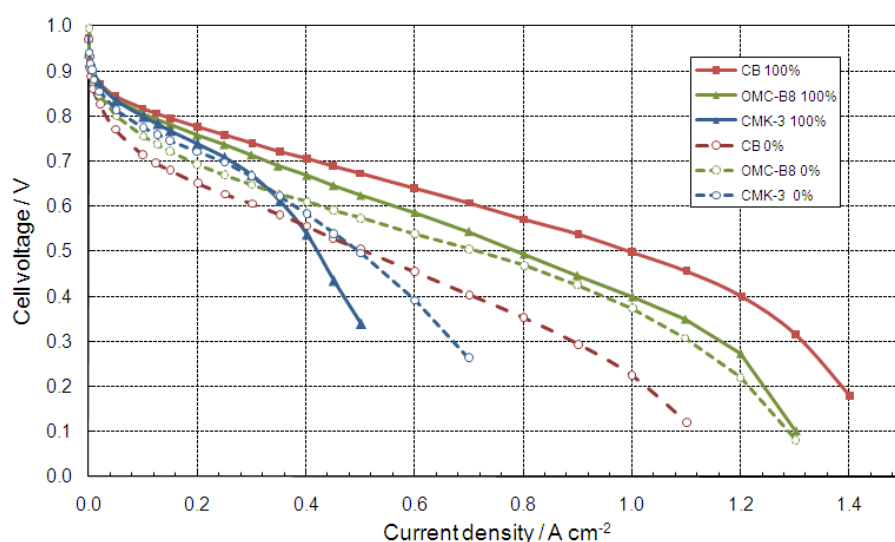


Figure 3 V-J characteristics showing the performance of MEAs with state-of-the-art (CB) versus OMC supports (CMK-3 and OMC-B8). The V-j characteristics were recorded at 65°C, ambient pressure. Air at the cathode was either water saturated (100%) or dry (0%). Pt loadings at the cathode were in the order 0.3 mg cm⁻².

The effect on the transport properties turned out to be very dependent on the humidity of the feed gases (Figure 3). Conventional MEAs perform best when fed with gases that are (nearly) saturated with water vapour (80-100% relative humidity). This high water content is required to enable the proton conduction in electrode and membrane. At high current density, when a large amount of product water is formed, the good proton conductivity is counterbalanced by poor oxygen transport that results from flooding of the pores of cathode. In conventional systems, the beneficial effect on the proton conductivity outweighs the flooding effect up to current densities in the order of 1 A/cm². It was found that for

- MEAs with OMC supported catalysts in the electrode operated under nearly saturated conditions the transport losses were exacerbated compared to carbon black based electrodes:
 - pore structure with uniform small pores impedes oxygen transport → probably blocking by water/Nafion, i.e. flooding occurs at lower current density

- larger pore size/ smaller carbon particles: improved oxygen transport as demonstrated by comparison OMC-B8 vs. CMK3
- proton transport losses increase as result of higher overall porosity of the electrodes → reduce thickness by increasing Pt/C ratio (60wt% Pt/CMK-3 achieved)
- electron transport losses seem to increase as the OMC is less graphitic than carbon black → use of an aromatic precursor instead of sucrose can remedy this
- However when operated with dry air it was found that these electrodes perform better than carbon black based electrodes:
 - improved water retention prevents drying out thus keeping the proton conduction in electrode as well as membrane at an acceptable level

The latter result is an important result as operation at reduced humidity is one of the requirements for to reduce the complexity and cost fuel cell systems. The fact that the small pores fill so easily with water indicated that, again contrary to traditional assumptions, the walls of these pores are hydrophilic, even though the synthesis included an etching step with HF.

Improved Design

Supportless Pt electrodes. Developments fuel cell research world-wide in recent years led to a growing concern regarding the stability of the carbon support. Especially during start/stop events but also during situations of partial fuel starvation the electrode supports may be exposed to high electrochemical potentials resulting in carbon oxidation, which leads to loss of electrode functionality. Use of more graphitic supports will mitigate these effects, but a more robust solution would be to eliminate the carbon support altogether. An example of such a catalyst is Pt black. However, this material has a low catalytic activity as a result of the low specific area. A low specific area can be outweighed by a high area specific activity. Such a high activity is exhibited by well-defined Pt surfaces of extended nanostructures such as nanorods and nanowires. For synthesis of such structures self-assembly methods are ideally suited. In this project two ways were investigated:

- a hard template method, i.e. the SBA15 template described above was filled with a platinum salt and reduced by H₂. Subsequent etching by HF of the silica resulted Pt nanowires.
- a soft template method. Pt nanowires are synthesized in a microemulsion of hexane in water, stabilised by a surfactant. Mixing with a second microemulsion containing a reducing agent results in Pt nanostructures. The surfactant molecules still adsorb strongly on the platinum, extensive non trivial cleaning steps are required to remove them.

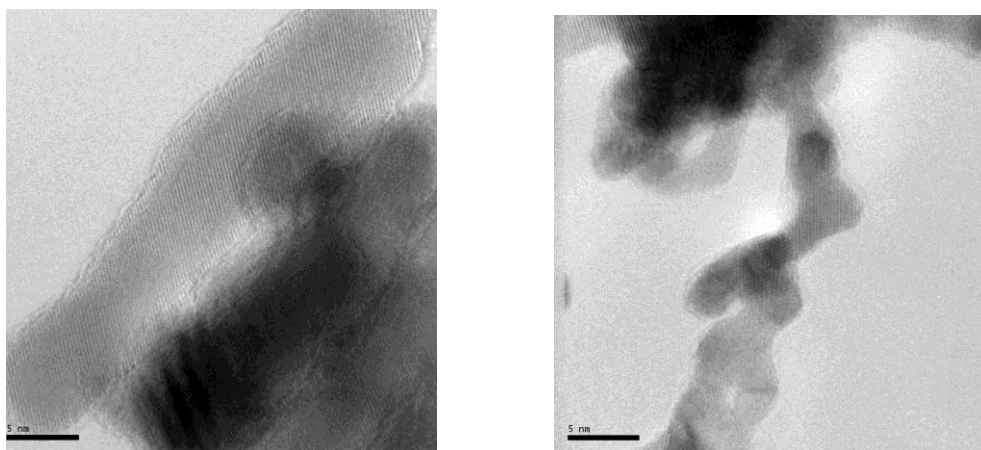


Figure 4 TEM mages of Pt nanowires synthesized using the hard (left) and soft (right) template method. TEM analysis was carried out at the JRC –IE, Petten, The Netherlands

TEM analysis of the samples showed that the intended structures had been formed, with diameters of nanowires from the hard template being in the order of 5 nm, in agreement with pore

sizes in the template. The soft template method resulted in nanowires as well, but with the surfaces seem less smooth, suggesting less extended structures. XRD results showed crystalline Pt in both cases, with the hard template structures having large crystallite dimensions as also found by TEM. Preliminary cell tests with the hard template wires showed good kinetic properties but also demonstrated the need for modification the electrode application. This was taken up in a subsequent ECN project.

1.4.2 Bicontinuous microemulsions

The objective of this task was to construct a working PEMFC electrode out of components that can self-assemble.

Initial Design

For a widespread implementation PEMFCs need to be robust in performance as well as utilize their components in an efficient manner. Current PEMFC technology is not optimized in meeting these challenges simultaneously. However, there is potential in using molecular self-assembly to help PEMFCs overcome their challenges. Molecular self-assembly is a bottom-up fabrication method and involves the spontaneous organisation of molecules into larger structures having customisable properties. The electrode being the most important functional part of a PEMFC can be self-assembled leading to control of the structure at the nanometer-scale, guaranteeing highly tuneable properties and enhancing performance while optimally using all its components. Microemulsions (nanostructured mixtures of immiscible liquids: aqueous and non-aqueous, thermodynamically stabilised by the help of surfactants) are the most attractive systems to build a PEMFC electrode, as they can be self-assembled reproducibly in the ambient, simplifying the manufacturing process. A particular type of microemulsion is the bicontinuous microemulsion (B μ E) that has two immiscible liquids in an interpenetrating structure and the surfactant molecules at the interface between the liquid channels. Such a structure may be advantageous for the functioning of a PEMFC electrode.

The basic functions of a PEMFC electrode are:

- Catalyse electrochemical reactions which is borne by its primary component, the catalyst
- Conduct electrons which is usually handled by an amorphous carbon material
- Conduct protons which is typically managed by an ion-conducting polymer

In addition, PEMFC electrodes have to provide easy access to gases (fuel and oxidant), control the amount of water and heat to name a few. The aqueous channels along with the surfactants at the interface in the B μ E are known to transfer protons. Besides, they can be used as micro-reactors to produce catalyst nanoparticles that can carry out the primary function of a PEMFC electrode. The non-aqueous channels can regulate the transport of gases. Electron conduction needs to be however supplemented by an amorphous carbon component that could be thoroughly mixed with the B μ E. Since the B μ E is a self-assembled structure and subject to changes with the ambient (very common during the operation of a fuel cell), a polymerizable surfactant turns out to be a suitable alternative. With the surfactants at the interfaces chemically linked by polymerization after the bicontinuous structure for the PEMFC electrode is realized, the structure can be immobilized. Thus, with all the functions covered a self-assembled B μ E and carbon based composite electrode seemed to offer a lot of promise for an optimally working PEMFC (see Figure 5). How it delivered to its promise was what was evaluated in this task.

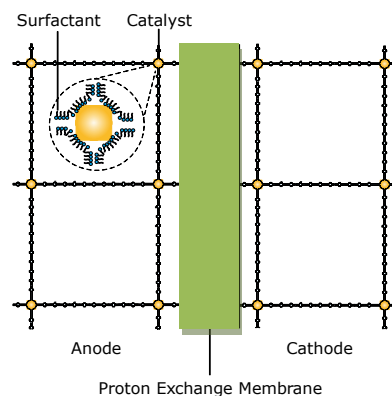


Figure 5 *Concept of a fuel cell having a self-assembled electrode based on bicontinuous microemulsion.*

Synthesis

Finding the right B μ E: After a review of existing literature a suitable components for a pilot B μ E was chosen with water as the aqueous component, n-heptane as the non-aqueous component and sodium bis(2-ethylhexyl) sulfosuccinate or AOT as the surfactant. Other combinations were also evaluated which include water/1-hexanol/Fluorocarbon surfactant. Several formulations of the components were prepared and tested with different experimental techniques (conductivity, dielectric and fluorescence spectroscopy, dynamic mechanical analysis, light and x-ray scattering, electron microscopy) to find out the formulation that had a bicontinuous nanostructure. Only a few compositions were found.

Making nanoparticle catalysts in the B μ E: By combining two B μ Es (one containing the catalyst precursor such as hexachloroplatinate and the other containing a reducing agent like hydrazine), monodisperse nanoparticles of catalyst (platinum, nickel etc.) can be synthesized at very high concentration. The B μ E helps to keep the catalyst nanoparticle distributed and caged in an infrastructure, which optimises their activity and prevents their degradation by recombination. This is unprecedented and has important technological implications. Besides monometallic nanoparticles, bimetallic nanoparticles such as platinum and nickel can also be prepared by this simple micro-reactor synthesis technique. Figure 6 shows a B μ E and in-situ grown nanoparticles.

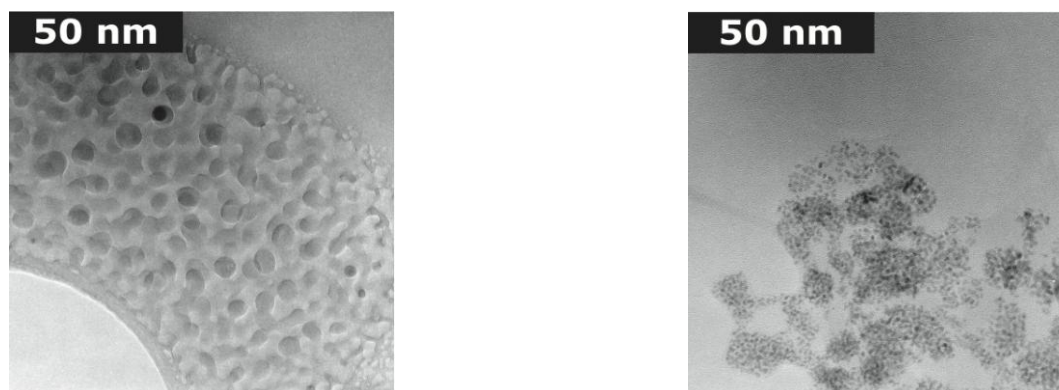


Figure 6 *TEM mages of water/1-hexanol/Fluorocarbon based B μ E (left) with ingrown Pt nanoparticles (right)*

Constructing a PEMFC electrode: The B μ E comprising of the in-situ synthesized catalyst nanoparticles is mixed with carbon black to produce a viscous ink which is then spread on a substrate (gas diffusion layer) and dried. The dried product forms an electrode and this is pressed with another such electrode and an electrolyte (Nafion® membrane) sandwiched in the middle to form the membrane electrode assembly or MEA (Figure 7).

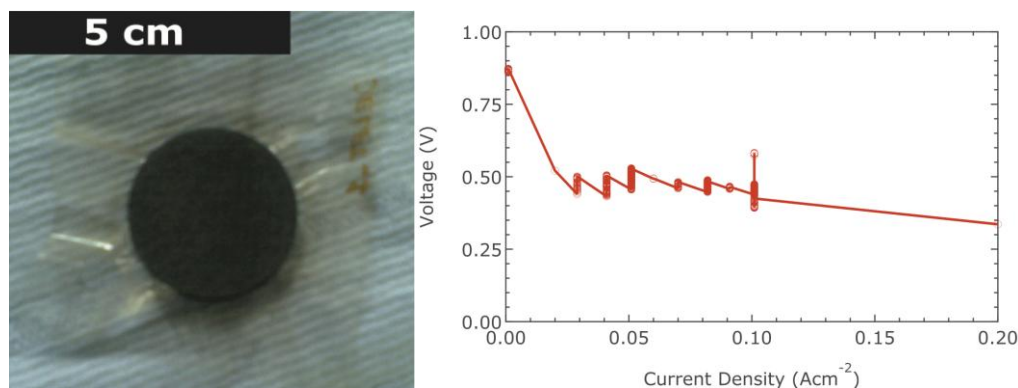


Figure 7 MEA made with self-assembled B μ E based electrodes (left) and the performance curve of the MEAs (right)

Characterization

An MEA with an ultra-low Pt loading of 0.02 mg cm^{-2} was able to deliver 0.1 A cm^{-2} at 0.58 V when supplied with hydrogen as a fuel and air as oxidant (Figure 7) corresponds to a power of 3 W per mg catalyst loading is which is more than twice that of the state-of-the-art technology.

Improved design

The B μ E with catalyst nanoparticles is a useful precursor to form interconnected carbon nanotubes, which has not been reported before this work. It was also found that the synthesis of noble metal catalyst nanoparticles by the B μ E method can render them magnetic which is also a significant discovery having widespread implications.

1.4.3 Polymerizable surfactant

The aims of this task were design and synthesis of a fluorosurfactant that

- has sulfonate as a polar group to conduct protons
- bears a polymerizable group
- forms stable micro/emulsions/higher ordered phases

Below the design, synthesis, phase behavior and polymerization in water of the polymerizable fluorosurfactant and related compounds is described.

Initial Design

To create stable self-assembled PEMFC electrodes, a polymerizable surfactant with the fluorocarbon backbone, $-\text{SO}_3^-$ as the polar head group and styryl group as a polymerizable moiety was designed (compound 1) as shown in Figure 8. To facilitate further studies on the behaviour as surfactant also a non-polymerizable variation was designed. The related fully fluorinated compounds 3 and 4 were also synthesized to be used as building blocks in fluorinated polymers (3), or for further study of the phase behaviour (4).

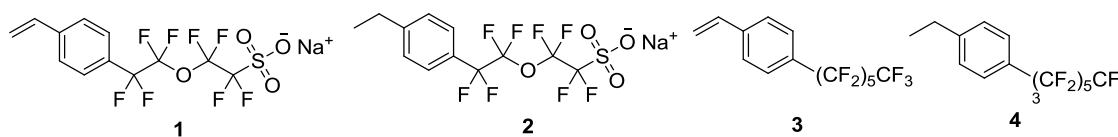
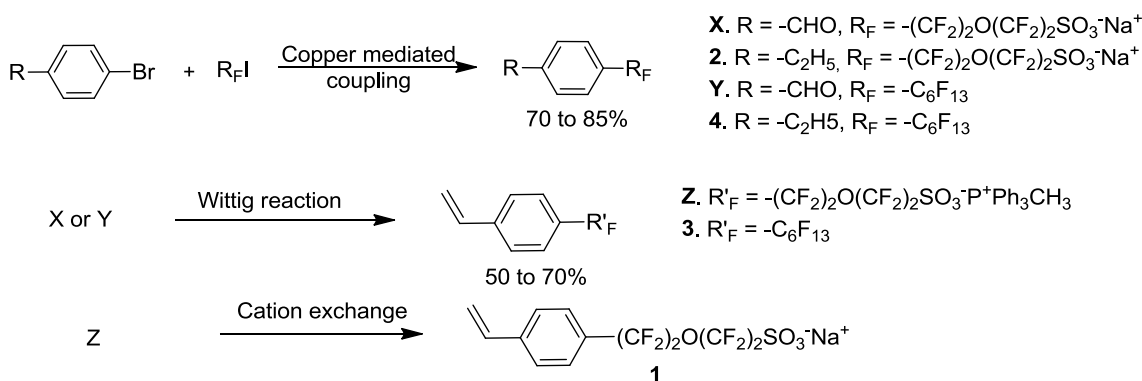


Figure 8 Fluorinated model compounds and surfactants

Synthesis

Scheme 1 shows the syntheses of compounds **1**, **2**, **3** and **4** which were carried out using mainly copper mediated cross-coupling between aromatic bromides and fluorocarbon iodide compounds. Similarly, to create styryl functionality, Wittig reaction was used as shown in Scheme 1. The intermediate fluorosurfactant **Z**, after exchanging the cation using a cation exchange column gave **1**, which was purified by column chromatography followed by recrystallization from toluene. The overall yield was around 50%.



Scheme 1. Scheme for synthesis of various fluorocarbon compounds⁴

Characterization

Phase behavior of **1** and **2** in dilute solutions⁵

The phase behavior of fluorosurfactants **1** and **2** in dilute aqueous solutions (<5% wt) were studied using surface tension measurements and ionic conductivity measurements. It was attempted to determine the aggregation and thermodynamic properties of compound **1** and **2** in dilute concentration. Figure 9 shows the combined graph of the surface tension and ionic conductivity data for fluorosurfactant **2** as an example.

Critical micelle concentrations (cmc), i.e. the concentration above which micelles start to form, for both surfactants were found to be in the range 30 to 50 mM by both techniques. The aggregation number determined from surface tension experiment was in the range of 25 to 30 whereas Gibbs free energy of micellization was found to be around 50 kJ/mol, for both **1** and **2**.

⁴M. N. Wadekar, E. J. R. Sudhölter, S. J. Picken, W. F. Jager, Synthesis of a Polymerizable Fluorosurfactant for the Construction of Stable Nanostructured Proton-Conducting Membranes, *J. Org. Chem.* **75**, 6814-6819 (2010).

⁵ M. N. Wadekar, E. J. R. Sudhölter, S. J. Picken, G. J. M. Koper, W. F. Jager. Manuscript in preparation

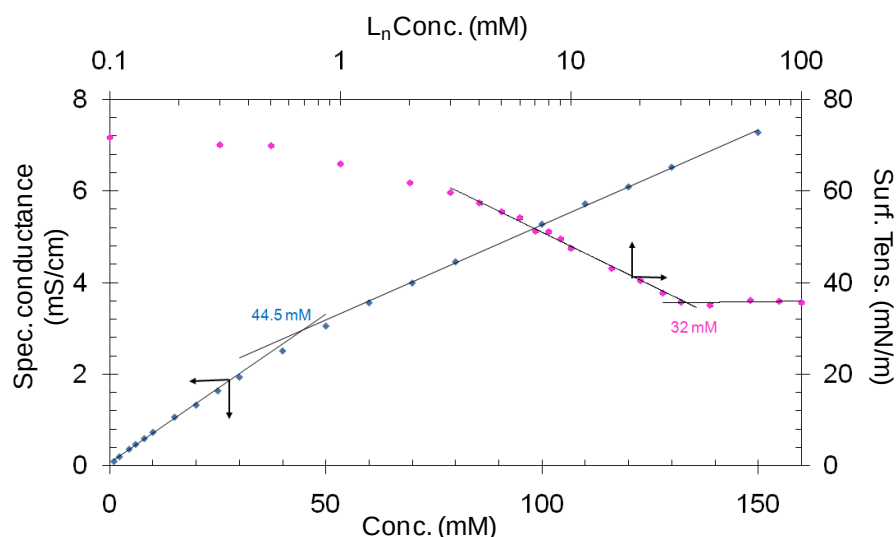


Figure 9 *Ionic conductance and surface tension study of surfactant 2 in water at dilute concentrations at 20 °C.*

Phase behavior of 1 and 2 in lyotropic liquid crystalline regime⁶

Fluorosurfactants **1** and **2**, unlike many other fluorocarbon sulfonate surfactants display lyotropic liquid crystalline phases (LLC) in water, from 60% up to 84% of surfactant weight. Since **1** shows LLC phases at the temperature above 50 °C, where it also easily undergoes polymerization, we found it difficult to investigate its LLC phase behavior. Thus LLC phase behavior of **2** was studied using polarized optical microscopy (POM), small angle X-ray scattering (SAXS) and freeze fracture electron microscopy (FFEM). In Figure 10, POM pictures under crossed polarized light of solutions of **2**, at 60%, 70% and 80% concentrations are shown. POM and SAXS experiments suggest presence of two mesophases regimes one from 60% to 70%, primary small angle X-ray scattering in this regime was absent as shown in Figure 11. POM pictures show typical oily streak pattern under crossed polarized light in this regime as shown in Figure 10a indicating weak ordering of the molecules. Another phase was from 70% to 84% was identified as lamellar phase by SAXS.

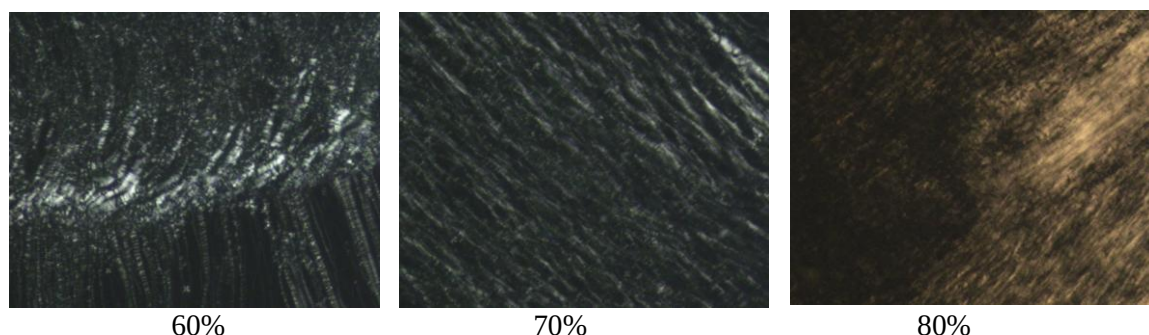


Figure 10 *Optical microscopy pictures of the 2 and water binary mixtures under crossed polarized light.*

⁶ M. N. Wadekar, E. J. R. Sudhölter, S. J. Picken, E. Mendes, D. Dganit, W. F. Jager. Manuscript in preparation

POM shows typical mosaic texture characteristic for lamellar phase in this region. More analysis of SAXS spectra shows that the surfactant molecules in both mesophases have interdigitated and/or tilted arrangement (Figure 11)

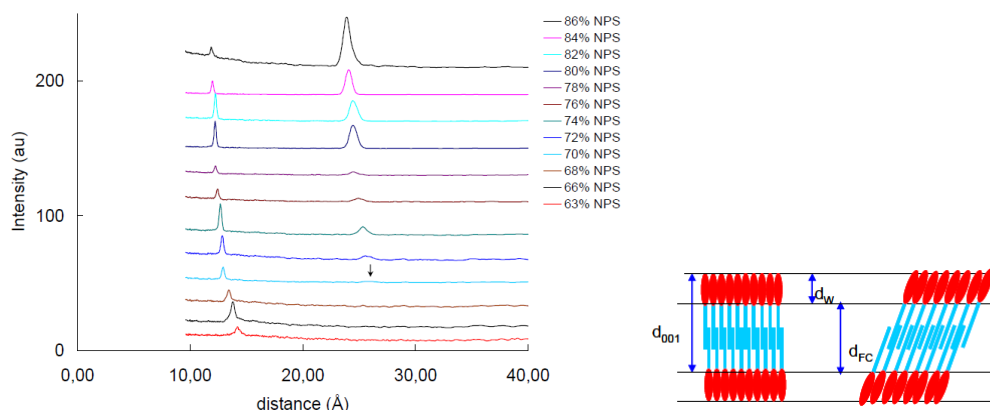


Figure 11 SAXS spectra for binary mixture of **2** and water at various concentrations and depiction of interdigitated/tilted arrangement of surfactant molecules.

FFEM pictures show rodlike aggregates of diameter 20 to 30 nm and length of >100 nm, in the 60% to 70% regime and lamellar sheets above 70% concentration as shown in Figure 12. SAXS spectra suggest that these rods should be supramolecular cigar like particles formed by rolling of interdigitated bilayers of surfactant **2**.

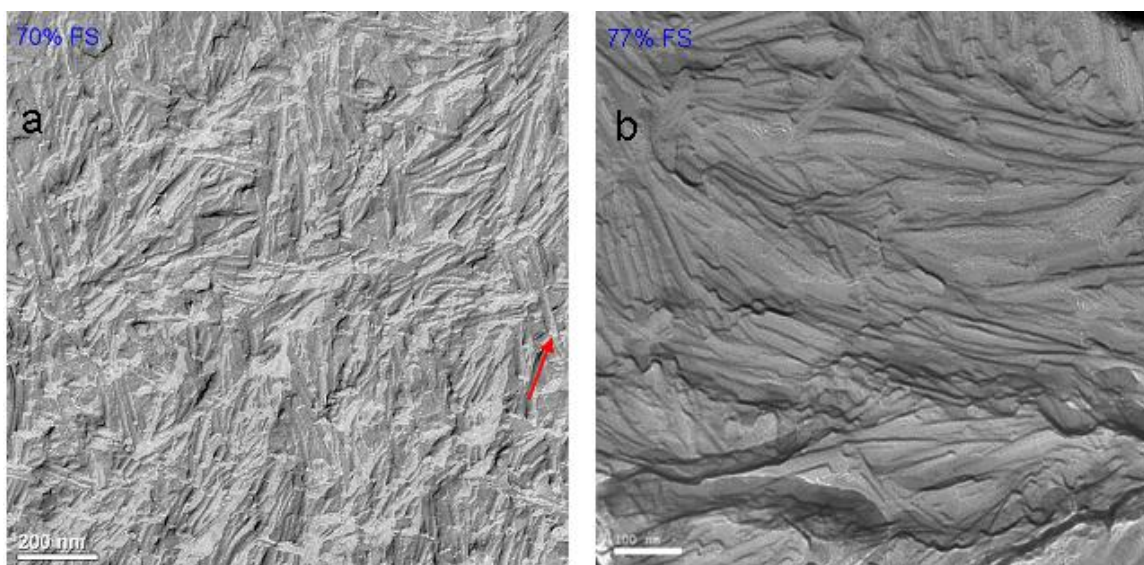
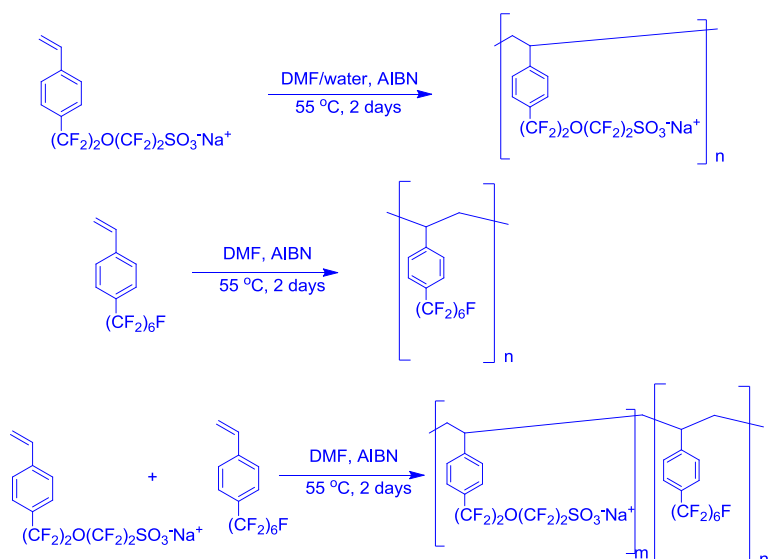


Figure 12 FFEM picture of fluorosurfactant **2** and water binary mixtures showing supramolecular rods (a) lamellar sheets (b)

Polymerization of **1** and **3**.

Solution polymerization of **1** and **3** were studied by free radical method in water or DMF as shown in scheme 2. Attempts to determine molecular weight by static light scattering and size exclusion chromatography of homopolymer of **1** failed due to strong aggregation behavior of polymer chains in the solvents used for the experiments.



Scheme 2. Free radical polymerization **1** and **3** to give homo and copolymers.

^{19}F NMR of copolymers proves that the composition of both monomers in the polymer chains was different than their feed ratio. The homopolymer of **3** was found to be insoluble in many organic solvents. Further analysis of the experiments to study thermal stability and glass transition of these polymers is being carried out.

Improved Design

The interesting morphology on a larger length scale shown by the (polymerizable) fluorosurfactants synthesized in this project suggest that they can be a good basis for (block)co-polymers to be used in membranes. This would allow for a larger concentration of sulfonic acid groups, while at the same time maintaining the low solubility in water. Such properties are extremely relevant for membranes that can operate under reduced humidity conditions.

1.5 Discussion

The research carried out in the project and described above demonstrates first of all the vital importance of the electrode structure for the fuel cell performance. It also shows that self-assembly techniques can lead to electrode structures with well-defined properties. Although such electrodes may not always come with an improved performance, they can be used to study structure-performance properties. The work on OMC-based electrodes has led to a better insight of the factors determining the utilization of the catalyst and transport properties. It was shown that a high utilization is not at conflict with small pore sizes, on the contrary the good water retention in such pores may enhance the accessibility of the catalyst sites. Contrary to traditional assumptions the small pores are not water-free and contributing to gas transport, they easily fill with water. This is an advantage when operating under relatively dry conditions, which is envisaged for more cost-efficient and robust PEM fuel cells.

Increased understanding of the very severe durability requirements for PEMFC has put some doubt on the viability of carbon supported electrodes. Here OMCs can provide a mitigation strategy. The corrosion resistance of the carbon increases significantly with its degree of graphitization. Most carbons show a substantial decrease of surface area on graphitization. In turn, this negatively affects the dispersion of the Pt on the carbon, resulting in lower active surface area or thicker electrodes. Using aromatic precursors, graphitic OMCs may be synthesized that have similar surface areas as their non-graphitic amorphous counterparts.

Another option, explored here, is to eliminate the carbon support and use the template methods to prepare extended Pt nanostructures not requiring a support. This is a very new development that is also receiving attention in other laboratories. However, it still requires a substantial R&D to incorporate such structures into a well operating electrode. Conventional thin film preparation methods used for fuel cell manufacturing may not be the best.

The durability requirements have also indicated the need for intrinsically robust structures. At this respect the self-assembly method based on bicontinuous microemulsions using a polymerizable surfactant is still an attractive option as it incorporates an intrinsic immobilization step for the structure which is at present lacking. This original design was not brought to completion as the development of the polymerizable surfactant alone proved to be very demanding and preparation of a 3-phase system was not possible. For further evaluation of the bicontinuous emulsion concept two further actions seem required:

- Polymerizable fluorosurfactants with longer tails should be synthesized for rich phase behavior and to obtain bicontinuous phases. The other polymerizable moieties like (partially) fluorinated vinyl groups, ethylene group should also be considered to attach to fluorocarbon surfactants.
- Three component microemulsions phases of the synthesized fluorosurfactants should be studied more systematically and in depth.

It must be noted that this is the first time the synthesis polymerizable fluorsurfactant surfactant has been reported in the literature.

The application of this surfactant is not limited to the bicontinuous microemulsion concept, it can in fact be used to synthesize fluorinated block-copolymers that at contrast with conventional random co-polymers such as Nafion may provide better phase separation and morphology in systems with increased content of sulfonic acid groups. Such materials are required for operation at low humidity conditions.

The study on electrodes from bicontinuous microemulsions using conventional surfactants has shown a good performance per mass unit of Pt, which is probably related to the monodisperse nature of the catalyst in the sample. Further research would be required to fully characterize this system, also with implementation of the polymerizable surfactant. A very interesting alternative use of bicontinuous microemulsion is the possibility of making interconnected nanotubes having embedded catalyst nanoparticles in them. As carbon nanotubes are much more graphitic than carbon black and as this concept reduces the mobility of the catalyst particles, this suggests an optimal basis structure for an effective and robust PEMFC electrode. Moreover, it has been realized that the bicontinuous microemulsion concept can play a role in regenerating electrodes in which Pt coarsening, a common degradation effect in PEMFC, has taken place.

1.6 Conclusions

- Various self-assembly methods for manufacturing (components) of PEMFC electrodes have been investigated.
- Valuable new insights into structure- performance relations have been obtained, especially using the unique properties of synthesized ordered mesoporous carbon supports.
- Electrodes based on mesoporous supports were shown to have superior performance at reduced humidity conditions compared to state-of-the-art electrodes.
- The originally envisaged electrode based on immobilized bicontinuous microemulsions has not been achieved. However, in the process new synthesis methods have been identified that can result in more robust and efficient electrodes. More specifically:
 - Supportless catalysts, i.e. extended Pt nanostructures
 - Electrodes with interconnected carbon nanotubes
 - Tailored fluorinated (block) copolymers with high sulfonic acid group content for use as proton conducting phase in electrodes as well as membranes.

2. Implementation of the project

2.1 Problems and solutions

The problems encountered within this project were primarily of a scientific nature, as described in the previous section. A relatively minor issue that led to some start-up difficulties was that the work plan and all other documents related to the EOS LT framework were in Dutch. Scientific and technical research has an international character with English as *lingua franca*, and English should therefore be the preferred language for most documents, certainly for all content related documents as proposals, work plan and progress reports, project information on the web-site.

2.2 Modifications of the work plan

The project had a delayed start at TU Delft, because the hiring of the two PhD students took about six months. This is the time required for careful selection from an international group of applicants. This late start at Delft was the reason for the extension of the end date to 1 September 2010.

2.3 Budget and cost

There have been several budget modifications asked for and granted. The net result is that a Materials budget of ECN has been transferred to Costs for Third parties to enable materials characterization outside ECN. Effectively at TU Delft a Materials Budget was shifted to Personnel, to enable extra input from the TU Delft staff.

A summary of budget and costs is given below. ECN has underspent the budget for Materials and for Third Parties, which it wants to use to compensate for additional personnel cost. The excess personnel cost at ECN results from a recalculation of the ECN personnel rates. The budget for TU-Delft was based on standard numbers for the guidance of PhD-students whereas in actual fact the guidance in this case was more involved because of differences in basic education and skills and differences in the quality of the students. In addition, the guidance of a postdoctoral fellow is included. Finally, the guidance by the promotor of the PhD-students was erroneously not included in the budget. Because of this, the Delft personnel budget was overspent.

Table 1 *Summary of budget and cost of the project.*

	Budget ECN	Cost ECN	Budget TU Delft	Cost TU Delft
Total	493 k€	550 k€	669 k€	830 k€
Personnel	289 k€	337 k€	389 k€	495 k€
50% suppl.	144 k€	169 k€	194 k€	247 k€
Equipment	-	-	12k€	9 k€
Materials	25 k€	18 k€	58 k€	67 k€
Third parties	35 k€	27 k€	16 k€	12 k€

Detailed specifications of costs incurred by ECN and TU Delft have been supplied to Agentschap NL, with Audit Certificates.

3. Contribution to the EOS LT objectives

3.1 Contribution to Sustainable Energy Targets

3.1.1 Contributions to PEMFC targets

The EOS LT objectives in the field of PEMFC were to further improve the state-of-the-art PEMFC technology to make it ready for transport and stationary applications. Reduction of cost, i.e. more efficient systems, as well as including improvement of durability and robustness were identified as key issues. To this end several more specific goals were identified. The goals directly relating to the SANEPFC project were:

- reduction of the overpotential associated with the oxygen reduction reaction
- development of PEMFC electrodes optimized for operation at 100-150°C with emphasis on reduction of noble metal content
- research into increase of life-time of fuel cells

The combination of the first two targets has led to the target mentioned in the introduction of this report, i.e. to improve the efficiency of the PEM fuel cell by reducing the cathode overpotential while concurrently reducing the Pt content of the cathode. The work in this project has:

- proven the reduction of the overpotential under reduced humidity conditions by using mesoporous supports
- led to fundamentally new insights regarding the relation between electrode structure and Pt utilization and transport properties
- resulted in synthesis of Pt nanostructures with expected improved durability
- shown the synthesis of well-defined, monodisperse, highly active Pt particles
- resulted in synthesis of carbon/catalysts networks with expected improved durability
- shown for the first time the synthesis of a polymerizable fluorsurfactant that can result in a more effective proton conducting phase

3.1.2 Contribution to a technological break-through

During the project duration it has become increasingly clear to the PEMFC community that in addition to requirements on performance and Pt loading (both directly translated into cost) of the PEMFC, durability issues will determine success or failure of this technology. For both performance and durability, the major contribution still has to come from alternative electrodes, in which the mass activity of platinum is driven to its maximum, and transport limitations are driven to their minimum. A better control of the catalyst layer, on design as well as on maintaining the beginning-of-life properties, is required. This has led to the recognition that the focus should be directed more than in the past on materials that are intrinsically stable under the harsh fuel cell conditions. The research carried out in this project has initiated the work at ECN on supportless catalysts and at TU Delft on electrodes of carbon nanotubes. Both these concepts allow for better control and durability.

A second breakthrough in the field of PEMFC has to be provided by the development of a class of proton conductors that can operate at low relative humidity. The synthesis, for the first time, of a polymerizable fluorsurfactant provides the way to the synthesis of a new type of block-copolymers that through their improved morphology can achieve more efficient proton conduction.

3.1.3 Implementation of the results and continuation of research

In 2010 the PEMFC group at ECN developed a road map for MEA development (Figure 13). In this road map it was envisaged that both the supportless Pt catalysts as well as catalysts on supported on a stable support would be further explored. In both developments the SANEPFC results were to be implemented: the Pt nanowires as described in section (Improved Design) as well as graphitic variants on the OMC materials (1.4.1 Initial concept) or the connected nanotubes from TU Delft (1.4.2. Improved concept). The decision taken by the ECN management at the end of 2010 to terminate the Hydrogen and Fuel Cell program implies unfortunately that this route to further development and implementation of results has been cut off.

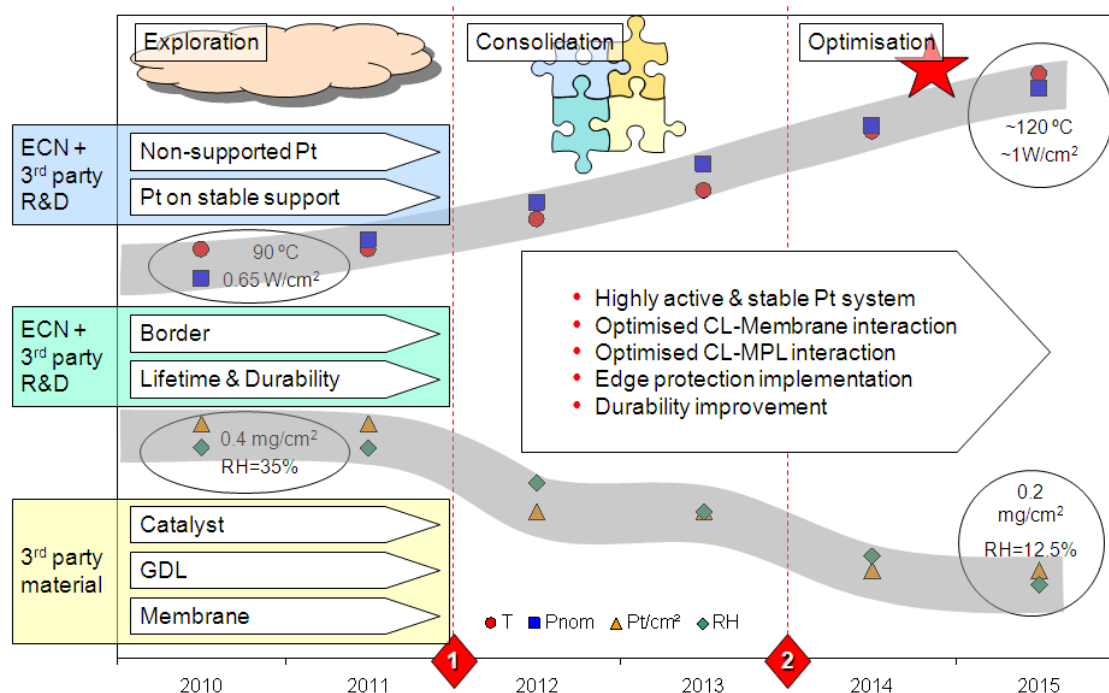


Figure 13 Road map for MEA development at ECN, 2010.

At TU Delft on the other hand various projects building on the knowledge, skills and collaboration acquired in Sane PEMFC have started at the end of 2010 or are about to start the first half of 2011. This involves two new PhD studies (ADEM and SHM-IOP) and a post doc position (EOS-NEO). The acquisition of these projects was the result of joint efforts of TUDelft and ECN.

The TU Delft Valorisation Centre has selected the patent application by Rutger van Raalten, Krishna Kowgi and Ger Koper [Patent NL 2002071, PCT/NL2009/050596] to be granted funding for business development. The TU Delft spin-off company Minus9 has accordingly been set up. This company develops nanocatalysts and nanonetworks (www.minus9.nl). STW has supplied two valorisation grants to foster the company on applications namely (Self-Assembling Nanocatalyst Electrode for Proton-Exchange Membrane Fuel Cells: a technical and commercial feasibility study) and (Chemically Linked Carbon Nanotube Networks: a technical and commercial feasibility study, CLICK).

Further joint efforts TU Delft and ECN have led to the acquisition of funding for other PEMFC related projects at Delft (PhD studies). Table 2 contains a full list of PEMFC projects at TU Delft.

Table 2 PEMFC projects at TU Delft

Title	Funding	Supervisors /Participants
<i>Minus 9 2011-2012</i>	TU Delft Valori- sation Centre STW	Minus 9 Rutger van Raalten, TU Delft Krishna Kowlgi
<i>Self Healing and -Assembling Rege- nerative Electrode for Proton- Exchange Membrane Fuel Cells</i>	IOP-SHM 2010-2014	Ger Koper SAS, Rutger van Raal- ten Minus9, Nedstack b.v.
<i>Nano-engineering of PEMFC elec- trodes and membranes using fluori- nated block copolymer morphologies</i>	EOSLT –NEO 2011	Wolter Jager NOC, Stephen Pick- en NSM, Bruno M. Ameduri Uni Montpellier
<i>Nanostructured, tricontinuous car- bon network electrode</i>	Adem 2010-2014	Ger Koper SAS, Stephen Picken NSM
<i>Hybrid superionic conducting PEM fuel-cell membranes manufacturing, structure, characterization.</i>	Adem 2010-2014	Stephen Picken NSM, Erik Kelder NSM
<i>Hybrid superionic conducting PEM fuel-cell membranes--dynamics</i>	Adem 2010-2014	Stephen Picken NSM, Erik Kelder NSM
<i>HOIF for PEMFC</i>	NanoNextNL (FES,submitted)	Ger Koper SAS

3.2 Improvement of knowledge position of the Netherlands

3.2.1 Contribution to knowledge, skills and research facilities

Specifically, the project has led to development at ECN of skills on of synthesis of:

- self-assembling systems
- carbon nanostructured carbon
- nanostructured Pt

At TU Delft the SANEOMEMFC project has initiated a second Dutch cluster of PEMFC related research in addition to the work at ECN. This may prove to be very valuable in the light of the shut-down of activities at ECN. The project has also empowered the purchase of advanced Dynamic Light Scattering equipment at TUDelft, required for research on micro-emulsions. Also, it has initiated work on (partially) fluorinated polymers at TUDelft, a subject not covered before at TU Delft.

Overall, the project has contributed to extending the research on PEMFC in the Netherlands to a more fundamental level that was lacking at the start of the project. Although fuel cells are emerging on the market it is also clear that there are still substantial scientific challenges to be met, which go beyond incremental improvement. As indicated above, breakthroughs are required to meet the future demands with respect to robustness and durability, as well as performance and cost. These breakthroughs will include novel materials as well as novel concepts and

will be facilitated by in-depth understanding of the fundamental aspects of the reactions of interest and relevant degradation processes. This requires a combination of academic and applied research.

3.2.2 Dissemination

The work in this project has been published in scientific journals and presented at scientific conferences, as well as in a patent application. A list is given below. At time of submission of this report the paper in J. Org. Chem. by Mohan Wadekar et al. is among the top -3 of most accessed papers of the J.Org. Chem. over the past 12 months, indicating international acknowledgement of the scientific significance and relevancy. Two PhD theses, by Mohan N. Wadekar and by Krishna N.K. Kowlgi, are in preparation at TU Delft.

Further publicity was given to the project when Rutger A. D. van Raalten won the Shell Master Prize 2007 for "Fuel Cell Optimization" at an elevator pitch grand finale on 14 February 2008 at Eindhoven, the Netherlands.

Krishna N. K. Kowlgi won poster prizes for "Self-Assembled Fuel Cell Electrodes" at the conference NWO-CW-studiegroep Vloeistoffen en Grensvlakken (Fluids and Interfaces) 2008 at Lunteren and for "A Revolutionary Fuel Cell" at the conference UK Polymer Colloids Forum - Young Researchers' Symposium 2008 at Greenwich.

Patents

1. R.A.D. van Raalten, N.K.K. Kowlgi & G.J.M. Koper, *Electrode compartment for a n electrochemical cell, a refreshing system for it tand an emulsion to be used therefore*, (2007), Patent NL 2002071, PCT/NL2009/050596.
2. Krishna Kowlgi, Ger Koper, Rutger van Raalten, *Carbon nanostructures and networks produced by chemical vapor deposition*, (2010), 2005365 (Patent Pending).

Mass Media

1. Broer de Boer, Platina-deeltjes in brandstofcel vormen zichzelf, *Energie+*, 3, 30 - 31(2008).

Articles published in peer-reviewed journals

1. M. N. Wadekar, E. J. R. Sudhölter, S. J. Picken, W. F. Jager, *Synthesis of a Polymerizable Fluorosurfactant for the Construction of Stable Nanostructured Proton-Conducting Membranes*, J. Org. Chem. 75, 6814-6819 (2010).
2. N. P. Lebedeva, A. S. Booij, and G. J. M. Janssen, *Cathodes for Proton-Exchange-Membrane Fuel Cells based on Ordered Mesoporous Carbon Supports*, ECS Transactions, **16**, 2083-2092 (2008).

Articles in preparation

1. M. N. Wadekar, E. J. R. Sudholter, S. J. Picken, G. J. M. Koper, W. F. Jager. Manuscript in preparation on *dilute concentration solutions of fluorosurfactants*.

2. M. N. Wadekar, E. J. R. Sudholter, S. J. Picken, E. Mendes, D. Dganit, W. F. Jager. Manuscript in preparation on *lyotropic liquid crystalline mesophases of fluorosurfactants*.
3. Krishna N. K. Kowlgi, Aditya Surjosantoso, Rutger A. D. van Raalten, Ugo Lafont, Ben Norder and Ger J. M. Koper, *Synthesis of High Density of Monodisperse Nanoparticles in Water Conduits of Microemulsions*, in preparation.
4. Krishna N. K. Kowlgi, Arend Booij, Gaby J. M. Janssen, Stephen J. Picken, Ger J. M. Koper, *Self-Assembled Electrode for Proton Exchange Membrane Fuel Cells*, in preparation.
5. Krishna N. K. Kowlgi, Zhwendeline Pieter, Patricia Kooyman, Stephen J. Picken, Ger J. M. Koper, *Carbon Nano-Networks*, in preparation.
6. Krishna N. K. Kowlgi, Ger J.M. Koper, Stephen J. Picken, Ugo Lafont, Lian Zhang and Ben Norder, *Synthesis of Magnetic Noble Metal (Nano)Particles*, in preparation.
7. Lian Zhang, Krishna N. K. Kowlgi, Stephen J. Picken and Ger J. M. Koper, *Anomalous Temperature Dependent Magnetisation of Magnetic Noble Metal (Nano)Particles*, in preparation.
8. Krishna N. K. Kowlgi, Ishrat Mubeen, Jan Aarts, Ger J.M. Koper, Stephen J. Picken, Ugo Lafont, Lian Zhang and Ben Norder, *Zero Magnetisation at Finite Magnetic Fields*, in preparation.
9. Gaby J.M. Janssen A.S. Booij and Eric F. Sitters, *Low Relative Humidity Operation of PEMFC Cathodes Containing Ordered Mesoporous Carbon Supports*, in preparation.

Oral Presentations

1. K.N.K. Kowlgi et al., *Making Noble Metals Magnetic*, NWO Meeting on Chemistry of the Solid State and Materials Science, Veldhoven, 16 February 2010
2. K.N.K. Kowlgi et al., *Self-Assembled Multifunctional Electrode*, Soft Matter Meeting Delft, Delft, 12 November 2009
3. Gaby Janssen, Natalia Lebedeva, Arend Booij, Eric Sitters, Martin Aalberts, *Cathodes for proton-exchange-membrane fuel cells based on ordered mesoporous carbon supports*, IEA Annex 22 on Advanced Fuel Cells, 2009 Fall Meeting, Argonne, IL, USA
4. K.N.K. Kowlgi et al., *A Revolutionary Fuel Cell*, 13th IACIS International Conference on Surface and Colloid Science and the 83rd ACS Colloid & Surface Science Symposium, New York, 16 June 2009.
5. Wadekar, M. N.; Jager, W. F.; Kowlgi, K. N. K.; Koper, G. M.; Janssen, G. J. M.; Lebedeva, N. P.; Picken, S. J. *A polymerizable fluorosurfactant for nanostructured proton conducting membrane*, Macro 2009, March 9-11, 2009.
6. K.N.K. Kowlgi et al., *Self-Assembly in Fuel Cell Electrodes*, 6th Dutch Soft Matter Meeting, Delft, 27 February 2009.
7. K.N.K. Kowlgi et al., *A Revolutionary Fuel Cell*, Johnson Matthey Practical License Company, Sonning Common, 20 February 2009.
8. K.N.K. Kowlgi et al., *Multifunctional Self-Assembly*, NWO-CW-studiegroep Vloeistoffen en Grensvlakken Lunteren, 9 February 2009.
9. M.N. Wadekar et al., *Polymerizable fluoroalkyl surfactant for improved PEMFC Electrodes*, Dutch Polymer Days, Lunteren, 2-3 February 2009.
10. Natalia P. Lebedeva, Arend S. Booij, and Gaby J.M. Janssen *Cathodes for Proton-Exchange-Membrane Fuel Cells Based on Ordered Mesoporous Carbon Supports*, Oral presentation for the 214th Meeting of the Electrochemical Society, Honolulu, 2008.
11. N.P. Lebedeva, A.S. Booij and G.J.M. Janssen, *Cathodes for Proton-Exchange-Membrane Fuel Cells Based on Ordered Mesoporous Carbon Supports*, oral presentation at the conference Progress MEA 2008, La Grande Motte, France, 21-24 September 2008.
12. M. N. Wadekar, W. F. Jager, K. N. K. Kowlgi, G.J.M. Koper, G. J. M. Janssen, N.P. Lebedeva, S. J. Picken, *Polymerizable Fluorosurfactants to Improve Performance of a PEMFC Electrode*, oral presentation at EUPOC 2008 Advanced Polymeric Materials

for the Energy Resources Exploitation: Synthesis, Properties and Applications, Gargnano, Italy, 1-5 June 2008

13. Gaby Janssen, Natalia Lebedeva, Arend Booij (ECN), Ger Koper, Krishna Kowlgi, Wolter Jager, Mohan Wadekar (TU Delft), *Improving the cathode performance of the PEM fuel cell: Challenges, strategy and some results*, The Advances in Hydrogen and Fuel Cell Research, Petten, 22 May 2008
14. Krishna Kowlgi, Ger Koper, Mohan Wadekar, Wolter Jager (TU Delft), Gaby Janssen, Natalia Lebedeva and Arend Booij (ECN), *Self-assembled Nano-structured Electrodes for Fuel Cells* The Advances in Hydrogen and Fuel Cell Research, Petten, 22 May 2008.
15. R.A.D. van Raalten, *Fuel Cell Optimization: Can stable platinum particles be synthesized in bicontinuous microemulsions?* MSc Defense, TU Delft, 27 September 2007.
16. G.J.M. Janssen, PEMFC research at ECN, Spring Meeting IEA Annex 16 on Advanced Fuel Cells, Helsinki (Fin), 7-8 June 2007.

Posters

1. M. N. Wadekar, E. J. R. Sudholter, S. J. Picken, G. J. M. Koper, W. F. Jager, *Fluoro-surfactant self-assemblies for functional nanostructured membranes*, Dutch Polymer Days 2010, Veldhoven 15-16 February 2010.
2. Wadekar, M. N.; Jager, W. F.; Koper G. J. M.; Kowlgi, K. N. K.; Janssen, G. J. M.; Lebedeva, N. P.; Picken, S. J.; Sudhölter, E. J. R. "*Synthesis of fluorinated building blocks for self-assembled proton conducting membranes*" The Scientific meeting in the Area of Organic Chemistry, Lunteren, The Netherlands, October 2009.
3. K.N.K. Kowlgi et al., *Self-assembled Multifunctional Electrode*, 2nd DCT Science Day, TU Delft, 29 October 2009
4. Wadekar, M. N.; Jager, W. F.; Kowlgi, K. N. K.; Koper, G.J. M.; Janssen, G. J. M.; Lebedeva, N. P.; Picken, S. J. *Polymerizable Fluorosurfactants to Improve Performance of a PEMFC Electrode*, Abstracts of Papers, 238th ACS National Meeting, Washington, DC, USA, August 2009, POLY-092.
5. Wadekar, M. N.; Jager, W. F.; Kowlgi, K. N. K.; Koper, G. M.; Janssen, G. J. M.; Lebedeva, N. P.; Picken, S. J. *A polymerizable fluorosurfactant for nanostructured proton conducting membrane*, Frontiers in Polymer Science, Mainz, Germany, June 2009.
6. Krishna Kowlgi, Aditya Surjosantoso, Ger Koper, Mohan Wadekar, Wolter Jager, Stephen Picken, Gaby Janssen, Natalia Lebedeva, *A Revolutionary Fuel Cell*, UK Polymer Colloids Forum - Young Researchers' Symposium 2008, Greenwich, 28-29 August 2008.
7. Krishna Kowlgi, Aditya Surjosantoso, Ger Koper, Mohan Wadekar, Wolter Jager, *Self-Assembled Fuel Cell Electrodes*, 17th International Symposium on Surfactants in Solution, Berlin, 18-22 August 2008.
8. Rutger A. D. van Raalten, Krishna N. K. Kowlgi*, Mohan N. Wadekar, Ger J. M. Koper and Wolter F. Jager, *Self-assembled PEMFC electrode*, NWO-CW-studiegroep Vloeistoffen en Grensvlakken, Lunteren, 11-12 February 2008.
9. K.N.K. Kowlgi et al., *Self-assembled Electrode*, DCT Science Day, TU Delft, 4 December 2007
10. Rutger A. D. van Raalten, Krishna N. K. Kowlgi*, Mohan N. Wadekar, Ger J. M. Koper and Wolter F. Jager, *Self-assembled PEMFC electrode*, 21st Conference of the European Colloid and Interface Society (ECIS), Geneva, September 10-14, 2007.

4. Outcome-indicatoren

4.1 Projectresultaten algemeen

1.1 Hoe is het technologisch resultaat van het project het best aan te duiden?

- ~~a. Proof of feasibility~~
- b. Proof of principle
- ~~c. Proof of concept~~
- ~~d. Prototype~~
- ~~e. Product/proces/systeem~~
- f. Anders, namelijk: **substantiële uitbreiding van kennis en vaardigheden op gebied van synthese met zelf-assemblerende systemen. Dit kan van groot belang zijn voor PEMFC component ontwikkeling.**

Toelichting:

1.2 Voor welke hoofdsector is het projectresultaat primair van belang?

- ~~a. Landbouw/visserij~~
- ~~b. Bouwnijverheid~~
- ~~c. Dienstverlening~~
- ~~d. Handel~~
- ~~e. Industrie~~
- f. Energie en water
- ~~g. Transport~~
- ~~h. Overheid~~
- i. Anders, namelijk:

1.3 Voor welke andere sectoren kan het projectresultaat ook interessant zijn?

- ~~a. Landbouw/visserij~~
- ~~b. Bouwnijverheid~~
- ~~c. Dienstverlening~~
- ~~d. Handel~~
- e. Industrie
- ~~f. Energie en water~~
- g. Transport
- ~~h. Overheid~~
- ~~i. Anders, namelijk:~~

1.4 Heeft uw project nog andere resultaten (zgn. spin off) opgeleverd?

- a. Ja, namelijk: **een methode om eenvoudig magnetische edelmetalen nanodeeltjes te maken.**
- ~~b. Nee~~

Toelichting:

1.5 Hebt u de resultaten, die u vooraf met dit project wilde bereiken, ook bereikt?

- ~~a. Ja~~
- ~~b. Nee~~
- c. Deels: **De gewenste Pt reductie is niet eenduidig gehaald, wel zijn er duidelijke ontwikkelingen richting een meer efficiënte en ook veel robustere elektrode.**

Toelichting:

1.6 Is het project voor u geslaagd?

- a. Ja
- ~~b. Nee~~
- ~~c. Deels~~

Toelichting: **Het project heeft de basis gelegd voor samenwerking tussen ECN en TU Delft voor**

PEMFC technologie. De zelf-assemblage technieken en de synthese van polymeriseerbare fluoro-surfactants vormen de weg naar nieuwe elektrode- en membraanconcepten.

1.7 In welke mate vindt u het project geslaagd, uitgedrukt in procenten?

- a. ~~0-50%~~
- b. ~~50-75%~~
- c. 75-100%
- d. ~~meer dan 100%~~

1.8 Als u minder hebt gehaald dan u verwachtte, wat is (zijn) daar dan de reden(en) van?

- a. Technisch
- b. ~~Personeel~~
- c. ~~Samenwerking~~
- d. ~~Financieel~~
- e. ~~Acceptatie eindgebruiker~~
- f. ~~Strategische bedrijfsoverweging~~
- g. ~~Wet/regelgeving~~
- h. Anders, namelijk:
Toelichting:

1.9 Wat gaat u met het projectresultaat concreet doen?

- a. Verder onderzoek, financiering (wordt gezocht) uit EOS: energie en samenwerking
- b. ~~Verder onderzoek, financiering (wordt gezocht) uit EOS: demo~~
- c. Verder onderzoek, financiering (deels) door marktpartijen
- d. Ontwikkelen van het product
- e. Anders, namelijk: **verder onderzoek op basis van o.a. Adem and IOP financiering**

4.2 Technologische innovatie

2.1 In welke mate zijn de *doelstellingen* die in uw aanvraag waren opgenomen ook gerealiseerd?

- a. ~~0-50%~~
- b. 50-75%
- c. ~~75-100%~~
- d. ~~meer dan 100%~~

2.2 In welke mate zijn de *technologische knelpunten* die in uw aanvraag waren opgenomen ook opgelost?

- a. ~~0-50%~~
- b. 50-75%
- c. ~~75-100%~~
- d. ~~meer dan 100%~~

2. Economie

3.1 Wat is uw inschatting van de time-to-market? (de tijd voordat het product verkrijgbaar is op de commerciële markt)

- a. ~~0-1 jaar~~
- b. ~~1-3 jaar~~
- c. ~~3-5 jaar~~
- d. ~~meer dan 5 jaar~~
- e. meer dan 10 jaar
- f. ~~geen marktintroductie~~

3.2 Welke knelpunten voor de ontwikkeling van de technologie zijn door het project in kaart gebracht of weggenomen?

Denk bij knelpunten ook aan sociaal-wetenschappelijke factoren, waarmee rekening dient te worden gehouden bij de ontwikkeling en implementatie van een nieuwe technologie, concept of systeem.

- a. Technische (o.a. doorontwikkeling)
- ~~b. Economische (o.a. leveringszekerheid)~~
- ~~c. Markttechnische (concurrentie)~~
- ~~d. Infrastructurele (o.a. inpassing in bestaande netten, duurzaamheid van grondstoffen)~~
- ~~e. Juridische (o.a. vergunning)~~
- ~~f. Sociale (o.a. acceptatie, gezondheid, veiligheid)~~
- g. Financiële (o.a. kostprijs en onvoldoende financiering)
- ~~h. Institutioneel~~
- ~~i. Geen~~

Toelichting:

3.3 Welke knelpunten voor verdere ontwikkeling zijn er nog?

- a. Technische (o.a. doorontwikkeling)
- ~~b. Economische (o.a. leveringszekerheid)~~
- c. Markttechnische (concurrentie)
- d. Infrastructurele (o.a. inpassing in bestaande netten, duurzaamheid van grondstoffen)
- ~~e. Juridische (o.a. vergunning)~~
- f. Sociale (o.a. acceptatie, gezondheid, veiligheid)
- g. Financiële (o.a. kostprijs en onvoldoende financiering)
- ~~h. Institutioneel~~
- ~~i. Geen~~

Toelichting: *Verder technische ontwikkeling is vereist voor producten ontwikkeld in dit project, die waarschijnlijk pas in de tweede of derde generatie brandstofcellen voor voertuigen gebruikt zullen kunnen worden. Aan de andere kant wordt de introductie van de eerste generatie brandstofcellen voor voertuigen nog belemmerd door de afwezigheid van een infrastructuur, onzekerheid over veiligheid van waterstof, en een hoge kostprijs. In Nederland wordt momenteel zeer sterk gesneden in geld voor onderzoek naar brandstofcellen. Dit betekent dat de internationale concurrentiepositie van Nederland duidelijk verzwakt.*

4.3 Kennis en kennisoverdracht

3.1 Welk effect heeft uw project gehad op de kennispositie van Nederland?

- ~~a. Sterke verbetering~~
- b. Verbetering
- ~~c. In stand houding~~
- ~~d. Verslechtering~~

3.2 Heeft er samenwerking plaats gevonden met het hoger onderwijs?

- a. Ja
- ~~b. Nee~~
- ~~c. Deels~~

Toelichting: TU Delft had een groot aandeel in dit project

3.3 Welke kennisproducten heeft het project opgeleverd?

- a. Octrooien
- b. Rapporten
- c. Publicaties
- ~~d. Anders, namelijk:~~

3.4 Wie bezit(ten) de intellectuele eigendomsrechten van de uit het project verkregen kennis? (o.a. aanvrager, partner, derden) **TU Delft**

3.5 Op welke manier(en) heeft u kennis over het project naar buiten gebracht? En hoe vaak?

- a. Openbaar eindrapport 1 keer
- b. Persbericht 1 keer
- c. Artikel
 - 1) In vakblad 2 keer
 - 2) In huis-aan-huis blad ...keer
 - 3) In regionale krant ...keer
 - 4) In landelijke krant ..keer
 - 5) Anders, namelijk..... ..keer
- d. Congres/workshop 30 keer
 - 1) Totaal aantal deelnemers: honderden personen
- e. Radio
 - 1) Nationaal ...keer
 - 2) Regionaal ...keer
 - 3) Lokaal ...keer
- f. TV
 - 1) Nationaal ...keer
 - 2) Regionaal ...keer
 - 3) Lokaal ...keer
- g. Internetpagina
 - 1) Eigen website gemaakt ja/nee
 - 2) Via websites van anderen ...keer
- h. Open dag ...keer
 - 1) Totaal aantal bezoekers ...personen
- i. Anders, namelijk:.... ..keer

4.4 Samenwerking

4.1 Welke partijen hebben in de samenwerking positief bijgedragen aan het projectresultaat?

Denk bij de bijdrage niet alleen aan een financiële bijdrage, maar ook aan inzicht in wet- en regelgeving, intellectuele bijdrage, bijdrage aan kennisoverdracht etc.

Naam partij 1: ECN

Project coördinatie, syntheses, karakterisering, disseminatie, opzetten projecten vervolg-onderzoek

Naam partij 2: TU Delft

Syntheses, karakterisering, disseminatie, patentverwerving, valorisatie patent, supervisie PhD studenten, opzetten projecten vervolg-onderzoek

4.5 Opmerkingen/verbeterpunten

5.1 Heeft u nog opmerkingen, dingen die u wilt toevoegen over uw project of projectresultaat die in de vragenlijst niet aan bod zijn gekomen? Die kunt u hier noteren.

5.2 Heeft u op basis van uw ervaringen met het subsidietraject bij Agentschap NL nog tips of verbeterpunten? Die kunt u hier noteren. ***Het gebruik van Engels in alle documenten en verslaggeving zou veel efficiënter zijn.***