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Project title: Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC

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1. Executive summary

The SMARTCat project is intended to provide new trimetallic catalysts (WP2) deposited on new support materials (WP3) expected to operate at high temperatures suitable for car applications. This involves a relevant high temperature membrane, which is developed especially for the project (WP4). Emphasis is also given to automated membrane electrodes assembly (WP4). Fuel cell tests in automotive conditions with selected MEAs (WP5) in agreement with harmonization protocol discussed with the JRC-IET are carried out. A technico-economic assessment has been achieved (WP5).

a) New trimetallic catalysts
The modelling of trimetallic structures has shown 0.05 eV reduction of OH binding energy on PtAuCo and PtAuNi rendering them highly active for ORR. Addition of small amount of Au is found to increase the stability of the catalysts. On the experimental side, the targeted exchange current was reached for Pt3NiAu, Pt3CuAu and Pt3AuCo ternary catalysts. The higher stability is obtained with the Pt6Cu2Au2/C catalyst with an activity loss of only 45% after 1000 cycles. Plasma sputtering deposition was designed to prepare low Pt content nanocatalysts of 220 cm$^2$ large area cathodes with Pt6Ni2Au2 and Pt6Ni1Cu1 loading. Molecular dynamics simulations of PtxPdyAuz, PtxNiyAuz PtxCuyAuz growth on model porous carbon have been carried out and leads to successful comparison with DFT and experiments.

b) New supports for high temperature operation.
Computational DFT techniques have been carried out for studying interactions between oxygen vacancy (Ov), doping Sb atom in SnO2, effect of Sb doping on the interaction between small Pt clusters and Ov-SnO2(110) surface. Segregation and transport properties at antimony-doped tin oxide (ATO)/Pt interfaces and at niobium-doped tin oxide (NTO)/Pt interfaces have been examined as well as transport properties. Stability and ORR of ternary catalysts Pt3NiAu and Pt3CuAu has been studied. On the experimental side, addition of Nb into the SnO2 support stabilizes the support and suppress the agglomeration of deposited catalyst particles. For the tri-metallic catalyst with Ni a significant diffusion of Ni out of the particles and onto the support is observed. This effect is suppressed when replacing Ni by Cu. Primarily work was put into synthesizing supported catalyst nanoparticles in a one-step flame synthesis.

c) Optimization and demonstration of MEA
Despite a huge amount of optimisation work during the project on the HT PYPO membrane, unfortunately no plausible route to prepare satisfactory fuel cells was found. On the other hand, the new polymer may find other applications in a hydrogen/bromine flow battery. For optimizing MEA fabrication using SMARTCat electrodes, new ink was defined and optimized for carbon supported Pt60Ni20Au20 trimetallic powder, and defining a pressing protocol for the MEAs manufacturing using the automated equipment. Constant improvement of the automated MEA Fabrication equipment led to highly reproducible features: achieve membrane size = electrode size + 5%; implementation of quality control procedure: 60 measurements per MEA, Optical measurement precision: 20µm Process reproducibility: 100 µm (based on more than 100 MEA). A rate of 70 of highly reproducible MEA/day is reached instead of the planned 60 MEA/day.

d) Fuel cell testing
The SMARTCat MEAs manufactured with classical screen printing method and with a classical loading exhibits a stack performance equivalent to reference MEAs: 0.8 W/cm$^2$. On contrary the low loaded PVD MEAs exhibit lower performances. In parallel to test, a technical economic study has been made in order to assess the capacity to use PVD catalyst. Despite a process cost estimated to 2.6 times more expensive than the conventional ink deposition, the cost assessment shows that it could became negligible at high production rate. If the SMARTCat PVD MEA would have reached the performance target of 1 W/cm2, it would have reduced the MEA cost by 30% and dropped below 20 €/kWgross. Nevertheless, the techno-economic analysis demonstrates the high potential of this coating technology.

e) Dissemination
SMARTCat has led to 13 publications in international peer reviewed journals, 7 invited lectures and 22 communications in international conferences. 2 patents have been delivered (2015, WP4), 8 patents applications have been submitted in 2017 (WP4). A successful dissemination activity was the European Fuel Cell Car Workshop held on March 1-3, 2017 in Orléans France. 80 participants (academics and industrials) joined the workshop coming from all Europe.
2. Context and objectives (not exceeding 4 pages)

A large-scale deployment of fuel cells in the automotive area hinges on reducing the manufacturing costs. A key point is the catalyst content, which is mainly restricted by the use of costly platinum. Today, a single cell provides 1.0 W cm⁻² with two electrodes of a total load of 0.4 mgPt cm⁻² leading to a power density of 2.5 kW g⁻¹ Pt. In a car, the delivered power should be 80 kW at maximum and 20 kW in constant drive situation. As a result, taking into account the cost of Pt (40€/gPt), fuel cells for automobile are still far from being economically competitive.

Beyond lowering the cost by reduction of the Pt-loading, several other technical advancements must be achieved in order to obtain high-performing and long-lasting fuel cells. The durability and stability of the PEMFC electrodes are some of the key points in need of substantial development as catalyst and support degradation leads to significant performance loss.

Changing the structural properties of the catalyst by alloying the platinum with a less noble material is known to enhance the durability of the catalyst [Ref: V. R. Stamenkovic et al, Nature Materials 6 (2007)]. Another well-known method for stabilizing the platinum-based catalysts is to improve the metal/support interaction by creating a molecular bridge between both materials. However this approach is not fully implemented and needs to be deepened.

With respect to the catalyst support, carbon black is commonly used and its degradation is one of the main problems to be overcome. Significant PEMFCs voltage losses can be observed once approximately 5-10 wt. % of the original carbon support has been corroded, independent of whether the carbon supports are graphitized or non-graphitized. Therefore, both alternative carbon materials, such as ordered mesoporous carbons and nanostructured carbons (e.g. carbon nanotubes, nanofibers, aerogels, etc ...) and non-carbon catalyst supports (oxides, carbides and nitrides) are being investigated. However, each approach has its pros and cons. Alternative carbon materials show better catalytic activity and stability in comparison to conventional carbon black, but are not more resistant to electrochemical corrosion. On the other hand, non-carbon materials are corrosion resistant but present poor electrical conductivity and low surface area.

Thus, SMARTCat establishes as main results to be:

- **New and innovative electrodes using tri-metallic low Pt-content based catalyst nanoparticles and nanostructured layers combined with new and corrosion resistant metal-doped oxide-based materials.**
- **Enable to optimize and to automate the production of MEAs with the new electrode concept.**
- **Prove the viability of the new concept for automotive applications.**

Such results are in complete consistency with the demands stated in topic SPI-JTI-FCH.2012.1.5 New catalyst structures and concepts for automotive PEMFCs.

The SMARTCat project will focus on new approaches to meet the demanding targets of the automotive industry.

**Catalyst design and synthesis**

The activity of classical Pt/C nanocatalysts, expressed in term of exchange current density j₀ calculated from the lower Tafel slope region (ca. 60 mV decade⁻¹) of the ORR polarisation curve is in the range of 10⁻⁴ mA cm⁻².¹ The increase of the exchange current density by a factor 10 is necessary to fit the fuel cell performance requirements of the present project. It is well known that bimetallic Pt based alloys are excellent catalysts for the Oxygen Reduction Reaction (ORR) taking place at the cathode of PEMFCs. In addition to decreasing the mass of platinum within the fuel cell, this type of catalyst leads to an increase in the catalytic activity by reduction of the oxygen binding energy.² As a consequence, bimetallic materials such as Pt₃M₁ₓ (M = Co, Fe, Ni and Cr) have been widely studied focusing on the correlation of their catalytic properties and stability with respect to the ORR and their electronic and crystallographic structure. Other noble metals such as Pd and gold have also been considered for the ORR realization under acidic conditions. Amongst pure metals, Pd leads to the second best ORR catalytic activity after Pt.

In comparison, very few studies have been performed on trimetallic catalysts for the ORR, including

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computational predictions of catalyst composition, activity and stability. Nanoparticles of PtNiFe have shown excellent electro-catalytic performances in fuel cells, but there is currently no data available on the robustness of such catalysts. Catalysts such as AuPt, PtNi, PtCo, PtVFe, PtNiCo with the properties of being active and stable with respect to the ORR have also been synthesized. Despite the low number of studies on tri-metallic catalysts it appears that:

1. The alloy of Pt with a less noble metal is highly beneficent for the ORR.
2. The interaction between two noble metals such as Pt-Pd, Pt-Au and Au-Pd increases the catalytic activity and the durability for the ORR compared to pure metals.
3. The platinum is necessary to obtain the best possible catalytic activity under acid conditions.

Trimetallic catalysts offer the potential of improved robustness and catalytic activity over the bimetallic alloys. Compared to the bimetallic systems, the third element can increase the stability, e.g. by forming a stabilizing subsurface monolayer to limit segregation, or the reactivity from novel alloyed core structures with a shell. The optimum morphology of the catalyst needs in depth investigations, both numerical and experimental, as morphology drives both activity/selectivity but also the stability of the atomic structure of the catalyst, which in turn will ensure the durability of the catalyst towards the fuel cell electrochemical reactions.

Besides to apply plasma sputtering to create “defect or anchorage sites” that are suitable to stabilize the Pt and alloyed Pt/core-shell clusters, we are also confident that using Pt-based trimetallic catalysts is a promising and alternative approach to enhance the catalytic properties and robustness of the fuel cell whilst rendering the technology economically competitive.

In order to access to a deeper understanding of the morphology role, SMARTCat will combine the expertise of DTU and CNRS to address theoretical and experimental research, respectively. CNRS has demonstrated for the past 20 years a world leading know-how in catalyst design and synthesis using simple chemical and plasma sputtering methods. On the other hand, DTU has an international reputation in the field of computational simulations especially quantum chemistry based, in the field of catalysis reactions and the calculation of catalyst properties.

Pt and Cost-reduction
The Pt content reduction should be the primary way for reducing catalyst cost in the fuel cell. An efficient way for lowering the catalyst content is to deposit the absolute minimum required quantity i.e. all the catalyst atoms are participating in the electrochemical processes. Moreover, the catalyst distribution in the active layer should correspond to an optimal delivery of the required current. At low current delivery, a homogeneous catalyst distribution over the active layer is expected, while at high current delivery, only the catalyst located at the electrode/membrane interface is operating. Operation in automotive conditions will require high current delivery, and hence, the catalyst location at the electrode/membrane interface is highly desirable. This implies that in order to reduce the catalyst content the catalyst must be organized as a gradient inside the active layer. This can be efficiently achieved by plasma sputtering. Indeed, plasma sputtering behaves like a versatile atom source with controlled kinetic energy and flux. This enables to control the diffusion of the catalyst atoms in the nanostructured gas diffusion layer. Moreover, the plasma sputtering technique is now widely used in industry. It is easily scalable and the economic efficiency has been assessed.

The CNRS partner has previously demonstrated a power density of 250 kW gPt⁻¹ using plasma sputtering deposition of Pd₃Pt catalyst at the cathode side loaded with 0.001 mgPt⁻¹ cm⁻² and 0.01 mgPt.cm⁻², while the anode was Pt free, and loaded with 10 µgPt.cm⁻². This key result enables us to propose plasma sputtering deposition as a powerful technology for ultra-low Pt loaded improved automotive fuel cells.

Corrosion resistant support material
Recent advances on robust and corrosion resistant non-carbonaceous electrodes have been achieved with promising performances relevant for automotive applications. Currently, there is still a lack on the fundamental understanding of the support properties and the catalyst-support interactions, especially on alternative materials. Non-carbonaceous materials such as oxides, carbides and nitrides have begun to emerge as promising alternative support due to their high corrosion-resistant properties, as well as their thermal and electrochemical stability under harsh electrochemical operating conditions. However, their application as electrocatalyst supports has been

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hindered by their (i) low specific surface area; (ii) poor electrical conductivity and (iii) low porosity. Although, efforts have been made to improve the physicochemical properties of these materials, the results vary widely\textsuperscript{4,5}.

Due to the oxidizable environment at the cathode in a PEM fuel cell, carbides and nitrides are believed to be partly oxidized changing their properties, e.g. electronic conductivity, affecting the durability of the electrode. Therefore, \textbf{SMARTCat will focus on metal-doped oxide materials, as titanium and tin oxides, which are more stable under cathode fuel cell operating conditions}. The disadvantages of such material, e.g. the stability of the doping atom, will be systematically addressed in order to tune the material properties to the requirements of a suitable catalyst support, e.g. by use of computational techniques to quantify the effect of doping atoms on the electronic conductivity.

Furthermore a fundamental understanding of the catalyst and the catalyst-support interaction is needed in order to obtain the best-optimized catalyst-support pair. Therefore, extensive theoretical modelling of the composition and the stoichiometry of the active oxide layer and the role of the morphology will be used.

The support durability/stability will be also addressed applying automotive degradation procedures such as start-up and shut-down and hence gaining information for modelling and understanding the degradation mechanism of conductive oxide and its effect on the electrode robustness.

\textbf{SINTEF Materials and Chemistry has already shown a world class experience in the field of synthesis of new support materials for catalysis. Thus, this partner will work close to DTU partner for elucidating the relevant properties of the conductive oxide materials to be applied to automotive PEM Fuel Cells.}

**MEA optimization**

In order to obtain the targets required in the JTI-FCH 1.5 topic, MEA optimization and demonstration at pilot scale will be included. MEA optimization and manufacturing have great impact on cell performances and cost. CEA partner has in house \textbf{modern equipment capable of producing MEAs in a semi-automatic manner will be used to be able to adjust the assembly process parameters, and hence ensuring the robustness, repeatability and flexibility with respect to material use and size of the MEAs}. Both state-of-the-art and high temperature membranes will be included enabling the developed electrode concept to be also evaluated with respect to state-of-the-art electrodes. The new catalyst and electrode concept will be directly tested and validated in view of the automotive application specified. This will ensure the appropriateness of the necessary up scaling required by the industrial needs.

\textbf{CEA is involved in numerous European projects concerning improvement of PEM fuel cells, among them AUTOSTACK. They have a well established international leading position in field of fuel cell systems, especially for automotive applications.}

SMARTCat has then built the best consortium gathering the world class skills and complementarities for a successful project. Indeed each, partner has demonstrated a know-how leading to international recognition in the field of fuel cells, especially by the high quality of the available facilities and of the reached performances, in terms of fuel cells delivered powers, robustness and durability.

The main objective of this project is to design new catalyst structures and catalyst support materials satisfying the cost and durability targets required by the call for the mass-market penetration of automotive PEM fuel cells.

In order to reach these goals the consortium will focus on a completely new catalyst/electrode concept: \textbf{Tri-metallic low Pt content based catalyst nanoparticles and nanostructured layers combined with new metal-doped oxide-based support material}.

Computational design of novel catalyst nanoparticles or multilayers, as well as modelling of the interactions with the support will allow a comprehensive insight into the catalyst appropriate morphologies/composition and stability on the new supports. The stability of the catalysts under operational conditions will also be used as a direct optimization procedure.

Both reducing Pt catalyst content and optimising catalyst design on a new support material will improve fuel cell efficiency, stability and durability and will contribute to lowering fabrication costs to a level


\textsuperscript{5} S. Sharma and B.G. Pollet, J. Power Sources 208 (2012) 96-119.
SMARTCat will address the following objectives:

- Deliver specifications/requirements for reaching the technical goals as a roadmap.
- Design an efficient new catalyst architecture using plasma technology based on electrochemistry selection and computer simulation.
- Establish a support selection criterion based on physico-chemical characterization and modelling for defining the most suited electrode support to the defined catalytic system.
- Assess the robustness regarding automotive operation conditions and fuel cell efficiency.
- Enable to automate the MEA production using state of the art (< 100°C) and high temperature membranes (120°C).
- Build efficient short-stack required for competitive automotive fuel cell operation.
- Low cost process and low Pt content will dramatically reduce the fuel cell cost, and which will lead to economically suitable fuel cells for automotive application.

The expected progress for the SMARTCat project is the following:

<table>
<thead>
<tr>
<th>State of the Art</th>
<th>Expected progress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>Trimetallic system without measurable ORR performance degradation during 5000h electrochemical testing.</td>
</tr>
<tr>
<td>Support materials</td>
<td>High corrosion resistant support (i.e. physic-chemically and morphologically stable) with a highly stabilization of the metal particles through the metal-support interaction under start/stop cycles (≥ 30 000) proved by both ex-situ (standard electrochemical cell) and in situ (PEMFC) experimental protocols. Increases at least 1.5 times the resistance of the catalyst to loss the surface area in comparison to carbon-supported catalyst. Expected targets are (0.44 A.cm⁻² at 0.9V), durability (start/stop cycles (≥ 30 000 ) and 5 000 h at dynamic operation) and cost (100 € based on MEA cost) Catalyst+support conductivity &gt;1 S cm⁻¹ (in the range of PEMFC operation temperature from -20 to 120 °C); pore sizes larger than at least 25 nm in the catalyst layer; exclusion of dissolution of the support material (e.g. doping); BET surface area larger than 50 m² g⁻¹</td>
</tr>
<tr>
<td>MEA</td>
<td>Fully automated fabrication at rate 60 MEA/day with large areas up to 500 cm², versatility versus type of electrodes and membranes. Power density at nominal power: &gt; 1 W cm⁻² at 1.5 A cm⁻² (single cell) at BoL 0.9 W cm⁻² at 1.4 A cm⁻² (single cell) at EoL &gt; 2 kW L⁻¹ (short stack) Lifetime &gt; 5,000 h at dynamic operation (car)</td>
</tr>
<tr>
<td>HT membranes</td>
<td>Proton conductivity ~ 15 mS/cm @ 40 °C, ~ 50 mS/cm @ 180 °C, spoiled by moisture contact, good resistance to CO 3 – 5 % in fuel proton conductivity &gt; 60 mS/cm @ 40 °C; &gt; 200 mS/cm @ 180 °C; good resistance to shutdown &amp; restart; similarly good CO resistance as current HT system based on PBI (tolerate 5 % of CO in fuel or air – note that current (PFSA based) systems are degraded by CO from exhaust of neighbouring vehicles)</td>
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3. Project main S&T results/foregrounds

Workpackage 1: Specifications

The purpose of the WP1 was to specify strategic targets and evaluation criteria of the activities with significant input from industrials applications. The work package 1 focused on the definition of characterization and testing protocols that will be used in WP4 and WP5. Relevant operating conditions for automotive fuel cell application, definition of package of in and ex situ characterization to be used for membrane/catalytic layers / MEA evaluation developed during the project have been defined as well as protocols for parametric study of the influence of working parameters on MEA durability and aging mechanisms (Temperature, gas stoichiometry, ...). In addition, protocols for selection of MEA for ageing tests and stack fabrication have been defined. This task was led by CEA with the participation of partners CNRS, SINTEF, and MxP.

Task 1.1 and 1.2 was respectively devoted to the definition of representative operating conditions and in situ testing protocols for single cells and stack and to ex situ characterization protocols for membrane/catalytic layers. These sub task are synthetized in deliverable D1.1.

The fuel cell test conditions are gathered in Table 1.

Table 1: reference operating conditions used during characterisation.

<table>
<thead>
<tr>
<th>Reference conditions</th>
<th>H₂ stoichiometry</th>
<th>Air stoichiometry</th>
<th>H₂ pressure (kPa)</th>
<th>Air pressure (kPa)</th>
<th>Maximum differential between anode/cathode (kPa)</th>
<th>Coolant liquid pressure (kPa)</th>
<th>Fuel cell temperature (output) (°C)</th>
<th>Anode relative humidity (%)</th>
<th>Cathode relative humidity (%)</th>
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<tbody>
<tr>
<td>H₂ stoichiometry</td>
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<td>Air stoichiometry</td>
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<td>H₂ pressure (kPa)</td>
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<td>Air pressure (kPa)</td>
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<td>Maximum differential between anode/cathode (kPa)</td>
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<td>Coolant liquid pressure (kPa)</td>
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<td>Fuel cell temperature (output) (°C)</td>
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<td>Anode relative humidity (%)</td>
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<td>Cathode relative humidity (%)</td>
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FCTESQA⁶ procedures dedicated to polarization curves are available on FCTESQA website. Procedure includes:

i) an initial stabilization phase in reference conditions (given by stack manufacturers),

ii) an increase step by step of the current up to the maximum current density, then

iii) a decrease step by step of the load from maximum current density down to 0 A and

iv) finally an increase step by step of the load from 0 A back to reference current density.

Polarisation curve is recorded during the decreasing current phase as shown on Figure 3. Step duration is not fixed by the procedure but a steady-state criterion is defined for each plateau used to record polarization curve.

In order measure the ElectroChemical Surface Area of MEA electrodes (ECSA) a cell inside a stack, electrochemical characterizations by cyclic voltammetry (CV) were carried out with an Autolab PG302N potentiostat associated with a 20 A booster device.

An Autolab PG302N potentiostat associated with a 20 A booster device was used to measure the ElectroChemical Surface Area of MEA electrodes (ECSA) a cell inside a stack by electrochemical characterizations by cyclic voltammetry (CV) and hydrogen crossover through MEA inside a stack by electrochemical characterizations by cyclic voltammetry (CV) at low rate (typically 1mV.s⁻¹).

Durability test will be performed at constant load conditions and under automotive cycle according JRC-IET document. Constant load test is described in FCTESQA procedures⁷ whereas automotive cycle will be calculated using the new European Driving cycle according to EU Directive 98/69/CE.

WP1 was also devoted to the definition of protocols for physicochemical characterizations of catalysts:

⁶ http://iet.jrc.ec.europa.eu/fuel-cells/downloads-0

- Metal loading in catalysts: determined by thermogravimetric measurements using a TA Instrument SDT Q600 apparatus under air from 25 °C to 900 °C. The metal loading of oxide supported catalysts have been determined by ICP-OES.

- Electrochemical characterization of catalysts: set-up consisted in a Voltalab PGZ 402 potentiostat controlled by a computer, a CTV 101 radiometer speed control unit and a rotating radiometer BMEDI 101 disk electrode (RDE). The counter electrode is a glassy carbon plate and the reference electrode a reversible hydrogen electrode (RHE). Electrochemical measurements were carried out in a 0.1 M HClO4 N2 saturated electrolyte (in ultrapure water, MilliQ from Millipore, 18.2 MΩ cm) at a sweep rate of 20 mV s⁻¹ and at 25 °C. Before electrochemical measurements, the catalyst/C electrodes underwent several voltammetric cycles between 0.05 and 1.25 V vs. RHE, until stable voltammograms were recorded.
  - Electrochemical active surface area (EASA) from Hupd region: determined from cyclic voltammograms (CV) by integrating the charge in the hydrogen desorption region corrected from the double layer capacity contribution
  - Electrochemical active surface area (EASA) from CO stripping measurement:
  - Evaluation of the activity and selectivity of catalyst towards the oxygen reduction reaction: the oxygen reduction reaction was studied by rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) methods. 3.3.1 Rotating disc electrode experiments (RDE)

The third task was devoted to protocols of components and MEAs selection definition. This work is detailed in deliverable D1.2. It focused on state of the art MEA’s performance measurements. Commercial MEAs (Solvicore, Gore, Paxitech, Johnson Mattey, AGC) and CEA MEAs assembled with homemade electrodes and commercial membranes (Chemours, Solvay) have been characterized.

Workpackage 2: Multi-metallic catalysts and electrodes

a) Modelling of trimetallic structures (core shell, alloys, monolayers) and ORR of selected trimetallic structures (DTU).

Atomic-scale simulations at the level of density functional theory (DFT) calculations have been applied in combination with genetic algorithms (GA) and machine learning, to search for improved tri-metallic catalyst compositions and nanoparticle structures.

As an outset for the calculations, we investigated the properties of binary and tri-metallic Pt-Pd-Au systems using model thin-film structures. By use of linear scaling relations, it was possible to establish activity volcanoes for the oxygen reduction reaction (ORR) on these systems, plotting the activity as a function of well-established descriptor like the OH- binding energy relative to the OH- binding energy on Pt(111), i.e. ΔE_OH - ΔE_Pt-OH. As shown in Fig. 1, a number of the tri-metallic catalysts were found to have increased activity compared to Pt(111) when Au was present in the sub-surface layers.

Fig. 1 Activity estimates for oxygen reduction of ternary thin film alloy surfaces with (a) pure Pt or Pd skin and (b) mixed Pt–Pd skin.

A detailed analysis of the properties of Au, showed that Au tends to segregate to the surface of Pt-based systems, but the presence of surface adsorbed O* or OH* under reaction conditions can sustain a partial coverage of Pt in the surface. Once Au segregates to the surface, it is thermodynamically preferred for the Au to migrate to under-coordinated step or kink sites, see Fig. 2. This effective Au-coating of the...
under-coordinated site is expected to reduce the Pt-dissolution and improve the durability of the catalyst.

![Fig. 2. Diffusion energy profiles from terraces to steps for a surface Au-atom on Pt(221). Color code: yellow: Au and light gray: Pt.](image)

In light of the promising results from the Au-addition to the Pt-based catalyst, we extended the trimetallic search to include the use of low cost transition metals. To enhance the mass specific catalytic activity, the computational analysis focused on the design and investigation of trimetallic core-shell nanoparticles in the range of 2-3 nm. We systematically investigated the catalytic activity of icosahedral core-shell particles with a transition metal (TM) core, an Au sub-surface layer and a Pt-shell (see Fig. 3 left). Using Co, Ni, Cu and Zn as the core material, it was possible to weaken the OH-biding energy and increase the ORR activity compared to Pt(111)

![Fig. 3 left) Schematic showing the complete icosahedral nanoparticle (top) and the cross-section of the tri-metallic nanoparticle (bottom). The atoms are colored showing the Pt shell (grey), Au subsurface (yellow) and M core (purple). Adsorption sites are also denoted on the complete particle, showing the edge-bridge position (1) and the atop position (2). Right) Pt–OH binding energies on the Pt162Au92M55 nanoparticles plotted relative to the Pt309 nanoparticle for binding at the atop (2) sites. The dashed red line indicates the comparable OH binding energy on the Pt(111) extended surface.](image)

The final part of the computational analysis included an analysis of the structure, stability and catalytic activity of the predicted tri-metallic catalysts, when deposited on the developed oxide supports. This work focused primary on the PtAuCu and PtAuNi systems, see the WP3 description of the details. These simulations combine DFT-level calculations and genetic algorithms (DFT-GA) in order to predict the structure of the tri-metallic particles on the oxide supports. This is, however, computationally very intensive, so we developed a computational ‘Machine Learning Augmented Genetic Algorithm’ (MLnGA) which can accelerate co-optimization of nanoalloy composition and structure. Applying the MLnGa method to a 147 atom Pt-Au cluster, we were able to demonstrate a speed-up of 5,000 times compared to the serial DFT-GA (Fig. 4)

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10. Jennings et al, to be submitted
According to DFT calculation at DTU, some Pt\(_x\)Pd\(_y\)Au\(_z\) composition could lead to catalyst with improved activity and stability towards ORR than pure Pt. Then, several binary and ternary catalysts based on Pd, Au and Pt have been first synthesized by a wet chemistry method and characterized by different physicochemical methods: TGA for metal loading, TEM for particle size and size distribution, XRD for structure, ICP-OES and EDX for composition, etc. The different catalysts were electrochemically characterized in terms of active surface area, activity (EASA) and selectivity towards ORR. Tables 1 gives the comparison of activity for the different binary catalysts synthesized expressed as \(j_0\). Tafel slopes and exchanged electrons 0.8 V. From the results on binary catalysts the proposed compositions of ternary catalysts for plasma sputtering process are given in Fig. 5 in the blue part of the ternary diagram. This proposition is based on activity (higher exchange current density \(j_0\)) and selectivity of catalysts (4-electron process for oxygen reduction towards H\(_2\)O) with lower Pt content\(^{11}\).

**Fig. 5:** ternary diagram representing the synthesized binary catalyst and the proposition of composition for the ternary one based on Pt, Au and Pd.\(^{11}\)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt</th>
<th>Pt(_5)Au(_5)/C</th>
<th>Pt(_5)Au(_5)/C</th>
<th>Pt(_5)Au(_5)/C</th>
<th>Pt(_5)Au(_5)/C</th>
<th>Pt(_5)Au(_5)/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j_0) (mA.cm(^{-2}))</td>
<td>(2.6 \times 10^{-4})</td>
<td>(1.7 \times 10^{-4})</td>
<td>(9.1 \times 10^{-4})</td>
<td>(0.1 \times 10^{-4})</td>
<td>(0.3 \times 10^{-4})</td>
<td>(2.9 \times 10^{-5})</td>
</tr>
<tr>
<td>Tafel slopes / mV dec.(^{-1})</td>
<td>63</td>
<td>59</td>
<td>63</td>
<td>59</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>(n) electrons @ 0.8 V</td>
<td>3.99</td>
<td>3.99</td>
<td>3.99</td>
<td>3.99</td>
<td>3.98</td>
<td>3.97</td>
</tr>
<tr>
<td>(n) electrons @ 0.55 V</td>
<td>3.99</td>
<td>3.99</td>
<td>3.98</td>
<td>3.98</td>
<td>3.90</td>
<td>3.76</td>
</tr>
</tbody>
</table>

Tafel slopes / mV dec.⁻¹  

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt/C</th>
<th>Pd₅Au/C</th>
<th>Pd₁₂Au/C</th>
<th>Pd₁₅Au/C</th>
<th>Pd₃Au/C</th>
<th>Pd₁₅Au/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>j₀ (mA·cm⁻²)</td>
<td>63</td>
<td>67</td>
<td>64</td>
<td>62</td>
<td>63</td>
<td>60</td>
</tr>
<tr>
<td>n electrons @ 0.8 V</td>
<td>3.99</td>
<td>3.99</td>
<td>3.99</td>
<td>4.00</td>
<td>3.99</td>
<td>3.98</td>
</tr>
<tr>
<td>n electrons @ 0.5V</td>
<td>3.99</td>
<td>3.97</td>
<td>3.97</td>
<td>3.97</td>
<td>3.93</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Table 1. Exchange current density (j₀), Tafel slopes and number of exchanged electrons for the oxygen reduction reaction on binary catalysts.¹¹

We have confirmed the interesting atomic ratios for the ternary PtPdAu/C catalysts, Pt₇₀Pd₁₅Au₁₅/C and Pt₅₀Pd₁₂₅Au₁₂₅/C materials were synthesized and characterized, and their electrocatalytic behavior towards ORR evaluated and compared to that of Pt/C catalyst. The Pt₇₀Pd₁₅Au₁₅/C catalyst displays slightly higher activity than the Pt/C one (18.5 mA cm⁻² and 17.5 mA cm⁻² at 0.85 V, respectively), although the catalyst contains 30 % less Pt atoms, so that the specific activity related to the amount of Pt in the catalyst is higher. The intrinsic activity of Pt₇₀Pd₁₂₅Au₁₂₅/C catalyst is ca. 247 mA mg⁻¹, i.e. 1.4 times higher than that of Pt/C. The Pt₅₀Pd₁₂₅Au₁₂₅/C catalyst displays the lower intrinsic activity (ca. 14 mA cm⁻²) but, considering that it contains 50 % less platinum atoms than the pure Pt/C one, it remains still interesting if the objective is to lower the platinum loading in electrode, leading to a specific activity of ca. 250 mA mgPt⁻¹.¹¹

DFT calculations at DTU also pointed out that some non-noble metals alloyed with Pt and Au in ternary systems could enhance activity and stability of the catalysts. Amongst them, nickel, cobalt and copper appeared interesting. Then binary and ternary catalysts based on Pt, Au and Ni (Me = Ni, Co, Cu) were synthesized, characterized and evaluated towards ORR (Table 2). All catalysts containing Nickel led to higher activity than Pt/C, with the highest activity for Pt₅₀Ni₁₅/C. Considering the ternary catalysts, Ni-containing catalysts (Pt₅₀Ni₁₂Au/C and Pt₅₀Ni₁₇Au₁₃/C) displayed again the highest activities (j₀, jk,geom, jk,metal and MA). Since the ratio Pt/Ni was fixed at 3:1, the lower activity of Pt₅₀Ni₁₇Au₁₃/C compared to Pt₅₀Ni₁₂Au/C is certainly related to the presence of gold at the nanoparticle surface in the case of the catalyst with the higher gold surface atomic ratio as evidenced from XPS and cyclic voltammetry measurements. The Pt₅₀Co₁₂₅Au/C and Pt₅₀Co₁₇₅Au₁₃/C materials led to electrocatalytic activities close to that of pure Pt/C, in terms of j₀ and jk at 0.9 V, although the electroactive surface areas were lower than that of Pt/C. Therefore, the mass activities were higher for the ternary systems than for the Pt/C catalyst, which indicated the beneficial effect of cobalt in the catalysts. Pt₅₀Cu₁₂₅Au/C showed catalytic activity, in terms of j₀ and jk at 0.9 V, higher than that of Pt/C, whereas that of Pt₅₀Cu₁₇₅Au₁₃/C were lower than that of Pt/C. The low catalytic activity of Pt₅₀Cu₁₇₅Au₁₃/C could be due to the high gold concentration at the particle surface since the Pt/Cu ratio has been fixed at 3:1. But interestingly, the mass activity of both copper-containing ternary catalysts are higher than that of platinum, Pt₅₀Cu₁₂₅Au/C displaying the highest catalytic activity, which indicated the beneficial role of Cu in the ternary catalyst conversely to what was observed in the case of the Cu-based binary systems.¹²

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
<th>Pt₅₀Ni₁₁/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESA (m²·g⁻¹)</td>
<td>47</td>
<td>31</td>
<td>37</td>
<td>33</td>
<td>33</td>
<td>34</td>
<td>43</td>
<td>64</td>
</tr>
<tr>
<td>b (mV dec⁻¹)</td>
<td>64</td>
<td>66</td>
<td>66</td>
<td>62</td>
<td>62</td>
<td>63</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>j₀ (mA·cm⁻²)</td>
<td>-2.5 × 10⁻⁴</td>
<td>-2.9 × 10⁻⁴</td>
<td>-1.3 × 10⁻³</td>
<td>-3.1 × 10⁻⁴</td>
<td>-3.7 × 10⁻⁴</td>
<td>-5.3</td>
<td>-7.5</td>
<td>-7.5</td>
</tr>
<tr>
<td>jk @ 0.9 V (mA·cm⁻²)</td>
<td>-5.3</td>
<td>-5.6</td>
<td>-12.7</td>
<td>-6.4</td>
<td>-7.5</td>
<td>-7.5</td>
<td>-77</td>
<td>-77</td>
</tr>
<tr>
<td>MA @ 0.9 V (A·g⁻¹)</td>
<td>-53.4</td>
<td>-59</td>
<td>-141</td>
<td>-84</td>
<td>-52.7</td>
<td>-52.7</td>
<td>-77</td>
<td>-77</td>
</tr>
</tbody>
</table>

The choice of the upper limit potential of 1.05 V vs RHE was restricted to limit the increase of activity by dealloying effect, and the protection of the platinum surface at which may have two effects: the limitation of the non noble metals acting as sacrificial anodes. In the case of Pt₆Ni₂Au/C, Pt₆Ni₁.₇Au₃.₃/C and Pt₆Co₂Au/C, the loss of ESA₀ₚḥ was accompanied with an increase of the ESA₀ₐʊₓ, i.e. of the surface Au atomic ratio, whereas, no increase of surface Au atomic was detected with the Pt₆Cu₂Au/C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt₆Co₃/C</th>
<th>Pt₆Co₅/C</th>
<th>Pt₁₄Au/C</th>
<th>Pt₁₄Cu/C</th>
<th>Pt₁₄NiAu/C</th>
<th>Pt₁₄CoAu/C</th>
<th>Pt₁₄CuAu/C</th>
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<tr>
<td>Pt₁₄Co₃/C</td>
<td>40</td>
<td>62</td>
<td>-3.5 × 10⁻⁴</td>
<td>-7.4</td>
<td>-81</td>
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<td></td>
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<tr>
<td>Pt₁₄Co₅/C</td>
<td>30</td>
<td>69</td>
<td>-6.5 × 10⁻⁴</td>
<td>-4.1</td>
<td>-53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt₁₄Au/C</td>
<td>40</td>
<td>69</td>
<td>-5.1 × 10⁻⁴</td>
<td>-3.6</td>
<td>-37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt₁₄Cu/C</td>
<td>39</td>
<td>72</td>
<td>-1.6 × 10⁻⁴</td>
<td>-3.0</td>
<td>-39</td>
<td></td>
<td></td>
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<tr>
<td>Pt₁₄CuAu/C</td>
<td>17</td>
<td>65</td>
<td>-2.3 × 10⁻⁴</td>
<td>-3.0</td>
<td>-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt₁₄NiAu/C</td>
<td>24</td>
<td>-</td>
<td>-2.9 × 10⁻⁴</td>
<td>-7.6</td>
<td>-134</td>
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<td></td>
</tr>
<tr>
<td>Pt₁₄CoAu/C</td>
<td>19</td>
<td>-</td>
<td>-1.0 × 10⁻³</td>
<td>-10.3</td>
<td>-117</td>
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<tr>
<td>Pt₁₄CuAu/C</td>
<td>15</td>
<td>-</td>
<td>-2.0 × 10⁻⁴</td>
<td>-5.4</td>
<td>-95</td>
<td></td>
<td></td>
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<tr>
<td>Pt₁₄Cu₂Au/C</td>
<td>15</td>
<td>-</td>
<td>-1.1 × 10⁻⁴</td>
<td>-6</td>
<td>-86</td>
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<td></td>
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<tr>
<td>Pt₁₄Cu₁₄Au/C</td>
<td>36</td>
<td>-</td>
<td>-2.7 × 10⁻⁴</td>
<td>-4.3</td>
<td>-79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt₁₄Cu₁₄Au/C</td>
<td>28</td>
<td>-</td>
<td>-3.7 × 10⁻⁴</td>
<td>-5.7</td>
<td>-91</td>
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<td></td>
</tr>
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</table>

Table 2. Electrochemical characterization of binary materials: ESA (electrochemical surface area), b (Tafel slope), j₀ (exchange current density), jₚ (kinetic current density) and MA (mass activity).

The order of activity of ternary catalysts in terms of kinetic current density @ 0.9 V vs RHE was Pt₆Ni₂Au/C > Pt₆Ni₁.₇Au₃.₃/C > Pt₆Co₂Au/C > Pt₆Co₁.₇Au₃.₃/C > Pt₆Cu₂Au/C > Pt₆Cu₁₄Au/C, whereas and the order of mass activity @ 0.9 V vs RHE was Pt₆Ni₁.₇Au₃.₃/C > Pt₆Ni₂Au/C > Pt₆Co₁.₇Au₃.₃/C > Pt₆Co₂Au/C > Pt₆Cu₂Au/C > Pt₆Cu₁₄Au/C. Therefore, in order to discriminate the catalysts for their use in a cathode of PEMFC, their stabilities have to be checked and compared.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ESA₀ₚḥ (mg cm⁻²)</th>
<th>ESA₀ₐʊₓ (mg cm⁻²)</th>
<th>ESA₀₅₇₅ (mg cm⁻²)</th>
<th>at% Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₆Ni₂Au/C</td>
<td>19</td>
<td>0</td>
<td>19</td>
<td>0</td>
</tr>
<tr>
<td>Pt₆Ni₁.₇Au₃.₃/C</td>
<td>24</td>
<td>3</td>
<td>27</td>
<td>11</td>
</tr>
<tr>
<td>Pt₆Co₂Au/C</td>
<td>15</td>
<td>0</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Pt₆Cu₂Au/C</td>
<td>28</td>
<td>3</td>
<td>31</td>
<td>8</td>
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</tbody>
</table>

Table 1. Evaluation of the Electrochemical Surface Area characterization of ternary materials before and after the aging test.

The aging study of ternary catalysts Pt₆MeₓAu/C (Me = Ni, Co, Cu) has been carried out by potentiodynamic cycling of the electrodes in O₂-saturated 0.1 M HClO₄ electrolyte. After every 200 cycles between 0.6 V and 1.05 V at 50 mV cm⁻¹, CV were recorded in de-aerated electrolyte in order to determine the ESA₀ₚḥ and ESA₀ₐʊₓ, as well as the Au surface atomic ratio. The choice of the upper potential limit was motivated by the necessity to limit the degradation processes due the carbon corrosion and detachment of nanoparticles, and further to only evaluate the stability of Pt₆MeₓAu nanoparticles. Table 3 compares the results obtained before and after the aging process for 1000 cycles. For all ternary catalysts, results indicated relatively low Pt surface loss compared with the pure Pt/C catalyst. The small changes in ESA₀ₚḥ were related to the low upper limit potential of 1.05 V vs RHE, which may have two effects: the limitation of the non noble metal dissolution rate which will lead to limit the increase of activity by dealloying effect, and the protection of the platinum surface atoms by the non-noble metals acting as sacrificial anodes. In the case of Pt₆Ni₂Au/C, Pt₆Ni₁.₇Au₃.₃/C and Pt₆Co₂Au/C, the loss of ESA₀ₚḥ was accompanied with an increase of the ESA₀ₐʊₓ, i.e. of the surface Au atomic ratio, whereas, no increase of surface Au atomic was detected with the Pt₆Cu₂Au/C.
In Fig. 6, the values of the kinetic current density @ 0.9 V vs RHE, $j_k$, are reported as a function of the number of aging cycles. For all catalysts, a very important loss of activity occurred for the first 200 aging cycles and then the value of $j_k$ tended to reach a plateau. Considering the Pt/C catalyst, the value of $j_k$ decreased from -5.3 mA cm$^{-2}$ to -2.35 mA cm$^{-2}$ after 1000 cycles, corresponding to ca. 55 % loss in activity. The activity loss after 1000 cycles reached ca. 70 % for Pt$_6$Ni$_2$Au$_3$/C and Pt$_6$Ni$_{1.7}$Au$_{1.3}$/C, both catalysts leading to the same activity as Pt/C after 1000 cycles although achieving higher initial activity. Pt$_6$Co$_{2}$Au$_3$/C catalyst lost 55 % of activity after 100 cycles, as in the case of Pt/C catalyst, but keep higher $j_k$ value than Pt/C. The higher stability was obtained with the Pt$_6$Cu$_2$Au$_3$/C catalyst with an activity loss of only 45 % after 1000 cycles and a final $j_k$ value of -3.2 mA cm$^{-2}$.

Beyond the classical degradation processes of nanoparticles (particle mobility/agglomeration, and/or 3D Ostwald ripening, and particle detachment due to the carbon support corrosion), the difference in electrocatalytic activity losses between the ternary catalysts involved changes in surface structures and compositions. The dissolution kinetics of the different non noble metals at the nanoparticle surface could also be proposed as explanation. But, if dealloying of the materials by progressive dissolution was the only degradation process, it should lead firstly to an improvement of the catalytic activity, which was not observed. It is worth to note that the highest activity losses were observed for the Pt$_6$Ni$_2$Au$_3$/C, Pt$_6$Ni$_{1.7}$Au$_{1.3}$/C and Pt$_6$Co$_2$Au$_3$/C catalysts, which underwent gold surface enrichment during the aging test. Such gold surface enrichment was already observed after aging tests in the case of Pt$_6$Pd$_3$Au$_3$/C catalysts$^{11}$ and confirmed by molecular dynamic calculation at GREMI$^{13}$. Therefore, the degradation mechanism of catalysts appears to be complex, involving, in addition to probable aggregation/Ostwald ripening processes, particle detachment, dealloying of non-noble metals from the particle surface and gold surface segregation in the case of ternary catalysts containing nickel and cobalt, whereas in the case of Cu based ternary catalyst the last process was avoided, which explains the highest activity after aging testing of Pt$_6$Cu$_2$Au$_3$/C material.

The best ternary catalyst in terms of initial activity for an application in the cathode of a PEMFC is the Pt$_6$Ni$_2$Au$_3$/C one. However, the Pt$_6$Cu$_2$Au$_3$/C catalyst displayed higher stability under potential cycling with an activity loss of only 45 % after 1000 cycles, against 70 % for the Pt$_6$Ni$_2$Au$_3$/C one. Moreover, the activity after 1000 potential cycles of the copper-based ternary catalyst is 1.4 times higher than that of the Ni-based one. One reason of the higher activity of the Pt$_6$Ni$_2$Au$_3$/C material is that in presence of copper the segregation of gold from the particle bulk is avoided, conversely to what was observed with Pt$_6$Ni$_3$Au$_x$ and Pt$_6$Co$_2$Au$_x$ materials.

**Workpackage 3: Highly Corrosion resistant and non-carbon based catalyst support**

**Catalyst support material**

Metal oxide catalyst support materials, more specifically tin-based oxides, were investigated to be used as cathode catalyst support in PEMFCs, offering high electrochemical stability and corrosion resistance for this application as compared to carbon$^{14,15,16}$. The following criteria were defined for screening and

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selection of support materials:
1. BET Surface Area: $\geq 50 \text{ m}^2 / \text{g}$
2. Electronic conductivity ($\sigma$): $> 0.01 \text{ S cm}^{-1}$
3. Microstructure: mesoporous with a pore size distribution (PSD) ranging from 20 to 150 nm

These criteria were fulfilled through tin oxide (SnO2) doped with different atomic level of Antimony (Sb) and Niobium (Nb), $\text{Sn}_{1-x,y} \text{Sb}_x \text{Nb}_y \text{O}_{2+\delta}$, $x,y = 0 - 0.15$, synthesized using Flame Spray Pyrolysis (FSP) and a modified Co-precipitation (mCoP) method. Surface area of as-synthesized support materials without any catalyst particles is plotted as a function of antimony and niobium doping level in Figure 1, for both FSP and Co-P powders. It is evident that the surface area increases with the doping level for both dopants and synthesis procedures, however the effect is less severe for the powders prepared by FSP. Sb and Nb is reported to segregate to the surface as the dopant level increases and hence, inhibiting the particle growth. This phenomenon is known as “solute drag inhibiting growth” where one component segregates easier to grain boundary \(^{17}\). The higher BET surface area of FSP powder compared to Co-P ones is mainly associated to their microstructure (higher microporosity).

![Figure 1. Surface area of as synthesized tin oxide powders prepared by FSP and Co-P as a function of Sb and Nb doping. Star in graph to the left indicate data from commercial material.](image1)

TEM images of as-synthesized and post treated (milling and heat treatment at 550$^\circ$C) powders of $\text{Sn}_{0.95} \text{Sb}_{0.05} \text{O}_{2+\delta}$ are presented in Figure 2. A significant growth of the crystalline particles is observed (reducing the surface area to ~60 m$^2$/g which is still above target), which is desired as it is expected to enhance the particles connectivity (electronic grain boundary effect) and hence also the electronic transport (conductivity) of the powders.

![Figure 2. TEM images of as-synthesized $\text{Sn}_{0.95} \text{Sb}_{0.05} \text{O}_{2+\delta}$ (left), and post treated (milled and heat treated at 550$^\circ$C, 1 hour) (right). The added rings are exactly 20 nm in diameter.](image2)

The electronic conductivity of as-synthesized tin-based support powders is presented in Figure 3 a). The conductivity increases by more than 3 orders of magnitude up to a Sb-doping level of 7 atomic %, in agreement with the literature.\textsuperscript{18,19} Doping with 5-valent Nb does not enhance the conductivity. The cause of this lowering conductivity in niobium doped samples is assumed to be due to insulating layers (or separate phase as mentioned above) of Nb\( (\text{Nb}_2\text{O}_3)\) forming on the surface of particles, however is added together with Sb with the intention of suppressing the Sb segregation towards the interface between Pt catalyst and support material, as previously demonstrated.\textsuperscript{18} As shown in Figure 3 b), the conductivity of the Sb doped FSP powders is significantly enhanced by the post-treatment (milling and heat treatment), exceeding that of the commercial reference sample and the Co-P powders for doping levels < 10% Sb as well as the targeted value for the project.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Electronic conductivity of as-synthesized Sn-based oxides prepared by FSP (a) and compared post-treated FSP powders, Co-P powders and commercial reference (b).}
\end{figure}

As Figure 4 demonstrates also the microstructure in form of pores in the range of 20-150 nm was obtained, however, a larger quantity of pores in the upper range is still desired.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Pore size distribution of Sb-doped tin oxides prepared by FSP.}
\end{figure}

**Catalyst – support interactions**

The effects of the support material on the deposition of Pt and trimetallic Pt60Ni20Au20 and Pt60Cu20Au20 catalyst particles in WP2 were investigated by TEM analysis. These studies prove that homogenously sized catalyst (both Pt and trimetallic) nanoparticles of ~4 nm have been successfully deposited onto the various oxide support materials. While a homogenous dispersion of catalyst nanoparticles was deposited onto supports of Sb- and Nb-doped \( \text{SnO}_2\), significant agglomeration of catalyst particles was observed on the surface of undoped \( \text{SnO}_2\), as seen in Figure 5 and Figure 6. Through EDS/EDX analysis it is also observed that the catalyst particles deposited both onto \( \text{SnO}_2\) and \( \text{Sn}_0.93\text{Sb}_0.05\text{Nb}_0.015\text{O}_2\text{.5} \) supports are Ni-deficient as compared to the intended composition.

(Pt$_{60}$Ni$_{20}$Au$_{20}$), whereas the diffusion of Cu from the Pt60Cu20Au20 particles is significantly less severe.

Figure 5. High resolution HAADF STEM images of SnO$_2$ support with Pt$_{60}$Ni$_{20}$Au$_{20}$ catalyst particle agglomerates.

Figure 6. High resolution HAADF STEM images of Sn$_{0.930}$Sb$_{0.055}$Nb$_{0.015}$O$_{2+\delta}$ support with Pt$_{60}$Ni$_{20}$Au$_{20}$ dispersed catalyst particles.

Support materials with catalyst particles prepared in one-step synthesis
In addition to the catalyst (Pt and trimetallic systems) deposition reported above, a new activity was initiated on preparing supported Pt catalyst nanoparticles onto doped tin oxide support in a one-step flame spray pyrolysis process. Microstructures of the one-step FSP powders, presented in Figure 7, show nicely dispersed ~1 nm Pt particles on Sn$_{0.935}$Sb$_{0.065}$O$_{2+\delta}$ support particles.

Figure 7. TEM images of ~1 nm Pt particles (20 wt.%) dispersed on Sn$_{0.935}$Sb$_{0.065}$O$_{2+\delta}$ by one-step FSP procedure.
**Electrode preparation with one-step FSP based supported catalysts**
Whereas procedures were in place for preparation of carbon based electrodes, the change of to a non-carbon catalyst support material gives rise to need for alternation and optimization of these procedures. By extensive investigations and tailoring of suspensions (including various milling processes for the starting powders) and use of automated ultrasonic spray coating, homogenous electrode layers of both commercial Pt/C and Pt/NATO (from one-step FSP) were prepared. Pt/C electrodes and Pt/NATO (one-step FSP) appears to have morphologies which could contribute to good mass transport (see **Figure 8**), previously identified as a main challenge and cause of low performance on fuel cells based on oxide supports.

![SEM micrographs of MEA with Pt/NATO (one-step FSP) and Pt/C electrodes, both prepared by ultrasonic spray coating.](image)

**Figure 8.** SEM micrographs of MEA with Pt/NATO (one-step FSP) and Pt/C electrodes, both prepared by ultrasonic spray coating.

**Fuel cell testing with ATO/NATO based MEAs**
ATO based membrane electrode assemblies (MEAs) were tested on 5 cm² cells and compared to both commercial Pt/C (60 wt% Pt/C) catalysts coated on Nafion 212 membranes and to commercially available MEAs from Gore. In general the performance of the MEAs with electrodes prepared by hand-held air brush using Pt/ATO (one-step FSP, 20 wt% Pt, 3% Sb-doping of the SnO₂ support) and commercial Pt/C resulted in performance inferior to that obtained when using Pt/C also in the cathode layer. At least parts of the problem is associated with poor mass transfer in the Pt/ATO electrode layer, and hence 50 vol% carbon (Ketjen Black) without any Pt was added to the cathode layer during electrode preparation. This resulted in improved performance, see **Figure 9**, confirming the issue of mass transfer in the electrodes prepared with oxide based support.
Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC

Modelling

Atomic-scale simulations at the level of density functional theory (DFT) and non-equilibrium Green’s function methods (NEGF) have been utilized extensively to investigate and predict the conductivity, stability and catalytic effects of the selected oxide support materials. The primary focus has been placed on the investigations of Sb and Nb dopants in SnO₂, in order to identify suitable doping levels and strategies which improve the electronic conductivity and stability of the catalyst-support interface for an extended period of time.

A key aspect in the modelling was investigations of dopant configurations and segregation to the support-catalyst interface, and to calculate how these properties would influence the electronic conductivity and stability of the doped oxide supports. The analysis was performed for Sb, Nb and mixed Sb-Nb systems in dopant concentrations ranging from 4.2 to 25% and significant difference were found for the three systems.

For Sb dopants, a strong thermodynamic driving force for segregation to the catalyst-support interface, i.e. ATO-Pt, was identified. It was found that Sb segregation to the top-most oxide layer was preferred, which could result in depletion of dopants in the subsurface region and ultimately a loss of electronic conductivity. A two-step doping strategy was therefore proposed, where a lower bulk Sb doping level could be supplemented with a high concentration of surface-Sb. As seen in Figure 10, this results in a higher electronic conduction and a more stable interface as the thermodynamic driving force for Sb-segregation has been eliminated [Fu et al., ACS Appl. Mater. Interfaces 7, 27782-27795 (2015)].
A similar analysis for the segregation of Nb towards and through the Pt layers in NTO-Pt yielded different results [Fu et al., Chem Mater. 29, 1641-1649 (2017)]. The Nb dopants were found to thermodynamically prefer segregation to sub-surface sites near the interface. An analysis of the thermodynamic barriers for leeching of Nb through the catalytic Pt-layers under ambient conditions, however, appear low in the absence of an applied bias, but at operating and start/stop conditions, the thermodynamic barriers increase significantly (see Figure 11 a). The segregations of Sn through the Pt layer in NTO-Pt displays a similar behavior, albeit the thermodynamic barriers are approximately 1.5 eV lower than for Nb. (Figure 11b). The observed difference for Sb and Nb dopants also led to a suggestion of possible co-doing of with Sb and a small addition of Nb.

As a final part of the computational stability analysis, simulations were performed to predict the structure of the Sb and Nb dopants in the catalyst layers. The results showed that the Nb dopants prefer sub-surface segregation, while Sb dopants show a preference for surface segregation, although the thermodynamic barriers for leeching are lower for Nb than for Sb. The observed differences in the segregation behavior of Nb and Sb dopants suggest a possible co-doing with Sb and a small addition of Nb.

Figure 10  Change of the electric current with respect to the increase of the Sb concentration at the interface. The purple spheres represent the Sbdopant atoms. Only the central regions are shown for geometries of the device [Fu et al., ACS Appl. Mater. Interfaces 7, 27782-27795 (2015)].

Figure 10  Change of the electric current with respect to the increase of the Sb concentration at the interface. The purple spheres represent the Sbdopant atoms. Only the central regions are shown for geometries of the device [Fu et al., ACS Appl. Mater. Interfaces 7, 27782-27795 (2015)].

Figure 11 a) Gibbs free energy diagram of the processes from the Nb segregation through Pt adlayers to the formation of the Nb$_2$O$_5$ bulk. The labels $C_i$ represent different configurations. Three conditions, i.e., the unbiased condition ($U = 0 \text{ V}, T = 25 \text{ °C}, pH = 1$), start/stop conditions of PEMFCs ($U = 1.2 \text{ V}, T = 80 \text{ °C}, pH = 1$), and operating conditions ($U = 0.8 \text{ V}, T = 80 \text{ °C}, pH = 1$) are taken into account, with the corresponding results shown in blue, red, and green, respectively. The Sn (Nb) atoms are represented by gray (azure) spheres. b) Similar analysis for Sn segregation through Pt adlayers to the formation of the SnO$_2$ [Fu et al., Chem Mater. 29, 1641-1649 (2017)].
and stability of two of the computationally predicted tri-metallic nanoparticles, i.e. PtAuCu and PtAuNi, when combined with the investigated conducting oxide supports (ATO). It is interesting to note that for the Pt$_{15}$Au$_{15}$Cu$_{15}$ system, the developed DFT-GA (Genetic Algorithm) code systematically identifies particles, where the copper and gold appear to form a stabilizing interface between the particles and the support and the platinum, where gold is found to cover the particle/island edges and may thus limit the dissolution of platinum, see Figure 12.

The DFT-GA code was also applied to investigate Pt$_{21}$Au$_{7}$Ni$_{7}$ on ATO, where the ratio was chosen to mimic the experimental ratios, i.e. Pt$_{60}$Au$_{20}$Ni$_{20}$, in order to understand the experimentally observed Ni-leeching and loss of activity on ATO compared to Pt$_{60}$Au$_{20}$Ni$_{20}$ on carbon. The calculations show a different ordering than that observed for the Pt$_{15}$Au$_{15}$Cu$_{15}$ system, where strong Au-Cu ordering was observed for at the oxides interface. For Pt$_{21}$Au$_{7}$Ni$_{7}$ on ATO, a strong clustering of the Ni-atoms is observed near the oxides, which is in good agreement with the observed Ni-leaching and loss of activity observed experimentally on ATO compared to carbon.

![Image](image_url)

Figure 12 Pt$_{15}$Au$_{15}$Cu$_{5}$ on the ATO support. Left: An initial randomly generated candidate structure from the calculations with the developed DFT-GA code. Right: A low energy configuration after 17 generations. Color code: Dark gray: Sn, red: O, purple: Sb, yellow: Au, light gray: Pt, and golden: Cu.

Workpackage 4: Optimization and Demonstration of MEA processing at pilot scale

**Development of the high temperature polymer synthesis**

This project was formulated on the basis of exploratory work in 2011-12 at (now defunct) Basic Membranes on membrane based on 1,4-poly-2,6-di(3-pyridyl)phenyleneoxide (PYPO), 20 cured after casting from solution.

In contrast with expectations and plans, a long delay was experienced before any high molecular weight polymer became available. In any case, from the spring of 2015 we were able to study film formation, curing and doping at a high rate of experimentation – now avoiding fiber “reinforcement” which had been shown to lead to film damage, especially during doping (swelling) in the early work at Basic Membranes. By using high concentrations of polymer we could avoid “cratering” type behavior caused by the incompatibility of substrate and casting solution that we absolutely needed to achieve liftoff after curing. This necessitated using the curing agent as a solid, dissolving during curing, to avoid dilution and lowering the viscosity of the casting solution.

What seemed to be an important breakthrough in doping occurred in the early fall of 2015. We found that increased viscosity plus thixotropy, by adding nanosilica to the 85 % phosphoric acid used, facilitated a homogeneous application, and also dealt with the stickiness of the film surface that made doping originally a nightmare – in the absence of a “paper carrier” that had assisted handling in the early explorations at Basic Membranes. When the film surface meets acid dopant, the instantaneous local acid

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20 D J Sikkema et al., US 8299202; EU 224.465 – to mxpolymers
21 D J Sikkema, US 9187599 – to mxpolymers
concentration is very high. At the desirable, substantial doping levels the film is a soft, tacky rubber (in the absence of silica on the surface).

Pinholes due to air entrained into the casting solution were eliminated in membrane by degassing the casting solution. Note that pot life of the casting solution amounts to minutes, not hours. Cured films of $>400 \text{ cm}^2$ size, 35 g/m² of polymer were made, as well as doped ones $>100 \text{ cm}^2$ size.

By February 2016 MEAs built by both CEA and HyET (Arnhem, NL) from such silica-coated, modestly doped films showed disappointing fuel cell performance and much higher impedance than expected from the work in 2011-12. Strong electrical insulation by the silica was observed and work was started to find an alternative to silica – which seems to be in rather a pure state on the film surface (indeed the acidic liquid is absorbed rapidly by the polymer and a fine powder remains on the surface, during this method of doping).

It became clear that free-standing films without silica handling aid were not an achievable target. Even with silica, high doping levels lead to difficult handling of the very soft rubber films. At the same time, an alternative vacuum mixer was tested as a means to pinhole-free films – it performed less well than the more expensive one tested in December. Nevertheless it was useful in subsequent work directed at supported films, using GDL or GDE + border material supports. Casting onto “half MEAs” proved much preferable to doping previously made film on “half MEAs” or “in” MEAs. The resulting (GDL-based, dummy-) MEAs could be evaluated by EIS (at HyET, Arnhem. NL). Taking the impedances at high frequency, where polarization & capacitive impedance (almost) disappears, bone-dry-condition proton conductivities in the range of 100…350 mS/cm were seen (see appended graph) at 150°C.

We finally succeeded in preparing a number of functional MEAs, using GDEs (with PBI but also with PYPO electrolyte in the inks) made for us by HyET, despite the difficulties of casting onto such GDEs with loose-powder catalyst surfaces. SEM inspection of such a GDE at Sintef showed that the originally feared “drowning” of catalyst by too deep a penetration of membrane material into the GDE was not a significant issue. Operating these MEAs at 150 °C with dry gases as an actual fuel cell (H₂ vs. air) showed, after 250 h, some softening and mobilization of membrane material in the active areas (not in the equally hot border areas) – i.e. thermoplastic behavior.

The observation of membrane softening in fuel cell operation led to investigation of a pyridine-chloranil adduct under acidic, strongly hydrogenolytic conditions with platinum catalyst, modeling (accelerated) ageing at the HT fuel cell anode. After 8 h, obvious degradation of our model compound had occurred. Upon finding strong indications of poor long-term stability of the (current) PYPO membrane system and a likely cause in reversal of crosslinking at the hydrogen/platinum anode, we decided to stop further experimentation with the current high temperature membrane system. We see no plausible route to prepare satisfactory fuel cells with the PYPO system as formulated.

**Optimization of large size MEA at lab scale**

In the frame of MEA development procedure on the one hand, the CEA identifies all manufacturer of MEA materials (GDL, PEM…) and then tests sample from all of them. Then, our know-how allows determining the better combination/synergy between all the components, according to processing/running/operating fuel cell conditions via a continuous development trial map. During this period, the CEA estimated the performances of various perfluorinated membranes (from Chemours (Nafion HP and Nafion XL) and Solvay) to identify the material which will serve as reference for the continuation of the studies and the comparison with MEA prepared in this project. The Solvay membrane shows the best performance at 105°C ($540\text{mW/cm}^2 @0.675V$) and at 115°C ($400 \text{ mW/cm}^2 @0.675V$).

The manufacturing protocol of these MEAs has been optimized, in order to be relevant for both membranes and electrode evaluations.
For a correct bonding of the electrodes with the membrane, a hot pressing is performed. In single cell 25cm², assembly parameters were optimized by CEA, a pressure of 3.5MPa and a temperature of 135 °C appear to be the best compromise between performance and durability.

For the assembly of large area MEAs, the pressure uniformity is an important parameter. Assembly test with a Fuji paper inserted instead of the membrane were made. The results of these tests show a high degree of heterogeneity of the assembly pressure in the plane (Figure 4). A variation of pressure can be noticed between 0.5 to 5 MPa as a function of the red level. Current density distribution observed by S++ system measurements also reveals the homogeneity of the GDE sealing. Variation of current density can be explained by a limitation of the gas diffusion due to the decrease of the porosity of the GDL following the excessive pressure. After optimization of the hot pressing protocol we obtain a uniform 3.5 MPa pressure under the active area (figure 2).

The MEA of SMARTCat project are based on the best CEA MEA. Specific changes SMARTCat project are carried on the cathode. These new cathodes of SMARTCat project are made from the trimetallic alloy catalysts.

Before testing low Pt loading electrodes obtained by PVD, electrode obtained by conventional ink formulation have been prepared and tested in small size (25 cm²) single cell assembling and compared to the best CEA MEA. As the synthesis of new catalysts is difficult, a first screening has been made from 200 mg of each catalyst. To achieve the cathodes with small amounts of catalyst the spray printing method was chosen. In this case, printing on carbon GDL (SGL 24 BC) has been selected. The ink formulated for the production of the cathode is composed of a mixture of catalyst, Nafion, water and ethanol. The catalyst loading is 0.38 mg/cm². For anodic gas diffusion electrode, the ink was prepared using commercial platinum supported on carbon using same way of cathodic solution.

Finally, the last step is the assembly of the membrane (PFSA) between the two GDE by hot pressing. This step is needed to both improving interfacial connection between GDE and membrane and providing cohesion in the assembly. The catalyst carbon supported Pt60Ni20Au20 show the best result of the trimetallic catalysts (see WP 5 report). Maximum power is 733 mW/cm² at 80°C whereas powers are equals to 607 and 505 mW/cm² at 105°C and 115 °C respectively.

Considering these results, Pt60Ni20Au20 was selected for the preparation of a first large size stack for fuel cell tests. The realization of large size MEA requires, considering the tries for the development of the deposit, quantities of the order of 4 grams of catalyst Pt60Ni20Au20. This catalyst was synthesized (cf WP2) by CNRS/IC2MP, SGL24BC GDLs used for this study are carbon GDLs.

Large size stack required 220 cm² GDE. For best catalyst dispersion homogeneity, we decided, after ink formulation adaptation to proceed by screen printing for ink deposition (figure 3).
Figure 3: screen printing used for gas diffusion electrode manufacturing.

Four 220 cm² cathodes were prepared, with loading rate from 0.255 to 0.445 mgPt/cm². 4 anodes loaded with a conventional Pt/C catalyst were also prepared. Their loading rate is 0.125 mgPt/cm².

Optimization of MEA at pilot scale

The goal of this sub task was to provide large size optimized MEA which can be integrated in stack, and whose production is ensured by automatic, reproducible, economic and pre-industrial means. The objective was the demonstration of the potential of the equipment to prepare 60 MEA/day. The equipment used for this study is an automatic machine designed in collaboration with Bertin Technologies, specialized in the manufacture of special machines. The equipment is localized at CEA Le Ripault, Monts, France. It is illustrated on figure 4

Figure 4: CEA’s automatic machine for MEAs manufacturing.

The principle of MEAs assembling is based on the management of different storage stations with the formatted raw materials. Given the very small thickness of the membrane, it is previously held between two half frames which are then moved by a manipulator arm equipped with an electromagnet. The operations of raw materials cutting and stacking in the storage stations have not yet been automated. A PLC (Programmable Logic Controller) provides automatic management of operations. The different workstations are mobilized simultaneously, with a control of the queues and the safety of the machine. The MEAs assembly is carried out in two pressing operations. The first makes it possible to attach the GDE to the membrane. Only the active area is pressed. A second press makes it possible to ensure good cohesion of the non-active zone. This splitting into two pressings allows to manage the pressure exerted on the materials by the compression plates and thus to ensure a well-controlled compression ratio in the GDE.
After optimization of the different pressing parameters, the productivity of the machine was tested during a day of 8 hours of work. For this study, the machine is configured for CEA F-MEA manufacturing. During this production day, it was possible to manufacture 71 MEAs in 8H (net of lunch time). The productivity of the machine is therefore 9 MEAs/hour. This productivity takes into account the times of preparation of the materials and the reloading of the storage stations. It also takes into account the uncertainties encountered during production (handling mistake or components positioning defaults). Anyway, the scrap rate is less than 3%.

The dimensional control of the MEAs is carried out using 2D optical measurements. A MICRO-VU (a camera associated with a motorized XY movement device) instrument was used, making it possible to do measurements with an accuracy of 20 μm (figure 22). The MEA are disposed under a glass plate to be maintained. The measures are done by the definition of a zero and reference axes of the MEAs, and then "auto learning" of points to measure. The camera itself determines the dimensions by making contrast difference. 44 control points distributed on the AME are realized. Statistic measurements showed that the average of the deviations are very small (<0.3 mm) and that the standard deviations are also very small (< 0.2 mm). These results demonstrate that the MEAs manufacturing process is very precise and very reproducible.

During this project, various ranks of membrane were used (Nafion on 212, 211, HP, XL) to evaluate the versatility of the equipment. The obtained MEA are all in accordance with requests. In addition, a first fluorinated and colored reinforcement compound was changed by a non-fluorinated compound so that the MEA are transparent out of the GDE.

The works also concerned the integration of an antiwicking function within the MEA. The antiwicking function consists in preventing the cooling fluid from getting in touch with the membrane.

This work was led in two phases. The first modification of the process consisted in working on the geometry of the membrane inserted into its transport frame. For that purpose, the process was modified to limit the membrane at the level of entrances and exit of coolant, but still in contact with the gas collector area. These modifications also allow reducing the consumption of membrane for the realization of the MEA. The used surface is reduced by 30 %. The fuel cell performances of these antiwicking MEAs are equivalent to that of non anti wicking MEAs. Besides, this modification was validated by measures of fuel cell ageing.

The work was then concentrated on the realization of full antiwicking MEAs, that is, MEAs in which the dimensions of the membrane are as close as possible to that of the electrodes (figure 5 and 6). Such MEAs allow to envisage optimal performances in terms of ageing still while reducing the cost of the MEAs because of the lower waste of membrane during the MEAs manufacturing.

![Figure 5: 220 cm² MEA](image1)

![Figure 6: antiwicking MEA](image2)

**Production of large size MEAs for fuel cell stack characterization (see WP5)**

Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC
This last sub-task was devoted to the furniture of large size optimized MEA which can be integrated in stack, and whose production is ensured by automatic, reproducible, economic and pre-industrial means. Three production runs were carried out to feed the work of task 5.

The first series of 4 MEAs was carried out in September 2016 using the GDEs prepared at CEA LITEN Grenoble from the carbon-supported trimetallic catalysts synthesized by the CNRS IC2MP in Poitiers. A second series of 8 MEAs was carried out in January 2017 using the GDEs prepared at the CNRS GREMI in Orléans. These GDEs were obtained by PVD. The catalyst is deposited by plasma sputtering on GDL SGL 24BC supplied by the CEA. For this series, the catalyst is Pt60Ni20Au20 and the loading rate in platinum of 50 μg/cm².

A third series of 6 MEAs was carried out in April 2017 using the GDEs prepared at the CNRS GREMI in Orléans. These GDEs were obtained by PVD. The catalyst is deposited by plasma sputtering on GDL SGL 24BC supplied by the CEA. For this series, the catalyst is a core shell NiCu@Pt6 and the loading rate is 100 μg/cm².

These MEAs were prepared on the CEA’s automatic machine. These three series of MEAs (figure 7) were delivered to CEA LITEN Grenoble for stacking and fuel cell testing (see WP5) in September 2016, January 2017 and April 2017 respectively.

![Figure 7: 220 cm² MEA: A (screen printing chemically synthesized Pt60Ni20Au20 cathode), B (PVD Pt60Ni20Au20 cathode : 50 µg/cm²), C (PVD core shell NiCu@Pt6 cathode 100 µg/cm²)](image)

**Workpackage 5: Fuel Cell Testing and Demonstration. Techno-Economic Assessment**

WP5 of the SMARTCat project dealt with experimental validation of improvement made respectively on membrane, catalyst, catalyst support and MEA manufacturing. In addition an economics study aimed to estimate the cost modification induced by the use of new materials in MEA and stack manufacturing. As a consequence, the aims of the WP5 within the project were:

- The support of the development of improved specifications.
- Provide data to align the research and development activities of WP2 and WP3 regarding activity and stability.
- Improvements of the MEA design (WP4) in order to achieve the performance targets.
- Confirm the final MEA concept regarding performance and costs.

To be able to test MEA improvements at stack level, CEA was provided a stack technology based on previous development for automotive application. These stacks based on stamped metallic bipolar plate were used on different European project and were integrated by SymbioFC in the Hy-Kangoo range extender system. The reference performances obtained with a PEMFC stack have been provided to WP2 and WP3. This stack, depicted in figure 1, was composed of stamped metallic bipolar plates with an active surface area of 220 cm². A complete description of stack was provided to SMARTCat partners during the first year of the project.
The performances are obtained in automotive reference conditions, summarized in table 1, with commercial MEAs (0.6 mgPt loading) and with reference MEAs (same loading), provided by CEA and manufactured using automatic tools which were used during the SMARTCat project. An example of results obtained is shown in figure 1.

**Table 2: Reference conditions used for automotive applications.**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ stoichiometry</td>
<td>1.5</td>
</tr>
<tr>
<td>Air stoichiometry</td>
<td>2</td>
</tr>
<tr>
<td>H₂ pressure (kPa)</td>
<td>150</td>
</tr>
<tr>
<td>Air pressure (kPa)</td>
<td>150</td>
</tr>
<tr>
<td>Maximum differential between anode/cathode (kPa)</td>
<td>50</td>
</tr>
<tr>
<td>Coolant liquid pressure (kPa)</td>
<td>150</td>
</tr>
<tr>
<td>Fuel cell temperature (output) (°C)</td>
<td>80</td>
</tr>
<tr>
<td>Anode relative humidity (%)</td>
<td>50</td>
</tr>
<tr>
<td>Cathode relative humidity (%)</td>
<td>50</td>
</tr>
</tbody>
</table>

In addition to activity dedicated to electrochemical characterisation of MEAs manufactured during the project, Work package partners were involved in European activities dedicated to development of reference protocols to characterise the MEAs for automotive applications lead by JRC-IET. According this activities, it was decided to add specific operating conditions and to use Fuel cell Dynamic Load Cycle for endurance tests.

During the second and the third years of the project, in agree with the development made in Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC.
WP2, WP3 and WP4, it was decided to begin MEAs development using only new catalyst developed within the project. Four MEAs provided by WP 4 and based on the WP2 best catalysts supported on carbon, have been characterised in CEA automotive reference conditions. These conditions are gathered in Table 2. As shown on the Figure 13 in which are depicted the polarisation curves recorded with MEAs manufactured with new catalyst and with commercial catalysts, the best performance is reached with commercial catalyst whereas the best results for new catalysts layer is obtained with Pt$_{60}$Ni$_{20}$Au$_{20}$ alloy. For all the tested MEA in these operating conditions, none MEA has reached the milestones of the project. Nevertheless it can be noted that these operating conditions are used as CEA references and are not in agree with automotive operating conditions.

![Figure 13: polarization curve recorded on SMARCAT MEAs with different tri-metallic catalyst in automotive low pressure conditions.](image)

Moreover as explained in deliverable 4.2, the low quantity of catalyst available for this test step are not sufficient to use optimized active layer structure. It can be confirm by the lower performances obtained on reference MEA manufactured using spray process (Figure 13). Cyclic voltammetries recorded on the different MEA shown that electrochemical performances are mainly linked to the active surface developed by the catalyst indicating that initial synthesis and electrode manufacturing will be a key factor to increase performance at MEA level.

According these results obtained at single cell level, Pt$_{60}$Ni$_{20}$Au$_{20}$ was chosen as cathodic catalyst for large area MEAs and stack manufacturing. Two 220 cm$^2$ stacks were then assembled using two kinds of MEAs made at CEA Le Ripault facilities (semi-automatic pilot line).

The first kind of MEA was manufactured in the frame of WP4 according classical screen-printing method. The second type was manufactured using Gas Diffusion Layer in which a low loaded catalyst was deposited using PVD techniques.

The two MEA kinds were assembled in two different stacks named 264-F2Sma and 272-F2Sma for screen printed MEA and PVD MEA, respectively. In order to easily compare the performances of SMARTCat catalysts and pure platinum ones, some reference MEAs were used to manufacture stacks.
On Figure 14 and Figure 15 are plotted the polarisation curves obtained on 264-F2Sma and 272-F2Sma respectively for SMARTCat MEAs and for reference MEAs. As shown on these figure, the MEAs manufactured with classical screen printing method and with a classical loading exhibits a performance equivalent to reference MEAs in Metallic bipolar plate stack. On contrary the low loading PVD MEAs exhibit lower performances. Durability measurement were made using FCDLC. Unfortunately, the two stacks durability are not able to reach the targets defined in the frame of the project with a degradation ten times higher than classical reported value. The deliverable D5.3 presents the main results obtained with the two stacks.

In parallel to test, a technical economic study has been made in order to assess the capacity to use PVD catalyst. The deliverable 5.3 establishes the manufacturing cost of SMARTCat MEA, considering that the process developed in laboratory within the project was transferred to industry. The value obtained was compared to the state-of-the art reference from Autostack Core project: MEA with platinum loading 3.5 mg/cm² and 1 W/cm². Due to its low performance, the SMARTCat MEA could not compete against the Reference. Nevertheless, the techno-economic analysis demonstrates the high potential of this coating technology.

It was found that some industrial PVD tools are designed already to easily integrate a continuous manufacturing line. Despite a process cost estimated to 2.6 times more expensive than the conventional ink deposition, the cost assessment shows that it could became negligible at high production rate. Concerning the choice of the trimetallic catalyst Pt₂AuNi, from an economic point of view, it does not seem relevant to replace the platinum load of PEMFC by Gold, more expensive, unless it enables to reduce catalyst quantities. If the SMARTCat MEA would have reached the performance target of 1 W/cm², it would have reduced the MEA cost by 30% and dropped below 20 €/kW_gross (production scale: 50,000 automotive stacks of 95 kW_gross).

Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC
4. Project potential impact and exploitation/dissemination activities

a) Scientific production
SMARTCat has led to 13 publications in international peer reviewed journals, 7 invited lectures and 21 communications in international conferences. 2 patents have been delivered (2015, WP4), 8 patents applications have been submitted in 2017 (WP4).
A PhD thesis entitled “Synthèse, caractérisation et évaluation électrocatalytique de catalyseurs plurimétalliques pour la cathode de la pile à combustible”, has been carried out and defended by Styven Demilta LANKIANG. It was delivered on August 30th, 2016 by Université de Poitiers, France.

b) Organisation of the European Fuel Call Car Workshop (EFCW2017)
EFW2017 was initially planned at month 42, but after discussion with FCH-JU, it was decided to postpone it to 1-3 March 2017, for allowing meeting of consortia planning to answer the 2017 FCH-JU call. So the milestone related to this event was completed by March 3rd, 2017 instead of month 42. The verification mean is the abstract book appended as Annex of this deliverable and details can be accessed on the website: https://efcw2017.sciencesconf.org
80 participants joined the workshop coming from all Europe.

The participants had the opportunity to meet and join potential consortia during the 2017 FCH-JU call period. This Workshop was a unique occasion for discussing both scientific and technological advances within the frame of the FCH-JU projects for having at midterm of H2020 a current status of the excellence research and Innovation in the fields of fuel cell car.
By contributing to this event, the participants highlighted Europe’s collective effort and advances and opened a new window on the Hydrogen Economy as an efficient way for reaching the EU climate change and COP21 goals.
Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC
Each topics had 2 invited lectures: one from an academics and one from an industrial.

A round table moderated by


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**Press Release I ORLEANS/ BRUSSELS I 21 FEVRIER 2017**

**Hydrogen and Fuel Cells: What recent advances in the automotive sector ?**

**Press conference**
**Thursday 2 March 2017 – 12 h**
Centre international universitaire pour la recherche - Hôtel Dupanloup
1 rue Dupanloup – 45000 ORLEANS

The press conference will be followed by a demonstration of hydrogen vehicles in the courtyard of the Hotel Dupanloup.

To establish recent advances made in Europe towards achieving the COP21 objectives in terms of transport and sustainable mobility using the fuel cells and hydrogen sector: these are the objectives of the "European Fuel Cell Car Workshop" to be held in Orléans 1-3 March 2017. It is organized by the CNRS and the SMARTCat project co-financed by the Fuel Cell and Hydrogen Joint Undertaking. The SMARTCat project aims at developing innovative catalysts for fuel cell cars. This workshop brings together researchers and manufacturers from major French and European SMEs and industrial groups to discuss the recent advances in hydrogen energy technologies and fuel cells in the field of automotive transport.

With 8 plenary lectures, 40 presentations (oral and poster) and a round table on research and innovation, the symposium will bring together more than 80 researchers dedicated to realizing the potential of fuel cell electric vehicles. The major European industrial groups (Toyota, Daimler, BMW, VW, Audi, Johnson Matthey Fuel Cells, ...), European and French SMEs (Anleg, Borit, NelHydrogen, Symbio, STEP, ...) will be present. These lectures and presentations, chosen for their innovative content, will be dedicated to the recent advances of the whole hydrogen value chain: fuel cell and hydrogen storage components, systems and motorization, and the approach of European automobile manufacturers in the deployment of fuel cell electric vehicles.

Specific time slots for discussions about new proposals for the 2017 call of the FCH2-JU will be arranged. The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) is a public private partnership supporting research, technological development and demonstration (RTD) activities in fuel cell and hydrogen energy technologies in Europe. Its aim is to accelerate the market introduction of these technologies, realising their potential as a means of achieving a carbon-lean energy system.

This workshop is supported by the FCH2-JU, The Région Centre Val de Loire, the Conseil Départemental du Loiret, and the city of Orléans.

**Press conference programme**

**Introduction : Fuel cell and hydrogen research in France**
Jean François Tassin, Deputy Director, Institute of Chemistry, CNRS

**Contributing to the deployment of the "hydrogen" sector through research and innovation**
Pascal Brault, Director of Research at CNRS in the Groupe de recherches sur l'énergétique des milieux ionisés (GREMI, CNRS/Université d'Orléans), délégué scientifique de la cellule énergie du

![SMARTCat Logo](SMARTCat.png)
**Systematic, Material-oriented Approach using Rational design to develop break-Through Catalysts for automotive PEMFC**
Recent advances in fuel cell materials
Deborah Jones, Director of Research at CNRS at the Institut Charles Gerhardt Montpellier (ICGM, CNRS/Université de Montpellier/ENSC Montpellier), Member of the FCH JU Scientific Committee

Hydrogen energy systems for transportation
Daniel Hissel professor University of Franche-Comté Belfort., Director of Fuel Cell LAB Institute, CNRS

Funding fuel cell and hydrogen R&D in Europe
Mirela Atanasiu, directrice unités opérationnelles et communications de la FCH-JU

A lunch buffet will be served after the press conference.

To know more:
Workshop Programme https://efcw2017.sciencesconf.org

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During the event a demonstration of 2 fuel cell cars (A Hydrogen taxi Hyundai i35 from HYPE company (Paris, France) and Kangoo electric vehicle with FC range extender) has been done. Possibility of driving them has been offered to participants.

The event was subjected to a French TV news on Friday 3rd (in French): http://france3-regions.francetvinfo.fr/centre-
As a satellite meeting, a “Hydrogen in Région Centre–Val de Loire” was organised on the occasion of the 2 MoUs between FCH-JU and Région Centre Val de Loire from one part and with Orleans City on the other part. L. Boillot and M. Atanasiu have moderated this meeting for meeting the stakeholders of the Region Centre – Val de Loire and for discussing the implementation of the MoU.

EFCW2017 was also the occasion for delivering a current status of Hydrogen and Fuel Cell for cars. It has been published online in CNRS Le Journal (in French): https://lejournal.cnrs.fr/articles/les-defis-de-la-voiture-a-hydrogene and CNRS News (in English): https://news.cnrs.fr/articles/hydrogen-cars-for-all

Social events in the evening were also really appreciated: Cheese and Wine party in Old city Hall of Orléans and a banquet with Slavic music.

c) Exploitation plan activities.

Involvement in the EFCW2017 preparation and venue has been time consuming and it has the effect of delaying the exploitation plan scheduled activities in deliverable 6.2.

As our project lacks from industrial partners, it was very difficult to build a strategy for communicating our results, and share them with industrials. Nevertheless, some issues have been completed.

First, interest for plasma deposition has generated interest for building a new consortium for the 2017 FCH-JU call. Indeed, as plasma deposition is a central tools in the submitted project InnOxiCat, Danish Power Systems (DK) and Xerolutions (SP) joined the consortium for benefiting of the expertise acquired during SMARTCat progress.

Second, following EFCD2015 organised by CATAPULT project, in 2015 near Montpellier, we started discussions with Tecnalia centre which was partner of NanoCat project, led by CEA, on the improvement of plasma sputtering deposition for electrode catalyst deposition. Such discussions should be deepen for mutual benefit.

Finally, we have been contacted by the Lurederra Centro Tecnologico for building a consortium based on plasma sputtering and Flame Spray Pyrolysis techniques developed in SMARTCat. Interest focused on metal oxide particle synthesis.

In the next coming months, the most valuable SMARCat results, mainly regarding ternary alloys with low Pt content, will be communicated to automotive OEMs and catalyst manufacturers for evaluation and potential collaborations. To this end a document summarizing quantified results will be written and send to contacts of these OEMs. The project results will be thus presented to automotive OEM for discussions and for building new projects. Johnson Matthey, Toyota-Europe, Daimler, … will be contacted before end of the year 2017.
5. Project website

SMARTCat website was victim of an SQL injection attack and was down for a few month. It has been recovered but using WordPress web free management tool. Current address is https://smartcatfchju.wordpress.com. CNRS is currently examining to redirect the initial address http://smartcat.cnrs.fr to this new one.