

# The 3rd CARISMA International Conference on Medium and High Temperature Proton Exchange Membrane Fuel Cells

Three approaches to better platinum catalysts at biannual conference

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The 3rd CARISMA International Conference was held at the Axelborg venue in Copenhagen, Denmark, from 3rd to 5th September 2012. The CARISMA conference series is specifically devoted to challenges in the development and testing of fuel cell materials and membrane electrode assemblies (MEAs) for proton exchange membrane fuel cells (PEMFCs) for operation at intermediate and high temperatures, i.e. above 100°C, for both transport and stationary applications. The conference series was initiated by the European CARISMA Coordination Action for Research on Intermediate and High Temperature Specialised Membrane Electrode Assemblies, with the first two conferences held in 2008 and 2010 at La Grande Motte near Montpellier, France. The scope of the conference series is scientific and its spirit is to encourage the free exchange and open discussion of recent findings in this important area.

The 2012 event in Copenhagen had around 150 participants from 20 countries in five continents. The majority of the audience was academic or from research organisations, but there was also industrial participation from 20 companies to put the research and development in perspective and to strengthen the link between fundamentals and applications. The oral programme comprised 50 speakers of whom 11 were invited. It was organised in 13 sessions, of which two were devoted to fuel cell catalysts and their supports. Other sessions covered membranes, MEAs, alkaline fuel cells, electrodes, system and stacks, and degradation. In addition there were 63 papers within the same fields presented in two poster sessions. The Book of Abstracts including the programme, selected presentations and posters can be downloaded *via* the conference homepage (1).

The focus of the present review is on a selection of those presentations dealing with platinum group metal

(pgm)-based fuel cell catalysts. Individual references to the presentations are not given. Instead names and titles are provided and the reader is referred to the Book of Abstracts (2).

### PEMFCs at Elevated Temperature

The idea of operating PEMFCs at elevated temperature dates back a few decades. One of the general advantages of the PEMFC is its low working temperature, conventionally 60–80°C, but there are a number of benefits if the temperature can be increased to above 100°C. The main drivers have been higher tolerance to fuel impurities, easier heat rejection, reduced challenges with water management and a higher value of the produced heat (3).

Catalysts, electrodes and cell architecture of the high temperature PEMFC (HT-PEMFC) are to a large extent shared with the conventional low temperature PEMFC. The major difference is the proton conducting electrolyte membrane, which must be thermally stable and maintain conductivity at the elevated temperature. A well-recognised breakthrough was made at Case Western Reserve University, USA, with the phosphoric acid doped polybenzimidazole (PBI) membrane (4). Hereafter, this and comparable systems have been explored by an increasing number of groups (5). The community of people involved in HT-PEMFCs is growing and a number of commercial enterprises are aiming at commercialisation of the technology on cell, stack and system levels. Many of the leading companies in this industry such as Elcomax (Germany), EnerFuel (USA), Samsung (Korea), Danish Power Systems (Denmark) and Serenergy (Denmark) were present at the conference.

### Catalysts

Similarly to low temperature PEMFCs and phosphoric acid fuel cells (PAFCs), Pt and its alloys are exclusively used as catalysts in HT-PEMFCs. High surface area carbon blacks (for example, VULCAN® XC72 or Ketjenblack® carbon blacks) have been widely used as the catalyst support, though it is well known from PAFC research that corrosion rates of these carbon materials are unacceptably high for long term operation. Higher operational temperatures impose even more challenges on the catalysts and electrodes. First of all, the doping acid adsorbs strongly on the catalyst surface and slows down electrode reactions. Moreover the high temperature aggravates the corrosion of the carbon support.

The work presented at this conference reflected the main challenges for PEMFC catalysts, namely cost

and durability. The presentations can be grouped in the following categories: Pt catalyst structures and application processes, alternative catalyst supports and Pt alloy catalysts. There were also a number of presentations on non-noble metal catalysts that are not included in the present review.

### Platinum Catalyst Structures and Application Processes

Gustavo Doubek (University of São Paulo, Brazil) and colleagues, in collaboration with Yale University, USA, presented a supportless approach for the design of stable catalyst architectures for HT-PEMFCs. This was done *via* Pt nanotubes or metallic glass nanowires. The glasses were thermoplastically moulded and subsequently activated through selective dealloying leading to a roughened Pt rich surface. Electrochemical cycling experiments showed that the activities of the metallic glass catalysts were constant or in some cases improved while the activity of a commercial ETEK Pt/C catalyst decreased under the same conditions. However, further development is needed to reach a practical electrode.

Shangfeng Du *et al.* (University of Birmingham, UK) have prepared single crystal Pt nanowires in the [111] direction for catalysts. Their catalyst layer of unsupported Pt nanowires was only 0.5 µm thick (see **Figure 1** (6,7)). In a potential cycling test against a commercial catalyst with methanol as fuel the nanowire catalyst showed higher stability.

An approach to ultra-low Pt anodes prepared *via* physical vapour deposition (PVD) was presented by

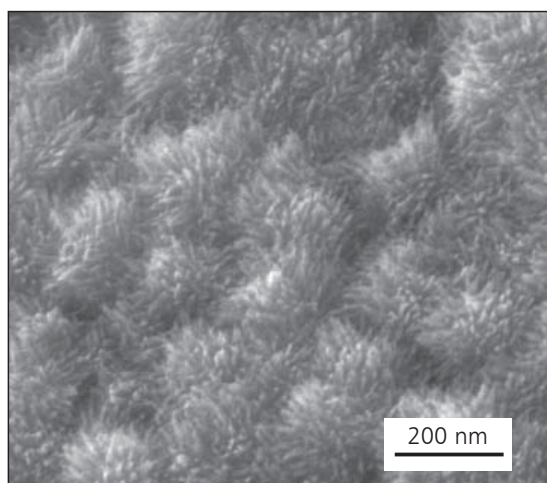


Fig. 1. Platinum nanowire thin film catalyst electrode (Courtesy of Shangfeng Du, University of Birmingham, UK)

Daniel Gonzalez *et al.* (Tecnalia, Spain). Catalysts were prepared with Pt loadings between 15 and 150  $\mu\text{g cm}^{-2}$  and particle sizes down to 10 nm. The preparation of anodes with Pt loadings down to 10 mg per kW was envisioned with this technique.

### Alternative Catalyst Supports

Alternative catalyst supports for Pt were addressed in a number of presentations. Some of these were modified carbon structures. Maria Daletou *et al.* (Foundation of Research and Technology-Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Greece) prepared pyridine functionalised multiwalled carbon nanotubes (MWCNTs), which showed increased Pt active surface utilisation and stable and robust behaviour at 180°C under hydrogen lean reformat conditions. The pyridine moieties helped distribute the Pt clusters (see **Figure 2**). The focus was on anode stability and the catalyst was tested with a phosphoric acid doped membrane (polyethers with pyridine units, Advent Technologies SA, Greece). Henri Perez (Commissariat à l'énergie atomique et aux énergies alternatives (CEA), France) *et al.* studied the oxygen reduction reaction (ORR) by organically grafted Pt electrocatalysts, carbon nanotubes and N-doped carbon nanotubes in combination. The grafting of the Pt particles was by organic moieties of different sizes bound by sulfur bridges. Test methods for porous electrodes were presented. Naotoshi Nakashima (Kyushu University, Japan) *et al.* presented PBI-wrapped carbon nanotubes as Pt catalyst support. Treatment with PBI increased the affinity of the support for Pt nanoparticles without prior oxidation. A similar approach on graphene as support

was taken by Anastasia Permyakova *et al.* (Technical University of Denmark). PBI treatment led to well distributed Pt particles. Amrit Chandan (University of Birmingham, UK) *et al.* made fuel cell electrodes with Pt catalysts supported on graphene oxide. Apparently, the sheet structure of graphene oxide led to poor gas transport properties, but this was solved by mixing in more spherical particles of carbon black.

Supports not based on carbon were the subject of several presentations. Magnus Thomassen *et al.* (SINTEF, Norway) used antimony-doped tin oxide (ATO) as a Pt support for the ORR. The Pt particles were about 3.5 nm diameter and well distributed. Accelerated testing showed high stability and minimal loss of electrochemically active surface area. The reference catalyst was from Tanaka. Catalyst supports of titanium dioxide and titanium oxycarbide (TiOC) with Pt applied by a colloid method were prepared by Alessandro Zana (University of Copenhagen, Denmark) *et al.* The electrochemically active surface area was much larger on TiOC than on  $\text{TiO}_2$ . Specific activity and mass activity were reported to be comparable to commercially available Pt/C catalysts. Carbide based supports were presented by Min Yin (Changchun Institute of Applied Chemistry, China) *et al.* and Antonio Luis Tomas Garcia *et al.* (Technical University of Denmark). Yin used tungsten carbide (WC) as a support for palladium and palladium-cobalt catalysts for formic acid electrooxidation and Tomas Garcia screened carbides of tantalum, molybdenum, niobium and chromium in hot phosphoric acid.

Finally, Jozsef Speder *et al.* (University of Copenhagen, Denmark) presented the support independent polyol method for Pt nanoparticle synthesis as a suitable way to decouple the particle synthesis from that of the support. This method allows the variation of process parameters to be avoided when applying the catalyst to the support. New catalyst supports can thus be studied without being affected by the Pt particle preparation.

### Platinum Alloy Catalysts

There were eight presentations on pgm alloys. Pt-Co alloys were presented by Alexander Schenk *et al.* (Graz University of Technology, Austria) and Ioannis Spanos and Matthias Arenz (University of Copenhagen, Denmark). The work by Schenk was performed in collaboration with Elcomax, a HT-PEMFC producer. Spanos compared eight different ways to prepare the alloy catalyst particles in terms of composition, active surface area and specific activity. Significant

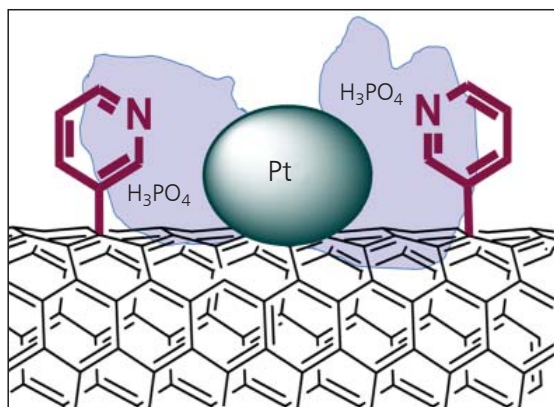


Fig. 2. Pyridine functionalised multiwalled carbon nanotubes as stable platinum supports (Courtesy of Maria Daletou, FORTH/ICE-HT, Greece)

variations were found. A third Co alloy presented was the Pd-Co by Yin *et al.* (Changchun Institute of Applied Chemistry, China) mentioned above. Gaurav Gupta *et al.* (University of Birmingham, UK) made Nafion stabilised Pt-Co alloy particles supported on Vulcan carbon black and graphene oxide. The active area was slightly higher for the graphene oxide based catalysts, but quite low in both cases. Nevertheless, the activity was reported to be high.

Jong Hyun Jang *et al.* (Korea Institute of Science and Technology, Korea) have studied the ORR activity of ruthenium-selenium on carbon in phosphoric acid. The aim was to find ways to mitigate the adsorption of phosphoric acid anions on the catalysts in HT-PEMFCs. A positive effect on the ORR after alloying of Ru with Se was seen in phosphoric acid. A platinum-gadolinium (Pt<sub>5</sub>Gd) catalyst was presented by Maria Escudero Escribano *et al.* (Technical University of Denmark). This alloy catalyst showed an activity similar to that previously obtained for platinum-yttrium (Pt<sub>3</sub>Y) (8), which has been identified as the most active Pt-based polycrystalline alloy for the ORR to date. The Pt<sub>5</sub>Gd catalyst also showed high stability during potential cycling with an upper potential of either 1.0 V or 1.6 V (9). Anton Vassiliev *et al.* (Technical University of Denmark) and Brian Benicewicz (University of South Carolina, USA) both presented recent work on direct conversion of dimethyl ether in a HT-PEMFC with Pt-Ru anode catalysts.

### Conclusions

The conference strongly supported the trend in fuel cell catalyst research towards higher stability and lower cost. Three main approaches can be identified. First, Pt application processes which result in better distribution of the catalyst surface. This includes non-supported nanostructured Pt. Second, the search for new and more stable supports. These can be nanostructured carbon materials or inorganic materials. Third, the development of Pt alloys and de-alloyed structures. It was evident at the third CARISMA International Conference that steady progress is being made in all three directions to improve fuel cell performance.

### Acknowledgement

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