SINTEF F23550- Unrestricted

Report

STAMPEM D 7-2
Report from Technoport 2012:
BPPs for PEM fuel cells and electrolyzers

Author(s)
Anders Ødegård

SINTEF Materials and Chemistry
Energy Conversion and Materials
2012-11-12

SINTEF Materialer og kjemi
SINTEF Materials and Chemistry

Address:
Postboks 4760 Sluppen
NO-7465 Trondheim
NORWAY

Telephone:+47 73593000
Telefax:+47 73597043

info.mk@sintef.no
www.sintef.no/mk
Enterprise /VAT No:
NO 948007029 MVA

KEYWORDS:
BPP
Bipolar plates
PEMFC
Fuel cells
Hydrogen

Report

STAMPEM D 7-2
Report from Technoport 2012:
BPPs for PEM fuel cells and electrolyzers

VERSION
1.0

DATE
2012-11-12

AUTHOR(S)
Anders Ødegård

CLIENT(S)
FCH JU

CLIENT'S REF.
303449

PROJECT NO.
806230

NUMBER OF PAGES/APPENDICES:
19

ABSTRACT

Abstract heading

This report is a summary of the presentations given at the Hydrogen session of Technoport RERC 2012: "Bipolar plates for PEM fuel cells and electrolyzers" and constitutes as Deliverable 7-2 in the FCH JU funded project STAMPEM. The project STAMPEM is a joint collaboration between SINTEF (Norway), MIBA Teer Coatings Limited (UK), Elring Klinger (Germany), Fraunhofer Institute for Solar Energy Systems (Germany), University of Birmingham (United Kingdom) and Fronius (Austria) and is dedicated to the goal of development of coatings for PEM fuel cell bipolar plates.

The workshop confirmed the general impression of high activity on BPPs for PEM technology. A wide variety of materials and concepts were presented, as well as different experimental techniques and procedures. No break-through technology was presented, but there are improvements done by several actors which are beginning to get interesting for commercial application. Both performance and costs are getting closer to the DoE requirements, however, it remains to confirm this in larger scale manufacturing and technical verification.

PREPARED BY
Anders Ødegård

SIGNATURE

CHECKED BY
Ingeborg Kaus

SIGNATURE

APPROVED BY
Egil Skybakmoen

SIGNATURE

REPORT NO.	ISBN	CLASSIFICATION	CLASSIFICATION THIS PAGE
SINTEF F23550	ISBN	Unrestricted	Unrestricted

Document history

VERSION	DATE	VERSION DESCRIPTION
Version No. 1.0	2012-11-12	Final version

SINTEF

Table of contents

1 Introduction

This report is a summary of the presentations given at the Hydrogen session of Technoport RERC 2012: "Bipolar plates for PEM fuel cells and electrolyzers" and constitutes as Deliverable 7-2in the FCH JU funded project STAble and low cost Manufactured bipolar plates for PEM Fuel Cells (STAMPEM), FCH JU project reference 303449. The project STAMPEM is a joint collaboration between SINTEF (Norway), MIBA Teer Coatings Limited (UK), Elring Klinger (Germany), Fraunhofer Institute for Solar Energy Systems (Germany), University of Birmingham (United Kingdom) and Fronius (Austria) and is dedicated to the goal of development of coatings for PEM fuel cell bipolar plates.

To be up-to-date on the progress within BPP for PEM technology, an open international workshop for sharing knowledge and scientific discussions with colleagues also outside of the project consortium was planned in the project. Practical reasons led to such an event before the STAMPEM project started; the Hydrogen session of Technoport RERC 2012 took place in Trondheim, Norway, at Rica Nidelven Hotel on April 16th and 17th.

Technoport RERC Research was the first part of the Technoport 2012 – Sharing Possibilities conference. Technoport and Centre for Renewable energy organize Technoport RERC research in collaboration.

TECHNOPORT
Sharing possibilities

Centre for Renewable Energy
NTNU SINTEF UiO
www.sffe.no

2 Scope of the BPP session of the Technoport 2012 conference

The transportation sector is expected to become the main consumer of hydrogen in the future energy economy. Leading automobile manufacturers have announced the launch of fuel cell vehicles in 2015 or even before. European energy companies are correspondingly preparing for large scale production and distribution of H_2 to cover the increasing fuel demand.

One key component in PEM technology, which contributes significantly to cost and needs improvement to meet lifetime requirements, is the bipolar plate (BPP). For transportation applications, it is clear that metallic plates currently offer the best compromise between electrical and mechanical functionality, weight and space saving, but cannot yet meet the corresponding lifetime and cost requirements.

According to a recent analysis for US Department of Energy, the cost of BPPs is still significantly higher than the cost target (~2.5€/kW, both DoE and EU/FCH JU). Lifetime of automotive PEM fuel cell stacks is currently approaching the target lifetime of 5000 hours, but bipolar plates used in these stacks are very expensive, as they are commonly based on high alloy stainless steel with a cost intensive coating. Alternative substrates and coating materials have not yet been developed to a level that allows commercial use, but are needed to achieve long-term stable and commercially viable bipolar plates.

The scientific focus of the Technoport RERC Research 2012 Hydrogen session was bipolar plates for PEM fuel cells and electrolyzers. Invited keynote speakers gave an introduction to the future hydrogen oriented economy and infrastructure, as well as state of the art bipolar plate overviews from both fundamental and applied perspectives.

3 Conference programme

Monday 16 April

- 11.00 – 11.30 (keynote): **Ulrich Bünger (Ludwig-Bölkow-Systemtechnik, Germany).** *Hydrogen as energy storage medium and fuel for transport*
- 11.30 – 12.00 (keynote): **Shinichi Hirano (Ford, USA).** *Metallic bipolar plate technology for automotive fuel cells*
- 12.00 – 12.30 (keynote): **Karren L. More (Oak Ridge National Laboratory, USA).** *PEM fuel cell metallic bipolar plates: Technical status and nitridation surface modification for improved performance*
- 12.30 – 13.00 (keynote): **Heli Wang (National Renewable Energy Laboratory, USA).** *Modified stainless steels for PEMFC bipolar plates*

- 14.30 – 14.50: **Gerald DeCuollo (TreadStone Technologies, USA).** *Development of low cost PEM-based metal bipolar plates*
- 14.50 – 15.10: **Kristian Nygren (Impact Coatings, Sweden).** *MaxPhase™ coatings on bipolar plates deposited by magnetron sputtering techniques in a high throughput industrial coating system*
- 15.10 – 15.30: **Muammer Koç (Istanbul Sehir University, Turkey).** *On the corrosion and contact resistance characteristics of micro-stamped metallic BPPs*
- 15.30 – 15.50: **Christophe Carral (Grenoble Institute of Technology / Université de Savoie / Université Joseph Fourier, France).** *Numerical analysis of stresses and strain in PEMFC generated during cell assembly*
- 15.50 – 16.10: **Torsten Knöri (DLR German Aerospace Center).** *Procedures and diagnostic methods for developing bipolar plates*
- 16.10 – 16.30: **Emile Tabu Ojong (Fraunhofer ISE, Germany).** *Advanced bipolar plates without flow channels, for PEM electrolysers operating at high pressure*

Tuesday 17 April

- 08.30 – 08.50: **Sonja Auvinen (VTT Technical Research Centre of Finland).** *Screening of plasma nitrided CrN coatings for PEMFC bipolar plate*
- 08.50 – 09.10: **Lars Kühnemann (The fuel cell research center ZBT GmbH, Germany).** *Bipolar Plate Technologies and Ex-Situ-Tests for Material Selection*
- 09.10 – 09.30: **Emilie Planes (Grenoble INP / Université de Savoie / Université Joseph Fourier, France).** *Polymer composites bipolar plates for PEMFCs*
- 09.30 – 09.50: **Anders Ødegård (SINTEF Materials and Chemistry, Norway).** *Research on bipolar plates for PEM technology at SINTEF*
- 09.50 – 10.10: **Zhigang Shao (Dalian Institute of Chemical Physics, DICP)** *Research on bipolar plates at Dalian Institute of Chemical Physics*

- 10.30 – 10.50: **Alejandro Ojarce (KTH Royal Institute of Technology, Sweden).** *Correlation between ex-situ and in-situ contact resistance of steels and coatings in PEMFC*
- 10.50 – 11.10: **Sigrid Lædre (Sør-Trøndelag University College, Norway).** *Ex-situ testing of nitrided CrN coatings for PEMFC bipolar plate*
- 11.10 – 11.30: **Justin Richards (Fraunhofer ICT, Germany).** *Corrosion studies on electro polished stainless steels for the use as metallic bipolar plates in PEMFC applications*
- 11.30 – 12.10: Discussions

Poster presentations:

Emilie Planes (Grenoble INP / Université de Savoie / Université Joseph Fourier, France):
Fast and accurate determination of the electrical conductivity on samples with various geometry: application to characterization of fuel cell's bipolar plates

Suwarno Suwarno (Norwegian University of Science and Technology):
Titanium-vanadium alloys for selective hydrogen absorption: the effect of alloy composition and additives

Michael Hiller (Miba Coating Group, High Tech Coatings GmbH, Austria):
Progress towards, thin, cost-effective coatings for PEMFC metallic bipolar plates by closed field unbalanced magnetron sputter ion plating

Most of the presentations are available here:
https://www.sintef.no/Projectweb/Stampem/Presentations/

4 Summary of the presentations

4.1 *Hydrogen as energy storage medium and fuel for transport*

Ulrich Bünger (Ludwig-Bölkow-Systemtechnik, Germany)
Hydrogen's role in the energy markets has been discussed widely and for many years. In the late 80s and 90s visions mostly anticipated its use as a universal and sustainable energy carrier to distribute fluctuating renewable energy around the globe following the sun in its daily rhythm (East-West) and its seasonal course (North-South). In the 90s, research and finally development of fuel cell based traction systems for transport have stimulated the development of applications from road, to rail, maritime and air transport. Major motivation for the transport sector was its vulnerability to an almost 100% dependency on fossil fuel (imports) and the urgent need to reduce pollutants and specifically greenhouse relevant emissions from internal combustion gasoline or diesel engines by substitution with fuel cells and renewable electricity.

With the looming shortage of fossil fuels, i.e. mineral oil, natural gas as well as coal, the growing concerns about the greenhouse effect, it was finally the Fukushima disaster which has become a game-change synonym to accelerate the introduction of renewable energy also into the stationary sectors. Here, the motivation was the integration of large amounts of fluctuating renewable electricity into the energy markets by large scale seasonal hydrogen storage as one major option. Even though this could be understood as a deflection from the use of hydrogen for transport, it was soon detected that hydrogen's newly discovered role would also support the hydrogen-for-transport strategy by supporting its infrastructure roll-out. Both applications are in good economic synergy concerning the development of production, distribution and storage infrastructures.

This contribution explained the motivation for the use of hydrogen for both the storage of electricity/energy at large scale and its use in the transport sector as well as the advantages of its dual use. The focus was on fuel cells as they serve as perfect end-use technologies complementing electricity markets and hydrogen for storage.

The conclusions from the presentation were:
- Hydrogen is posed for commercialization by 2015, in mass markets after 2020
- There is a need for hydrogen for energy storage after 2025 which requires strategic planning
- Gas grid may play an important role in Germany, economic case must be worked out
- Actors from all energy sectors need to synchronize their strategies to end divergence

- Most relevant synergy expected from hydrogen as vehicle fuel and energy storage
- Hydrogen for renewable electricity storage is expected to experience different solutions
- Hydrogen energy market will drastically outgrow hydrogen industry demand in long term

4.2 *Metallic bipolar plate technology for automotive fuel cells*

Shinichi Hirano (Ford, USA)

Bipolar plates account for a large fraction of fuel cell cost. In this area, graphite-based materials have been used in previous technology demonstrations at Ford. However an alternative metallic bipolar plate technology shows promises to achieve cost and performance targets, and is amenable to high volume manufacturing processes. Metallic bipolar plate technology is also expected to significantly improve volumetric power density, which is a critical requirement for automotive applications.

Ford has been experimenting with some metallic bipolar plate materials. One is nano-meter range gold (Au) coatings on stainless steel substrate materials, a.k.a. Au-nanoclad® supplied by Daido Steel (Japan). It was confirmed that the use of 10 nm thick coating helps to retain the noble properties of Au. Another one is so called Au-dot technology supplied by TreadStone Technologies, Inc. (Princeton, NJ). This metallic bipolar plate consists of a stainless steel substrate with corrosion resistant thin film coat. Thermally treated Au dots are deposited to create a highly electrically conductive path between surface of the plate and stainless steel substrate. Au dots cover only a small percentage of bipolar plate surface area. While Au is an expensive commodity, however the amounts of Au for both configurations are very small and should not pose a large cost penalty. Ex-situ materials evaluation tests indicate excellent electrical and corrosion resistance properties for both materials and meet the USDOE target. And in-situ tests with short stacks with 300 cm^2 active area were performed. Au nanoclad 20-cell stack was successfully operated through 2,500 hours of durability cycle test simulating real world operating conditions. Au-dot 10-cell stack was operated for 1,000 hours successfully. Post analysis revealed no significant corrosion issue for either material.

Summary of the presentation:

- Ex-situ and in-situ test results show that Au-nanoclad® and Au-dot materials have a significant potential to be used in automotive fuel cell stacks.
- Au-dot baseline material has room to improve area specific resistance (electrical conductivity) which can improve fuel cell performance.
- While Au is an expensive commodity, the amounts of Au for both configurations are very small and should not pose a large cost penalty.
- A Ford 20-cell stack development with improved Au-dot technology materials is undergoing further durability cycle testings with TreadStone Technologies, Inc.

4.3 *PEM fuel cell metallic bipolar plates: Technical status and nitridation surface modification for improved performance*

Karren L. More (Oak Ridge National Laboratory, USA)

The technical status of metallic bipolar plates for proton exchange membrane fuel cells (PEMFC) was overviewed from a materials development perspective. Stainless steels, aluminium alloys, etc. are of great interest for bipolar plates because they are amenable to low-cost/high-volume manufacturing methods such as stamping, offer high bulk thermal and electrical conductivities, low gas permeability, relatively low cost (depending on alloy content), and can be readily made in foil form ($\sim \leq 0.1$ mm thick) to achieve high power densities. However, the corrosion behavior of most metals in the aggressive PEMFC operating environment (~60-90°C acidic conditions, aerated and reducing, varying potentials) results in high interfacial electrical contact resistance from the formation of resistive surface oxides and/or poisoning of the fuel cell membrane from dissolution of metal species from the plates, both of which can significantly degrade cell performance. These considerations have led to intensive worldwide activity devoted to development of coatings and/or surface modification approaches (borides, carbon/carbides, nitrides, conductive oxides, refractory and precious metals, etc.) to improve the performance and durability of metallic bipolar plates.

Current literature trends for lower cost coated metal alternatives:

- Nano Gold variations (layers and composites)
  - may be only option if encounter frequent excursions >1V
- Carbon-based surfaces
- Cr-nitrides
- Electrochemical treatments

Summary of nitridation work:

- Promising manufacturability and single-cell fuel cell results obtained for stamped, laser welded, gas nitrided Fe-(20-23)Cr-4V alloy foils
- Quartz lamp nitriding shows promise for low cost, robust surfaces
- May be able to extend approach to existing commercial SS foils
  - favor ≥ 20 wt.% Cr ferritic (nitride forming additions Ti, V, etc)
  - best chance with quartz lamp (grow passive oxide layer with nitride particles)
- Concern for nitrided surfaces if frequent operation excursions > 1V

4.4 *Modified stainless steels for PEMFC bipolar plates*

Heli Wang (National Renewable Energy Laboratory, USA)

The future demand of fuel cell vehicles requires mass production of bipolar plates. The good mechanical strength, high chemical stability, ability for massive production, wide range of choices, relatively low cost and existing high speed high volume production pathways (like stamping) makes the stainless steels excellent candidate materials for PEMFC bipolar plates. The challenges of the metallic bipolar plate are the higher surface contact resistance due to the surface metal oxides (though providing excellent corrosion resistance) and possible contamination to the membrane due to the dissolved metal ions.

As a loop to explore suitable materials/coatings for PEMFC bipolar plates, the interfacial contact resistance and corrosion resistance of different stainless steels have been investigated in simulated PEMFC environments. Alloys with promising results are selected as base candidates for further development. Coatings and surface modifications (including nitridations) are applied to the candidate stainless steels, and the surface modified stainless steels are tested again in the PEMFC environments to provide feedbacks for further improvements in alloy compositions and processing procedure. Different modification methods generate different surface chemistries on stainless steels. For PEMFC bipolar plate application, nitridations of stainless steels are among the best.

Presentation conclusions:

- Tested over 20 bare metallic alloys (mainly stainless steels) in simulated PEMFC environments (Austenite, Ferrite, duplex, low-N);
- Some candidate steels showed very low corrosion rate; (DOE sub-target on corrosion rate was achieved);
- ICR with bare alloys still high;
- Passive films provided corrosion resistance, as well as the reason of high ICR;
  => Ways to decrease ICR needed.
- Austenite (300), Ferrite (400) and Duplex (2205) steels were deposited with ~0.6 µm SnO_2:F coating.
- Behavior of original coated steels depends strongly on the substrates. In general, coated lower grade steels showed more improvement than that of coated higher grades.

- Adding a pre-etching process resulted in modified coating. Modified coated steels shifts the ICR down. However, modified coated steels (444 and 446) showed poorer corrosion resistance than the original coated ones.
- Successful development of nitrided Fe-based alloys (AISI 446 and AL29-4C).
- Nitridation of SS foils using pre-oxidation and nitriding cycle yielded mixed nitride/oxide surface layer with significant improvement in ICR and corrosion resistance.
- Drawback was the 800-900C runs done for 24 h (long cycle = high cost). Likely solution is short preoxidation and then nitride quickly in purified N_2-$4H_2$ environment.
- Corrosion resistant in PEMFC environments and/or ICR are issues for bare SS as bipolar plates;
- Nitridation is one of the best solutions.
- Electrochemical nitridation provides an economic method to modify SS surface. One of the applications would be for PEMFC bipolar plates.

4.5 *Development of low cost PEM-based metal bipolar plates*

Gerald DeCuollo (TreadStone Technologies, USA)

It has been reported that using metal bipolar separate plates can reduce the polymer electrolyte membrane (PEM) electrochemical stack weight & volume by 40-50%, compared with current graphite bipolar plates. The major barrier for such metal bipolar plates is the severe corrosion conditions during stack operation. TreadStone is working with industrial partners in the fuel cell, electrolyzer, electrochemical compressor and flow battery (Energy Storage) markets to demonstrate and optimize TreadStone's patented technology and processing techniques for these commercial applications.

Most substrate metals do not have the adequate corrosion resistance in PEM-based electrochemical stack environment resulting in rapid performance degradation due to the formation of the electrically resistive surface oxide scale, and potential contamination of MEA by the dissolved ions from the metal plates. Various corrosion protection techniques have been investigated to prevent the metal plate corrosion. Some of these technologies have developed the corrosion resistant metal plates that can meet the performance requirements. However, it is still a challenge to have the metal bipolar plate that can meet both the performance and cost requirements.

TreadStone has developed and patented proprietary design and processing technologies that protect low cost stainless steel (such as 316 or 304SS) for PEM-based applications. The majority of the metal surface area (>98%) is covered with the low-cost corrosion resistive but non- or poor conductive material. A corrosion resistance and highly electrically conductive material (such as Au) forms a pathway for electron transport, in the form of small conductive vias (dots) penetrating through the non-conductive layer. The conductive dots have a dimension as small as several micrometers, are distributed (<1-2%) on the metal surface significantly reducing the cost. The average distance between the conductive vias is 20-70 mms. The dense distribution of conductive vias ensures a uniform current distribution between the gas diffusion layer (GDL) and metal bipolar plate.

TreadStone has conducted the proof of the concept experiments to demonstrate the low electrical contact resistance between GDL and metal plates with small gold particles covering a small portion of the whole surface area. It was found that the electrical contact resistance is related not only the total coverage of gold on the surface, but the dimensional structure of the gold vias. Higher gold coverage and smaller gold vias will lead to the lower contact resistance.

In summary, TreadStone have successfully demonstrated using commercial available stainless steel as the bipolar plate substrate for PEM-based applications. Using metal plates, replacing standard graphite plates, reduces 40~50% stack weight & volume of the stacks at much lower costs.

Presentation summary:

- Metal plates are an important component for PEM electrolyzers and fuel cells for cost reduction and long term durable operation.
- PEM electrolyzer developers are interested to the low cost metal plate technologies to replace expensive alternatives
- TreadStone's metal plate technology has been demonstrated for low temperature PEM fuel cell applications
    - 8000+ hours single cell test
    - 1000 hours stack test under automobile dynamic operation condition
- TreadStone's technology has potential to be used in PEM electrolyzers
- The long term durability test is on-going with industrial partners
- The investigations using TreadStone's metal plates is underway for energy storage flow batteries and electrochemical hydrogen compressors

4.6 *MaxPhase™ coatings on bipolar plates deposited by magnetron sputtering techniques in a high throughput industrial coating system*

Kristian Nygren (Impact Coatings, Sweden)

The multifunctional role of the bipolar flow field plates (BPP) in the fuel cell (FC) stack as a cell separator, gas distributor and current collector set high demands on their properties regarding weight, formability, corrosion, conductivity and cost. While stainless steel meets many of these requirements, the material is vulnerable to the hostile environment in a FC, which may degrade its function after long term use (> 5 000 hr).

Thin protective coatings (< 1 μm) deposited by physical vapour deposition (PVD) may offer a cost effective way of protecting the plates from degradation during cell operation. In addition to maintaining favourable functional properties (electrical and chemical) in the FC environment, the coatings should also meet the U.S. department of energy (DOE) cost requirements of about 1 $/kW. The choice of coating process together with the physical design of the BPP should therefore be considered already in an early stage in the fuel cell stack development.

Impact Coatings is currently offering MaxPhase™ as a low cost coating material suitable for stainless steel BPP, thus replacing the need for expensive precious metal coating. The InlineCoater™ system features a high throughput, short cycle deposition of MaxPhase as a cost efficient surface treatment. However, due to the wide variety of BPP geometries and substrate material quality, development of alternative deposition methods and substrate-specific adaptation may be necessary in order to further enhance productivity and thus meeting the DOE cost goals.

Two PVD methods are compared; DCMS (direct current magnetron sputtering) and HiPIMS (high power impulse magnetron sputtering) in order to deposit MaxPhase™ coatings on model BPP for evaluation in lab-sized, single cell fuel cells. The results show that MaxPhase™ coatings on BPP produced in InlineCoater™ are promising candidates to meet the production cost goals as recommended by DOE.

Conclusions from the presentation:

- MaxPhase™ coatings perform as gold coatings
    - 2,000 hours in stack test
- Results suggests that 50 nm CrN by PVD (compared to 500 nm & 1 μm) is too thin for fuel cell coatings with a large quantity of iron ions being released.
- Coating costs: 2 EUR/BPP (700 cm2/BPP, volume production)
    - Further cost reduction up to 90 % possible

4.7 *On the corrosion and contact resistance characteristics of micro-stamped metallic bipolar plates*

Muammer Koç (Istanbul Sehir University, Turkey)
The bipolar plate is one of the critical components in polymer exchange membrane fuel cell systems (PEMFC) as it constitutes big chunk of total stack weight and stack cost. Stainless steels, among other various materials, are considered as the prominent choice of bipolar plate material due to their inherent characteristics satisfying the requirements of PEMFC bipolar plates, such as mechanical support and strength to stack, flexibility, high heat, and electrical conductivity as well as chemical stability. Moreover, their forming into complex shapes can be performed conveniently at reasonable cost levels. Nevertheless, they are prone to corrosion under typical fuel cell working environment, and increased contact resistance may thus, arise.

A series of investigations, therefore, were performed to reveal the effects of several parameters on the contact and corrosion resistance of bare and coated metallic bipolar plates. These parameters included material type (SS304, SS316L, SS430, Ni270, Ti Grade I and II), forming method (e.g. stamping, and hydroforming), process condition (stamping force, speed, hydroforming pressure, rate) etc. Results, mostly conforming to reported findings in the literature, indicated that both corrosion and contact resistance performances are not at desired levels set by U.S. Department of Energy. A second set of studies was then conducted on PVD coated bipolar plates with SS316L as material of choice. Effects of coating type (TiN, CrN, ZrN), coating thickness (0.1, 0.5, 1.0 μm), forming method, manufacturing sequence (forming then coating vs. coating the blanks then forming into bipolar plate), corrosion test type (potentiodynamic and potentiostatic), and test condition (anodic, cathodic conditions), corrosion exposure on interfacial contact resistance (ICR) were evaluated at this stage. Coatings performed differently as ZrN was found to be the best in terms of corrosion resistance satisfying the DOE target and followed by CrN and TiN while TiN was the best performed in ICR tests yielding the lowest contact resistance. Apart from contact and corrosion resistance, a tribological effect study on long-term manufacturing of bipolar plates was also performed.

Presentation conclusions:

- Uncoated Samples
    - The channel size and hydroforming pressure by modifying contact geometry was found to be significant factors on ICR.
    - Stamping and hydroforming did not yield any certain pattern in most cases.
    - Do not meet DOE target level.

- Coated Samples
    - Effect of coating and coating thickness were the most significant effecting parameters.
    - Effect of manufacturing method and die geometry were insignificant.
    - Stamping with high punch speeds seem more appropriate for mass manufacturing of metallic BPP.
    - Coating before forming looks promising and is worthfurther investigation.

4.8 *Numerical analysis of stresses and strain in PEMFC generated during cell assembly*

Christophe Carral (Grenoble Institute of Technology / Université de Savoie / Université Joseph Fourier, France)
The design and assembly of fuel cells can influence significantly the efficiency of the stack. Experimental measurements show that the method of clamping the stack, which governs the compression rate of the MEA, is a critical parameter to get the best performance of the system [1]. Finite element analysis (FEA) has then often been used for predicting the state of stress and strain in the different elements of the stack. These numerical analyses are however based on either a single cell (3D), or a single tooth/channel structure in a bipolar plate (2D). The comparison with experimental results is then difficult or impossible. Large

deviations, up to 60%, between predicted stresses and experimental ones have been reported, by Lee et al, in a single cell stack. To improve knowledge about mechanical state generated within a stack during its assembly, a 3D finite element model of a 16-cells stack was developed. This model, composed of the MEA, the elastomer seal, the bipolar plates and the end plates, takes into account the real design of the different elements, such as the channels exhibited in the bipolar plates. The linear and non-linear mechanical properties of the different layers are also integrated.

The deformation of the different MEA has thus been evaluated with the help of the proposed FEA model; the determination of this parameter can be considered a pertinent parameter, because will help us, in the future, in the optimization of the design or the assembly of fuel cells. To verify these results, experimental measurements are now in progress, and require the development of a specific compression bench. The goal is to evaluate, in fine (small), the displacements, on different scales, from each bipolar plate, and to compare these values to FEA data. This study should thus bring an original contribution to the knowledge of the mechanisms involved during the clamping of the fuel cell, in order to optimize the design of the bipolar plates (dimensions, thickness) and to define the optimal properties of the different layers materials.

Conclusions from presentation:

- The minimum variation in the deformation in the MEA is observed at the middle of the stack.
- Similar results are observed for stacks composed by 16 or more cells.
- Two distinctive regions have been revealed:
- MEA n°1 - 4: Mainly governed by the bending of the end plate
- MEA n°5 - 16: Also depends on the mechanical properties of the Bipolar Plate

4.9 *Procedures and diagnostic methods for developing bipolar plates*

Torsten Knöri (DLR German Aerospace Center)
Today's polymer electrolyte fuel cells (PEFCs) are applicable only within a limited operating range. This limitation restricts the spectrum of possible applications and hinders their flexibility during operation. Hence, one of the most important targets in fuel cell research is to expand the range of the operating temperature. Thereby, the continuous operation at elevated temperatures or an extended temperature range for a limited time is an important consideration. In order to avoid critical operating conditions, to ascertain a sufficient durability and performance of a fuel cell stack, special concepts regarding bipolar plates, the cooling strategy, the membrane electrode assemblies as well as a closer look on the water management are essential. Furthermore, the operating strategy of the stack has to be adapted with respect to all of the stacks' components.

In this way, operating temperatures from 60 up to 130 °C can be realized. An elevated temperature range shall be applicable for short durations of approximately 1 hour. The presentation explained the steps of development of bipolar plates and endplate to meet the requirements. In addition, a DLR measurement technique for the determination of local current density distribution (PCB technology), local electrochemical impedance spectroscopy, calculations on the structural behaviour of the design was shown.

4.10 *Advanced bipolar plates without flow channels, for PEM electrolysers operating at high pressure*

Emile Tabu Ojong (Fraunhofer ISE, Germany)
In the vision to establish hydrogen as energy carrier in a wide range of applications, PEM water electrolysis has been recognized as an efficient and environmentally friendlier alternative to other technologies. But, although a lot of progress has been made in PEM electrolyser technology in recent years, there are still several challenges in order to realise full commercialisation and competitiveness in the market, such as: high capital cost due to expensive materials and production methods, and, short life time due to low chemical resistance of some of its main components. The bipolar plate is one of the components that bear the most

cost and chemical stability issues of a PEM electrolyser. Therefore, the manufacturing cost and chemical stability of bipolar plates must be optimised in order for PEM electrolysers to become more assertive in the renewable energy market.

Traditionally, carbon composites have been widely used as bipolar plate material for PEM fuel cell applications because of their high chemical resistance, although they have generally, low mechanical stability and high electrical and thermal resistance. Recently though, various metals have been considered as viable options, due to their high electrical and thermal conductivities and good mechanical strength. However, the chemical stability of metals in humid and acidic environments such as in PEM electrolysis, as well as high cost for machining remains a serious drawback in their usage. Corrosion on the anode side and, hydrogen embrittlement on the cathode side, are the main chemical degradation bottlenecks that hinder the use of metal bipolar plates in PEM electrolysers.

In framework of the EU sponsored NEXPEL project, Fraunhofer have tested several candidate metals as well as coating configurations, for corrosion stability in a simulated PEM electrolysis anode environment. Also, contact resistance measurements have been performed. The effect of hydrogen embrittlement on the cathode side has been addressed and the best solution as material for PEM electrolyser bipolar plate is presented. A cost analysis model has been used as the tool to evaluate the influence of material and production technology costs on the overall costs of bipolar plates and thus PEM electrolyser. It was found that, a significant portion of the cost is due to the machining of flow channels on metal bipolar plates. In this work, Fraunhofer propose an advanced and cost effective stack design concept without machined flow fields on bipolar plates.

Concluding remarks in the presentation:

- In-situ tests with short stacks, 5 cells and then 10 cells
    - 150 cm^2 cell active area
    - 1,8 V nominal cell voltage
    - 1 A/cm^2 current density
    - Up to 30 bar operating pressure
- Characterisation after up to 1000 hours of operation
- Concerns about hydrogen embrittlement of titanium
- Questions about titanium self ignition
- Further investigation on other coating configurations and surface modifications

4.11 *Screening of plasma nitrided CrN coatings for PEMFC bipolar plate*

Sonja Auvinen (VTT Technical Research Centre of Finland)

Different CrN coatings on SS 316L were studied with a multi single cell, in which several parallel samples can be tested cost-efficiently in-situ in similar conditions. All tested coatings were manufactured in the same manner. First a layer of Cr was deposited on the SS 316L surface and subsequently plasma nitrided to obtain a CrN layer. Different manufacturing techniques for the Cr layer were used. Physical vapour deposition (PVD by Impact Coatings AB) and electro deposition for hexavalent Cr (by Kromatek Oy) and trivalent Cr (in-house at VTT) were used to produce coatings with several different thicknesses. Hexavalent Cr is toxic but its mechanical properties are good. Trivalent Cr is more environmentally friendly but the process is more complicated.

In the fuel cell tests SS samples were placed inside the cell between the flow field and gas diffusion media. Test duration was four weeks (650 hours) with low constant current, high temperature and fully humidified hydrogen and air. The interfacial contact resistance (ICR) of the coated SS was the most important characteristic measured. Other properties studied were the amount of iron and chromium ions released from the steel and adsorbed to the MEA and GDLs and the contact angle of water on the coating surface. With some coatings the structure was inspected with XRD or SEM.

The ICR values of some of the samples were very good (5 mΩ cm^2) before exposure to the fuel cell environment. After the fuel cell test all the values were increased but still acceptable (11-14 mΩ cm^2). The results of the iron analysis of the MEAs and GDLs varied as both high and low values were measured. Some samples had visual changes in their surfaces implying some kind of degradation, which was also observable in the iron contents of the MEAs. The water contact angle results varied between samples both prior to testing and in the post-test measurements.

Summary from the presentation:

- Three different methods to produce CrN
    - Plasma nitridation was applied to
        - PVD Cr
        - Conventional electrodeposited hexavalent Cr
        - New electrodeposition process for trivalent Cr
- Iron release results were good for all but the thinnest CrN layers
- ICR values varied
    - Best results from 5 µm and 10 µm hex-CrN
    - Trivalent CrN has potential for low ICR as well if the process is further developed
- Most stable contact angle with trivalent CrN and 10 µm hexavalent CrN

4.12 *Bipolar Plate Technologies and Ex-Situ-Tests for Material Selection*

Lars Kühnemann (The fuel cell research center ZBT GmbH, Germany)

For many years, the development of compound materials consisting of a polymer and various carbon compounds for injection moulding of bipolar plates has been developed in Duisburg. As criteria, the resulting electric conductivity of the bipolar plates, the chemical inertness and gas tightness are of superior interest. In a first approach, material for PEMFC with perfluorinated, sulfonated membranes (PFSA) has been successfully used in a series production process. In further work, materials for high temperature PEMFC with phosphoric acid doped PBI membranes were investigated. Even this process was recently established successfully, a short stack underwent a first durability check for 500 operational hours with very good results.

For compact fuel cell stacks, metallic bipolar plates are usually preferred. Here, corrosion protection, forming of the delicate flow field structures and laser welding of two half plates to form a bipolar plate are the technologies to be addressed. Within a current project, a stack based on hydro-formed metallic bipolar plates will be realised. The application is a range extender for a battery electric vehicle, a Fiat 500. Consequently ex-situ-tests are applied at ZBT to conduct the material selection for stack and peripheral components. Approaches and specific results regarding materials for metallic bipolar plates, coolant and cooling cycle are presented.

Summary from the presentation:

- Stationary applications are addressed by injection molded composite bipolar plates for low temperature and high temperature PEMFC at ZBT
- Automotive applications are addressed by hydroformed metallic bipolar plates in cooperation with industrial partners
- Many ex-situ (and also in-situ) methods are available for materials, components and stacks
- Pre-assessment of metallic substrates for bipolar plates is conducted by ICR-measurement, immersion test and analysis of leached ions
- A graphite coating was found to be a promising candidate for corrosion protection
- 6 candidate cooling media were tested by an ex-situ immersion test, and one was selected as suitable for PEMFC application without ion exchanger

4.13 *Polymer composites bipolar plates for PEMFCs*

Emilie Planes (Grenoble INP / Université de Savoie / Université Joseph Fourier, France)
Many different materials for bipolar plates have been investigated. Non porous graphite remains however the reference materials leading to the best durability and performance. As a result of material and manufacturing costs of the graphite plates, extensive efforts have been made to develop alternative materials, essentially metallic and composite bipolar plates. The lack of corrosion resistance and the high density induce strong limitations to the use of metals. The alternative solution consists in polymer composites that combine the processability and mechanical properties of the polymeric phase and the conductivity of the carbon fillers. This communication provided a state of-the-art review for the current development, manufacturing and structure-property relationship of polymer composites designed for bipolar plates applications. Both thermoset resins and thermoplastics were considered and combined with many different carbon fillers: graphite, carbon fibers, carbon black, carbon nanotubes…The interests and disadvantages of these formulations were presented in terms of processability and most relevant properties (electrical and mechanical properties). Different combinations were suggested in order to reach the two main requirements of the materials used for this application. A debate on the optimization of electrical and mechanical properties was proposed.

Generally:
- graphite must be incorporated as a primary component
- carbon fibers, carbon black and carbon nanotubes can be added to improve/change properties

4.14 *Research on bipolar plates for PEM technology at SINTEF*

Anders Ødegård (SINTEF Materials and Chemistry, Norway)
SINTEF has experience within corrosion testing and protection of steel from working with the oil industry for several decades. Knowledge on protective coatings from this work, combined with new coatings and thin film technology is now being applied to develop improved BPP for PEM technology. SINTEF coordinates the Nordic project NORCOAT, where the partners PowerCell, Impact Coatings, VTT, Outokumpu and Kromatek are aiming at a low cost and durable coating for PEM fuel cell BPPs. Very promising developments have been achieved. SINTEF are also cooperating with NTNU and HIST on development of coatings, initially carbon -and epoxy based. Available techniques and equipment at SINTEF/NTNU was presented together with selected results from the on-going projects. One of them was from accelerated tests, where results from ex-situ and in-situ experiments were compared. These were made on Coatings from Impact Coatings, which show performance satisfying the DOE requirements. Some initial results from in-situ measurement of ICR, where a gold coated wire placed inside the cell, were presented.

4.15 Research on Metal Bipolar Plates with Surface Modification

Zhigang Shao (Dalian Institute of Chemical Physics, DICP)
DICP have studied modified metal plates for both PEMFC and URFCs (Unitized Regenerative Fuel Cells). For PEMFC the following concepts have been pursued:
- Ag-PTFE/316L SS bipolar plate
- C-Cr/316L SS bipolar plate
- (CrN/Cr)6/316L SS bipolar plate

While for URFCs the following concepts have been pursued:
- Ag/Ti bipolar plate
- Ti-Ag/Ti bipolar plate
- Ti-Ag-N/Ti bipolar plate

Summary of the presentation:

- Ti-Ag-N nanocomposite film is for the first time applied as modification layer on Ti bipolar plates for URFCs.
- After coated with Ti-Ag-N nanocomposite film, Ti plates show enhanced corrosion resistance, conductivity and hydrophobicity.
- SEM results show that Ti-Ag-N film is honeycomb-like and Ag cluster or nanoparticle is embedded in Ti_2N matrix.
- The enhanced corrosion resistance and conductivity is attributed to the combination of corrosion resistant Ti_2N and excellent conductivity of Ag.
- Coating Ti-Ag-N films on Ti plate show a promising potential application in URFCs.

4.16 *Correlation between ex-situ and in-situ contact resistance of steels and coatings in PEMFC*

Alejandro Ojarce (KTH Royal Institute of Technology, Sweden)

A low and stable contact resistance between bipolar plates (BPP) and gas diffusion layer (GDL) is one of the most important requirements for new BPP materials. The in-house fuel cell hardware used in this study provided the opportunity to conduct both ex-situ and in-situ measurements of contact resistance using the same set-up and the same BPP sample.

Operating conditions such as; current density, temperature and water content of gases were compared with MEA (in-situ) and without MEA (ex-situ). It can be assumed that depending on the BPP material there might be large differences between ex-situ and in-situ contact resistance mainly due to dynamic changes in MEA thickness, water-and heat-production at the cathode. It was observed that the voltage drop due to contact resistance in the in-situ measurements had a dynamic nature.

Conclusions from the presentation:

- The effective contact area between GDL and BPP is crucial for the magnitude and stability of the contact resistance, especially for poorly conductive materials such as uncoated stainless steels
- The contact resistance decreases with increasing temperatures, probably due to thermal expansion of the fuel cell components.
- The contact resistance decreases with increasing RH of the gases, probably due to membrane swelling. On the other hand, a large increase in pressure drop due to the presence of liquid water affects the contact resistance negatively.
- Current density has a dual effect on the contact resistance. While an increased current density increases the temperature of the cell and therefore has a positive effect on the contact resistance, it may also increase the water production and the pressure drop at the cathode, having a negative effect on the contact resistance.
- The changes in contact resistance could easily have been mistaken for other ohmic losses, such as metal ion poisoning of membrane, if the direct measurement of the contact resistance would have not been carried out.

4.17 *Ex-situ testing of nitrided CrN coatings for PEMFC bipolar plate*

Sigrid Lædre (Sør-Trøndelag University College, Norway)

SS 316L bipolar plates with etched flow fields were put through potentiostatic- and potentiodynamic electrochemical measurements in sulfuric acid electrolytes. Stainless steel bipolar plates without coating were put through these measurements in order to study the stability and thickness of the oxide layer formed on the stainless steel surface. The electrochemical tests were performed in electrolytes with various pH, which was done by altering the molarity of the sulfuric acid. Fluoride and chloride were added to the electrolyte for some of the tests, in order to study the effect the halides have on the stainless steel surface.

Interfacial Contact Resistance (ICR) measurements where performed before and after each electrochemical test.

Even though bare stainless steel possesses several of the qualities desired for a bipolar plate, it does not fulfill the U.S.department of energy's (DOEs) targets for conductivity (resistance). It is thus desirable to investigate coatings for SS316L bipolar plates. Stainless steel bipolar plates with CrN coatings were studied by use of the ex-situ measurements described above. The coated plates were delivered by VTT, technical Research Centre of Finland. The Cr had been applied to the stainless steel surface by use of both Physical Vapour Deposition (PVD) and electrodeposition, and both hexavalent and trivalent Cr was used. In order to obtain CrN the Cr had also been plasma nitrided.

Stainless steel plates polarized in electrolytes with pH values of 2.87 and higher showed corrosion currents in the same order of magnitude as the 1 $\mu A\ cm^{-2}$ target set by DOE for 2015. The ICR requirement for bipolar plates of less than 10 $m\Omega\ cm^2$ was, however, not fulfilled for the same plates.

Conclusions from the presentation:

- Both the corrosion test setup and the ICR test setup makes it possible to do ex-situ testing easier and faster than when the PEM fuel cell is in operation.
- Low pH might not be the best way to accelerate the corrosion process of the stainless steel.
- The CrN coated bipolar plates showed very promising ICR.
- Further work will focus on development and testing of self produced coatings.

4.18 *Corrosion studies on electro polished stainless steels for the use as metallic bipolar plates in PEMFC applications*

Justin Richards (Fraunhofer ICT, Germany)

In the tests the corrosion resistance of six stainless steel materials (316L, 316Ti, Al276, Al265 and Al6XN) in bulk form and after an electrochemical surface treatment was studied by linear sweep voltammetry. The electrolyte used for the corrosion analysis consisted of fluoride (1.8 ppm F^-) and sulphate ions (12.5 ppm SO_4^{2-}).

The electro polishing procedure varied in current densities (50 and 100 $mAcm^{-2}$) and polishing time (15 and 10 min) as well as in proportion of the constituent parts of the used electrolyte (methane sulfonic acid and 1,2-propanediol). In addition to the electrochemical characterization of the stainless steel specimen a microscopic analysis gave information on the surface structure of the tested samples.

The untreated samples exhibited an increasing corrosion resistance by the order of Al276 < Al265 < Al6XN < 904L < 316Ti < 316L. Of the untreated samples only 316L and 316Ti met the DOE target for the corrosion current density (< 1 $\mu A/cm^2$).

After the electrochemical treatment in a solution containing 30 % methane sulfonic acid and 70 % 1,2-propanediol the corrosion current for Al6XN, Al276 and Al265 decreased by more than 50 % in comparison to their bulk specimen.

The electrochemical test results showed influences on the corrosion resistance by the composition of the electrolyte and also by the erosion rate during the electro polishing process. The samples polished with a 50 A/cm^2 current density for 15 min exhibited lower corrosion currents at a potential of 0.6 V vs. NHE compared to those polished at 100 mA/cm^2 for 10 min.

In conclusion:

- Electrochemical corrosion properties of Al276, Al265 and Al6XN regarding LT-PEMFC applications can be improved by an electro polishing process.
- 316L, 316Ti and 904L showed an increase of corrosion currents.
- All polished samples exhibited an increase in resistivity.
    - Lowest Al265 with ~10-50% increase
- More tests are necessary to find the optimized electro polishing solution for each stainless steel material.
- The electro polishing procedure has to be individually selected for stainless steel materials to provide better corrosion resistance.

4.19 Posters

Emilie Planes (Grenoble INP / Université de Savoie / Université Joseph Fourier, France):
Fast and accurate determination of the electrical conductivity on samples with various geometry: application to characterization of fuel cell's bipolar plates
There is a need for a method to measure the electrical properties of samples with very irregular geometric features and without altering their shape. The four-point probe method is commonly used for measuring electrical conductivity, but the sample's geometry should be controlled or even altered for accurate measurements. Based on the literature, a method is proposed that fulfills all the above mentioned requirements to determine the electrical properties on samples with various geometry (shape and thickness). This is based on the determination of correction factors for the four-point probe method taking into account the real geometry of the sample and evaluating edge effects related to the position of the probes. Both experimental and theoretical approaches were performed and compared to validate the method. As an example, the dispersion in electrical properties of bipolar plates made of commercial composite formulation will be presented. It will also be emphasized that the results can be used for the local measurement of the electrical conductivity and thus for the study of the electrical properties anisotropy of the bipolar plates, and the relationship to the filler dispersion in the composite. In conclusion there is a hope that the technique may eventually be employed in order to develop a better understanding of the formulations and process of bipolar plates.

Suwarno Suwarno (Norwegian University of Science and Technology):
Titanium-vanadium alloys for selective hydrogen absorption: the effect of alloy composition and additives
Not relevant for the topic of the STAMPEM project.

Michael Hiller (Miba Coating Group, High Tech Coatings GmbH, Austria):
Progress towards, thin, cost-effective coatings for PEMFC metallic bipolar plates by closed field unbalanced magnetron sputter ion plating
Closed field unbalanced magnetron sputter ion plating (CFUBMSIP) produces dense, well adhered coatings, and both transition metal nitrides and graded, nano-composite, non-hydrogenated amorphous carbon, demonstrating the combination of properties required in this application. The quality of the coatings allows coating thickness to be minimised (typically <1micron) while still providing adequate functionality and longevity, and of course this is also critical to the minimisation of production costs. Ultimately this technology is compatible with low-cost manufacturing techniques similar to those already employed for many automotive parts.

The poster described the progress towards the industrial production of CFUBMSIP coatings for the metallic BPPs, using high rate reactive magnetron sputtering for transition metal nitrides (including CrN, TiN and ZrN) and carbon-based coatings (from elemental metal and solid graphitic magnetron sputtering targets). The characterisation of the coatings, in terms of their properties, relevant to the PEMFC application was described, and future developments were discussed.

5 Summary of the workshop

The workshop confirmed the general impression of high activity on BPPs for PEM technology. Germany, USA and Asia lead R&D in this topic. A wide variety of materials and concepts were presented, as well as different experimental techniques and procedures. Most studies are on modified SS bipolar plates, in particular on low cost coating materials and techniques. Besides coating materials themselves, an increased effort in the fundamental research, e.g. degradation mechanism, operating temperatures, etc would bring significant development to this topic.

Performances seem to meet the requirements, but the cost is still very much higher than the DoE-requirements, so more work will be need to be focused on this topic. No break-through technology was presented, but there are improvements done by several actors which are beginning to get interesting for commercial application. Both performance and costs are getting closer to the DoE requirements. However, it remains to confirm this in larger scale manufacturing and technical (stack, long term) verification.

Input to STAMPEM/remaining questions after the workshop:

It may be helpful to obtain durability cycle test for the fork lift/tow truck application in order to match this with a comparable accelerated corrosion stress test.

Karren More stated that plates must be stamped first then nitrided. It would be interesting to know which effect do the temperatures from 900-1000 °C have on the dimensional accuracy of a stamped 0.1 mm 316L plate.

Karren More stated concern for nitrided surfaces if frequent operation excursions > 1V. Would EK or Fronius have a mitigation strategy for the high (<1.4V) start up/shut down potentials?

The mechanical properties of candidate coatings should be correlated with suitability for stamping. It seems unlikely that the mechanical properties of a carbon/polymer composite would be suitable for coating followed by stamping. To get adequate conductivity, a high carbon loading is required, however, this would also make the coating very brittle.

It might be helpful to measure the in-situ compression of the STAMPEM stack using Pressurex™ paper and compare with ex-situ tests.

SINTEF

Technology for a better society

www.sintef.no