

Final Publishable Summary Report of the Project “Novel catalyst materials for the cathode side of MEAs suitable for transportation applications” (CATHCAT)

Executive Summary

The aim of the CathCat project was to investigate Pt- and Pd-rare earth alloys as catalysts for low temperature fuel cells, and advanced support materials to enhance both activity and durability of actual catalyst layers. The project targeted the entire process chain from theoretical materials screening and validation, materials synthesis, preparation and characterization of model compounds and actual nanosized catalyst powders to MEA fabrication and single cell testing.

A comprehensive understanding of the detailed physical mechanisms that lead to the enhanced catalytic activity of Pt-rare earth alloys for the oxygen reduction reaction was achieved by close collaboration between theoretical work and experimental studies on model alloys. It was shown that the formation of different compressive strains in the Pt skin layers induced by the underlying alloy lattice parameters determine the ranking in catalytic activity, but that there is a limit to the maximum possible strain, so that the maximum of the activity volcano cannot be reached with these alloys. Also the dependence of the catalytic activity of nanoparticles on the size was studied and understood, and the performance degradation of the alloys could be explained. Different approaches for the preparation of larger amounts of practical catalyst materials were pursued, including vacuum-based methods, i.e. sputtering, chemical reduction in solution-phase and dry methods, and electrochemical methods. Sputtering allowed to prepare thin catalyst films with correct composition and good catalytic properties. The electrochemical methods permitted to deposit the rare earth metals, but did not yet succeed in making catalyst material. The dry method resulted in the preparation of Pt-Y nanoparticles that showed a better performance than an excellent commercial Pt benchmark catalyst, but did not yet permit to control the particle size. The efforts to prepare these catalysts in a form and amount suitable for MEA testing was much more difficult and time-consuming as originally anticipated. With respect to Pd-based catalysts, the influence of particle size on the electrocatalytic properties and stability as well as the nature of the support were studied using electrochemically deposited Pd on HOPG and nitrogen-doped HOPG. Pd-Y alloys and Pd-Ce alloys were studied. In the latter case, through combined theoretical and experimental efforts, an understanding of the lowered catalytic activity of the alloy as compared to pure Pd was understood. Aside from the studies regarding Pt and Pd rare earth catalysts, several other binary catalysts like PdCu catalysts were prepared and tested.

Studies on nitrogen-doped HOPG did not unequivocally demonstrate a beneficial influence for the catalytic activity of Pd catalysts. However, a large set of different N- and S-doped mesoporous carbon materials were prepared and demonstrated to be beneficial for ORR activity of supported Pd and Pt. Similarly, advanced oxide supports demonstrated improved performance in ORR experiments. Different deposition methods were tested on these materials and oxide-carbon composites, and photochemical deposition proved the best option for simple Pt catalysts.

MEA single cell testing was carried out on Pt-based benchmark MEAs and several MEAs with catalyst materials and advanced support materials from the project. However, the only actual alloy samples tested were not present in optimized catalyst layers, as only one set of PtY/carbon powder had been prepared for MEA testing. Nevertheless, they performed better than pure Pt present in the same configuration, but still worse than the benchmark MEAs. None of the MEAs tested so far surpassed the performance of the

benchmark MEAs so that further efforts regarding catalyst preparation and optimization of the catalyst layer structure and loading are required in future work.

Summary description of the project context and the main objectives

The electrochemical oxidation of reactants in fuel cells represents, from a thermodynamic point of view, a very efficient way to convert chemical energy into electrical energy. When using hydrogen as fuel, fuel cells represent a very attractive choice as power supply for electric vehicles, with zero local emissions and driving ranges around 500 km. However, the true efficiency is much lower than the thermodynamically possible one. In low temperature proton exchange membrane fuel cells (PEM FCs) this is mainly due to the electrode reactions and especially to the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. At present, there is demand for a significant increase in electrical efficiency and higher volumetric and gravimetric power densities of fuel cells. State-of-the-art catalysts for both anode- and cathode-side are based on noble metals, mainly Platinum. Especially in mass production, the platinum would significantly add to the total system cost. Also, the production of Pt is not sufficient for widespread implementation of the technology at current loadings. Finally, the lifetime of the fuel cells needs to be improved. The FCH JU has set the following technical targets in the 2011 call regarding performance and durability of PEM fuel cells: Pt loading below 0.15 g/kW, preferentially below 0.1 g/kW, at a BOL efficiency above 55%, BOL powers $> 1 \text{ W cm}^{-2}$ @ 1.5 A cm^{-2} , and a lifetime above 5000 h. The aim of the CathCat project was to improve the performance and reduce the cost of PEM cathodes by development of new alloy catalysts based on Pt or Pd as one constituent and Rare Earth Elements as the second constituent. For Pt it was known that these alloys form a thick compressed Pt overlayer during initial de-alloying, leading to a significant enhancement of the catalytic activity. Such an enhancement would lower the amount of catalyst required and therefore the cost. For Pd the impact of alloying was not known but considered an interesting option to convert the cheaper but less active and less stable Pd into an attractive catalyst material. In addition, advanced support materials based on the one hand on doped carbon and on the other hand on oxide based support materials were supposed to be studied and combined with improved catalysts. The project was funded within the call "Next generation European MEAs for transportation applications" and addressed mainly the topic SP1-JTI-FCH.2011.1.5 and in part SP1-JTI-FCH.2011.1.6. The following Multiannual Implementation Plan (MAIP) and Annual Implementation Plan (AIP) targets were planned to address:

- **Electrochemically stable and low-cost catalysts for polymer Membrane and Electrode Assemblies (MAIP)**
- **Development of catalysts and electrode layers allowing for significant reduction in precious metal catalyst loadings (AIP)**
- Demonstration of high temperature properties under low relative humidity, including conductivity and mechanical robustness (AIP)
- Demonstration of long-term stability under automotive fuel cell conditions (AIP)
- BOL and EOL performance targets as specified in the call (Pt loadings $< 0.15 \text{ g/kW}$, BoL $> 55\%$ efficiency, BoL Power density at nominal power : $> 1 \text{ W/cm}^2$ at 1.5 A/cm^2 , Lifetime (EoL) $> 5,000\text{h}$ at dynamic operation (car)* applying typical load profiles (accelerated life tests), Maximum EoL degradation $< 10\%$ in rated power density, Power density $> 0.9 \text{ W/cm}^2$ at 1.4 A/cm^2 at EoL, operation temperature: up to $130 \text{ }^\circ\text{C}$ (AIP)

- Catalyst support corrosion linked to shut-down and start-up or fuel starvation (AIP)
- Catalyst dissolution, migration and re-precipitation linked to voltage excursions typically experienced in case of automotive load profiles (AIP)
- Catalyst particle growth causing loss in active catalyst area at high cell potentials (low load or idling conditions) (AIP)
- Enhanced knowledge and advice of how to prolong PEM fuel cell lifetime including properties of next generation materials with improved stability (AIP)

However, the main focus was on the performance targets, namely to prepare catalyst-support combinations for better performance, while the durability issues were of interest, but to a lesser extent. Also the major focus of the project was on the materials.

The starting point of the research were significant advances in the theoretical understanding of the deciding factors determining the rate of the ORR at different pure metal and later also alloy surfaces [1-5]. A number of Pt based alloys form after initial de-alloying Pt skin structures with an outer layer of Pt showing a different lattice constant compared to bulk Pt [6, 7]. This shifts the Pt d-band center and alters the binding energy of ORR intermediates (strain effect [8]). If the skin layer is only one monolayer thick and the underlying layers have a different composition, then the electronic interaction between other elements and the Pt skin also can change this binding energy (ligand effect [9]). While the focus of attention in literature was originally on alloys like Pt₃Ni or Pt₃Co, that show improved catalytic activity, but low stability and a strong tendency to de-alloying, in later work several Pt rare earth alloys were shown to combine increased catalytic activity with enhanced stability, starting with Pt₃Y and Pt₃Sc [2], later also including Pt₅Gd [6]. These studies were planned to be expanded within CathCat, complemented by the research on active support materials, ultimately aiming at improved MEAs made from these materials and innovative support materials that meet the targets above.

The project was structured into six technical work packages (WP2-WP7), while one work package (WP1) was dedicated to coordination and dissemination. A theoretical work package at DTU had the objective to study all remaining Pt-rare earth alloys of interest, to calculate the binding energies for the ORR intermediates, to study the influence of strain on the binding energy and to expand these considerations also to Pd alloys. They were closely interacting with experimentalists in order to verify and refine the theoretical considerations. One work package was dedicated to the preparation and structural characterization of materials (WP3) and one to the electrochemical characterization especially with respect to the ORR reaction (WP4). For the catalysts, both model alloys and nanoparticulate samples were considered. Originally vacuum-prepared surface alloys were considered as best model system, but then it turned out that the use of polycrystalline bulk alloys is the best option. In addition also arrays of nanoparticles on single-crystalline support materials were targeted. The challenge with the preparation of Pt-rare earth alloys lies in the extremely low standard potential for the reduction of the rare earth ions, and thus the extreme reactivity of the corresponding metals towards oxygen and moisture. Therefore it was planned to explore different preparation methods, besides vacuum based methods, in order to develop scalable synthesis methods and to scale then these method up for production of sufficient material for single cell MEA testing. The effect of carbon doping was planned to be studied first using well-defined model samples, and then to transfer the methods to technically applicable carbon powders. For

oxides different materials, especially doped titania, and composites of these oxides with different types of carbon were devised. All those materials were to be tested in WP4 for the ORR activity, the stability and the structural changes after the electrochemical workload. In WP5 the preparation of benchmark (or reference) MEAs and of MEAs with actually developed new materials were to be prepared, tested in WP6 for their fuel cell performance in single-cell fuel cell test stands and in WP7 for their durability and the structural changes after durability testing. It was expected that MEAs with clearly improved performance characteristics could be obtained. Aside from low temperature fuel cells using Nafion as the membrane material, also high temperature fuel cells using membranes from Advent technologies were included in the project.

Description of the main S & T results/foregrounds

In the following, the main research results of all partners are shortly summarized. One major effort was to pursue methods for allowing the preparation Pt-rare earth alloy catalysts. Different partners explored a number of different techniques. The task was very challenging as rare earth metals are very unobtainable and extremely reactive, with a high affinity to oxygen, which makes their complete reduction to the metal extremely difficult. In Table 1, the three major methods that are considered to be upscalable are compared in more detail to each other. Otherwise the following major results have been obtained:

- The preparation of size-selection nanoparticles in a cluster source permitted the successful preparation of Pt-rare earth nanoparticles of different size and the study of their electrocatalytic performance and structural properties. However, material for MEA cannot be made in this way due to upscaling issues. (DTU)
- The high temperature reduction of mixed Pt and Y precursor material led after careful and systematic optimization of the preparation to the formation of Pt-Y alloys, which still contained some amount of Y_2O_3 . Material for catalyst testing was fabricated using that method. As a substrate mesoporous carbon was chosen. The alloy formation was proven by XPS. (UniPd)
- The electrochemical reduction of Pt was successful from both ionic liquids and organic solvents. The electrochemical reduction of Yttrium was not successful, as passivation processes and possibly disproportionation of Y^{2+} happened. The reduction of Lanthanum was accomplished from ionic liquids and organic solvents, and there are indications that actually a metal was deposited. (TUM)
- The sputter-deposition permitted the reproducible fabrication of Pt-rare earth alloy films that may be well suited for nanostructured thin film catalysts, and possibly could be transferred also to nanoparticle deposition. Annealing resulted in surface segregation of the rare earth component though, while immersion in acid led to desired dealloying and Pt skin formation. (CUT)
- The reduction with alkali in water-free THF in order to make Gd nanoparticles failed in alloy formation, only Pt NP on Gd_2O_3 were found. (UP-IC2MP)

- Attempts were made to adopt the polyol or the NaBH₄ method for these catalysts but did not succeed. (FORTH)

Table 1. Summary of Synthesis Routes for Pt-rare earth nanoparticles

Method	Advantages	Disadvantages	Opportunities
Electrochemical Deposition from ionic liquids	<ul style="list-style-type: none"> • Particle Size Control by duration of potential pulse should be facile • Potential control permits composition control • Upscaling possible. 	<ul style="list-style-type: none"> • Careful elaboration of potentials and precursor concentrations required for simultaneous co-deposition at the right composition • High sensitivity towards residual moisture • Repeated addition of Pt precursor required for consumption of all Gd as lower concentrations of Pt required. • Difficulties in purchasing water-free precursors for Pt. • Currently high cost due to low volumes of chemicals, lack of procedure for retrieving unused precursors from electrolyte and strict requirements on water and air content (Glovebox required). 	<p>Quantities accessible with current setup: for 70 ml solution with 0.025 M Pt precursor and 0.1 M Gd precursor: ~ 0.4 g Pt₅Gd catalyst, as Pt precursor should not be entirely consumed rather 0.2 g catalyst</p> <p>Technical Upscaling Potential: Reasonably good. Further upscaling to industrial scale with bath composition monitoring and adjustment possible.</p> <p>Cost with current setup (precursor and IL cost only): IL: 1.50 € / g (ab 1 kg) Pt-Precursor: 200 € / g Pt Gd precursor: 108 €/g Gd For above solution: 120 € Gd + 74 € Pt + 105 € IL = 300 €</p> <p>Reproducibility: no data available yet</p> <p>Time of Synthesis: on the scale of h, possibly faster</p> <p>Ease of production: difficult, once all parameters have been optimized, this should become simpler.</p>
Single target co-sputtering	<ul style="list-style-type: none"> • Vacuum-based method starting already from 	<ul style="list-style-type: none"> • Current setup does not permit continuous production or 	<p>Quantities accessible with current setup: 3-27 nm thick films</p>

	<p>elemental rare earth metal atoms</p> <ul style="list-style-type: none"> • Deposition of thin films with 3-27 nm thickness feasible • High specific activity as determined by RDE: for 27 nm thick film 13.4 ± 0.3 mA/cm² initially, after stability test 10.5 ± 0.9 mA/cm²; for 3 nm thick films: 8.5 ± 0.5 mA/cm² initially, corresponding to mass activity of 3.5 ± 0.3 A/mg_{Pt} • Method can be used for preparation of thin films, but also collection of nanoparticles in ionic liquids should be feasible. 	<p>preparation of large samples.</p> <ul style="list-style-type: none"> • Current setup only suited for thin films 	<p>Technical Upscaling Potential: Sputtering already proven to be compatible with large-scale fabrication of low-emissivity windows. 3M has developed an all-dry, roll-to-roll-based production method of NSTF-electrodes, for use in fuel cells, based on sputtered thin films. Collection in ionic liquid for nanoparticle preparation another option.</p> <p>Cost with current setup: Costs for target materials and operating costs of sputter system.</p> <p>Reproducibility: high</p> <p>Time of Synthesis: Could be improved, probably by at least an order of magnitude, using a modified sputtering-target with improved cooling.</p> <p>Ease of production: Intermediate. For small samples preparation is very facile once the correct sputtering conditions are established. For larger samples major adjustments would be required to maintain constant composition.</p>
High temperature chemical reduction	<ul style="list-style-type: none"> • New route for Pt based bimetallic catalysts synthesis • Synthesis method is simple and carried 	<ul style="list-style-type: none"> • Incomplete reduction of yttrium salt • Presence of yttria in the sample 	<p>Quantities accessible with current setup: from 100 mg to 2 g of Pt_xY.</p>

	<p>out with easily accessible instruments</p> <ul style="list-style-type: none"> • Higher catalytic activity (MA, mass activity and SA, specific activity) than Platinum standard 50% (TKK) • High electrochemical stability of catalyst • Possible scalable synthesis • Low loss of platinum during the synthesis • Size control of nanoparticles • The amount of Pt in Pt_xY alloy was reduced with respect to Pt/C while the catalytic activity versus the oxygen reduction reaction and stability is maintained or even improved • Small spherical nanoparticles (2-5 nm) with narrow distribution dimensional size • No presence of chlorides or sulphates 	<ul style="list-style-type: none"> • Not all platinum is alloyed, best sample at present 41 % of Pt_xY alloy by XPS • Difficult control of reduction environment 	<p>Cost with current setup: 190 € g⁻¹ of Pt_xY on mesoporous carbon, Pt precursor 5 g 868.00 €, Y precursor 25 g 50.20 €, Mesoporous Carbon 25 g 386.00 €</p> <p>Technical Upscaling Potential: the upscale can be easily accomplished by employing bigger furnaces.</p> <p>Time of Synthesis: 6 h for sample precursor preparation 7-10 h for the synthesis of Pt_xY on mesoporous carbon catalyst</p> <p>Reproducibility: data not available</p> <p>Ease of production: the synthesis does not required sophisticate instrumentations or harsh experimental conditions</p>
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Technische Universität München (TUM)

TUM was active in WP3, WP4 and WP7 and coordinated the project. In WP3 the main activity was on the electrochemical deposition of catalyst materials. Numerous experiments in non-aqueous media on the electrodeposition of Pt, Y, La and Gd were carried out. While the deposition of Pt nanoparticles was successful in all solvents tested (organic solvents and ionic liquids, cf. Figure 1),

the deposition of the rare earth elements was more challenging. Y showed interesting results, but the deposition failed. The findings for the other rare earth elements studied were better, and the deposition of Lanthanum was accomplished from several media, as demonstrated by measurements with the electrochemical quartz crystal microbalance (EQCM, cf. Figure 2). Experimental techniques included the electrochemical quartz crystal microbalance, scanning probe microscopy techniques, SEM, EDX and other.

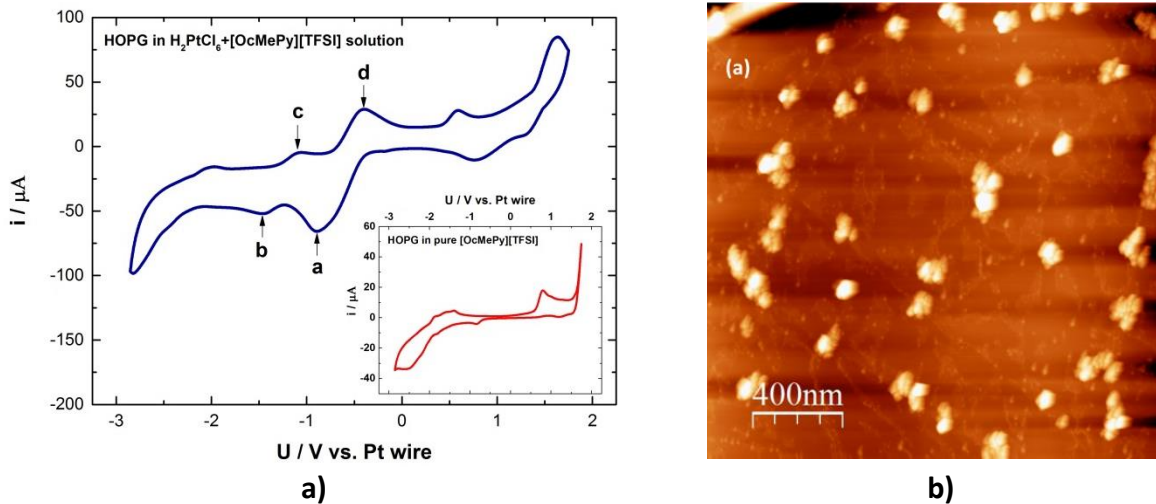


Figure 1. a) Cyclic voltammogram of a Pt precursor in an ionic liquid. The peaks labelled a and b correspond to the stepwise reduction of Pt(IV) to metallic Pt(0). b) Pt nanoparticles after electrodeposition imaged by atomic force microscopy.

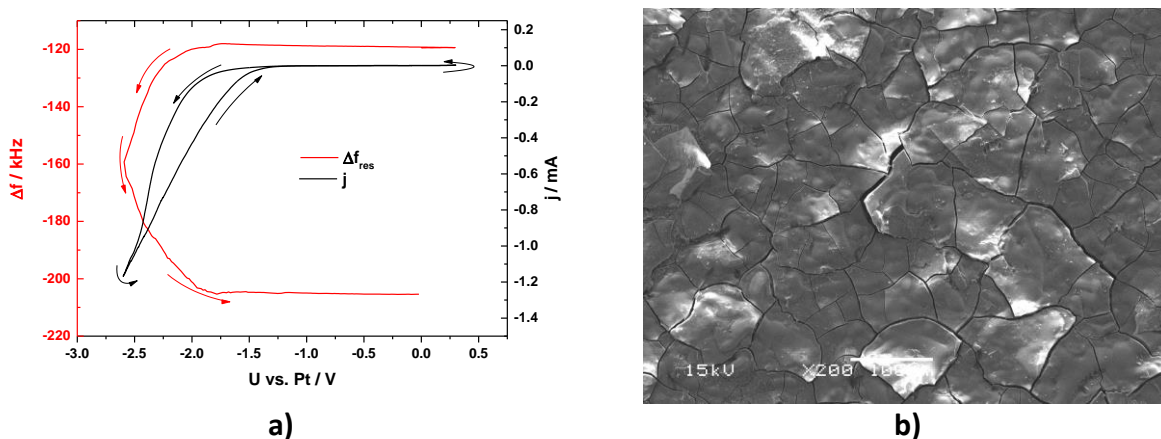


Figure 2. Voltammogram of La electrodeposition from an organic solvent. The red curve shows the resonance frequency change of the quartz resonator. One of the two Au electrodes (one on each side of the resonator) served as working electrode, onto which the La was deposited. The lowering of the resonance frequency clearly demonstrates successful deposition. b) Electron microscope image of a layer formed after transfer through air.

A further activity in WP3 and WP4 was related to the advanced support materials, where there was a collaboration with UniPd. Within that collaborative work, TUM studied the electrochemical deposition of Pd nanoparticles supported on both HOPG and nitrogen-doped HOPG prepared at UniPd, their catalytic activity, the size-dependence of the catalytic activity for fuel cell related reactions, and the stability of the particles in electrolytes of different pH. The results of these efforts are explained in the section of UniPd that also carried out extensive surface science studies

of these samples with XPS. The research led to two joint papers with UniPd and one third paper giving further details about the Pd / HOPG system by TUM.

TUM in depth applied the rotating disc electrode technique in order to study the catalytic behavior. A large number of experiments was carried out in order to optimize the deposition conditions of the catalyst ink on the glassy carbon support materials, and to perform to correction of background currents and IR drop (cf. Figure 3). Several catalysts provided by Ion Power and by UniPd were then tested with these methods.

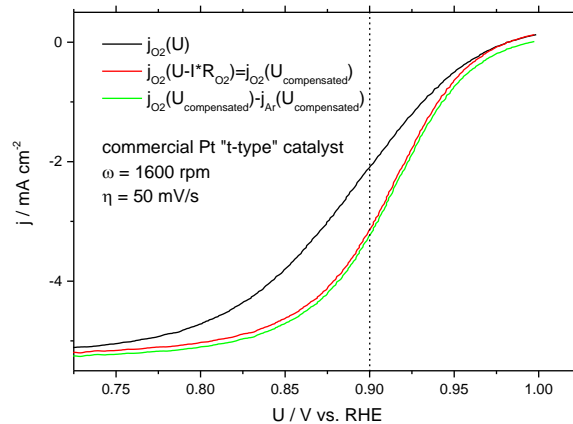


Figure 3. Characterization of Catalyst Material with the rotating disc electrode technique as measured (black curve) and after correction for uncompensated resistance (red) and background current correction (green).

TUM also studied model samples provided by CUT with STM. In WP7, the focus was on the analysis of MEAs obtained from Toyota. For each type of MEA, there was one that had not be used, and others after fuel cell performance and durability testing. The changes in the thickness of the cathode layer was analyzed by cross-sectional SEM, and changes in the particle size distribution were studied by TEM.

Joint Research Centre- European Commission (JRC)

JRC carried out testing of (benchmark) MEAs according to the harmonized European conditions that were developed in a joint effort by JRC, several FCH JU projects, OEMs and suppliers in the past few years, and contributed intensely to solving questions regarding the testing procedures and the MEA specifications.

Université de Poitiers (UP-IC2MP)

The main efforts of UP-IC2MP were in WP3, however also the electrochemical properties of prepared materials were studied. UP-IC2MP was active both in catalyst as well as in support material preparation. In the catalyst synthesis initially the carbonyl method and the water-in-oil method were employed with the aim of generating Pt-Y or Pt-Gd alloys. Those studies resulted in Pt-Y₂O₃ and Pt-Gd₂O₃ catalysts instead that showed nevertheless interesting catalytic behavior in RDE testing and an effect of induced strain in the particles. The Y-based catalyst was prepared in an amount sufficient for MEA preparation at Ion Power. In collaboration with FORTH, the catalyst was also studied on modified carbon nanotubes. Later the reduction from water-free media using

the alkalide reduction reaction was attempted. While the reduction to rare earth metal was possible, the alloy formation failed, only Pt NP on Gd_2O_3 were found.

With respect to Pd-based alloys, PdCu nanorods were fabricated by a procedure involving MOF precursors. The Pd oxidation peak could barely be observed in the voltammograms of these alloys. The addition of Cu into Pd NPs resulted in formation of a bimetallic PdCu nanoalloy. PdCu based on the MOF precursor showed a better ORR performance than PdCu based on other precursors and pure Pd catalysts, demonstrating a positive effect of the surface defects induced by alloyed PdCu NPs prepared from HKUST-1.

In order to exploit the strong metal-support interaction, mixed electron- and cation conducting transition metal oxides were investigated ($Ti_{0.7}M_{0.3}O_2$; M = Ru, Mo, Y, Nb and Ce). A new synthesis method was applied to disperse the oxide nanoparticles in a carbon matrix. Pt was deposited using a photo-deposition method. The activity of Pt supported on TiO_2/C prepared with the new synthesis method showed a slight improvement in the ORR activity, which was related to microstrain. It was also possible to further modify this interaction (*i.e.* Pt-Oxide) through TiO_2 doping with a second metal (*i.e.* Y and Ce). This interaction apparently favors a compression or relaxation in the TiO_2 lattice promoting the performance towards ORR in acid medium.

A nanocomposite Pt- CeO_x/C electrocatalyst was prepared as well using a MOF route and carefully characterized. A nanocomposite formed by CeO_x , porous carbon and Pt NPs is present after the heat treatment at 900 °C in samples prepared by carbonyl chemical route adopting sacrificial MOF(Ce). The presence of MOF(Ce) could stabilize and avoid the agglomeration of Pt NPs during heat-treatments.

Danmarks Tekniske Universitet (DTU)

At Danmarks Tekniske Universitet (DTU)-Center for Atomic-scale Materials Design (CAMD) DFT calculations were carried out to predict activity and stability of highly active catalysts. The range of compositions of suitable Pt(Pd)-rare earth (RE) element alloys to be studied was selected. The focus was on catalysts with Pt:RE ratios of 3:1 and higher to prevent leaching out. Since a several layers thick Pt skin forms on Pt-RE alloys, ligand effect and f electrons had not to be considered. Experimental lattice parameters for the Pt alloys were taken to determine the strain, and the OH binding energy was modelled. The influence of surface reconstruction was discussed, and comparison to experimental activities made. All Pt-RE alloys exhibit activities higher than that of Pt, but it was not possible to reach the maximum of the activity volcano. More detailed studies, in collaboration with the Center for Individual Nanoparticle Functionality (CINF), led to a detailed understanding of the correlation between catalytic activity, structure, and stability of the Pt-RE catalyst materials. Several joint publications with DTU-CINF have been published. For studies on a Pd-Ce alloy, the scaling relations between the binding strength of different intermediates were reinvestigated. The theoretical findings were confirmed at UniPd by experimental studies on a Pd model alloy, and published in a joint paper.

At DTU-CINF, studies on polycrystalline Pt-RE alloys were carried out. ORR RDE measurements of sputter-cleaned Pt₅Gd showed a 5-fold increase in activity relative to Pt at 0.9 V in 0.1 M HClO₄, and Pt₅La and Pt₅Ce more than a 3-fold enhancement. Also alloys with samarium, terbium, dysprosium, and thulium were studied. Angle resolved XPS (AR-XPS) was performed before and after testing for reconstructing the surface structure. Depth profiles of the alloys after electrochemistry exhibited the formation of a thick Pt overlayer, as previously observed for Pt₅Gd. The catalysts were very stable, losing less than 15% of their initial activity after 10 000 cycles between 0.6 V and 1.0 V in case of Pt₅Gd. The initially most active alloy was Pt₅Tb that however showed larger activity losses during cycling. Therefore the Pt₅Gd alloy represented the best compromise between activity and stability. Further studies concerned UHV prepared Pt(111)-Y surface alloys, and mass-selected Pt_xGd nanoparticles. The latter also demonstrated exceptional catalytic activity, and the maximum mass activity was obtained for particle sizes of around 8 nm, which also contributed to a good stability. These findings confirmed theoretical predictions.

Chalmers Tekniska Högskola AB (CUT)

CUT participated in WP3 and WP4, working both on preparation of alloy thin films as well as on the preparation of nanostructured model alloys.

Thin film deposition of platinum and its alloys is a key step to prepare model electrodes within this project. Thin films of pure Pt can be deposited using standard sputtering or evaporation. To be able to deposit thin films of Pt alloys CUT investigated two modifications of the standard methods.

In single-target co-sputtering, clips from foil of the alloying material are inserted onto the Pt-target, see Figure 4a. When sputtering from that target both Pt and the alloy material from the clips will be co-deposited. The number and area of the clips control the composition of the alloy. In successive evaporation Pt and the alloying material are evaporated as thin films on top of each other. Annealing is done on the thin films to form the alloy. The relative thicknesses of the thin films determine the alloy composition.

Using our developed method of single-target co-sputtering, with clips from foil of yttrium being fixated on the surface of a Pt sputtering target, thin alloy films were fabricated. Characterization by XPS shows metallic Y remaining after ORR-measurements (red double-peak in Figure 4b). This is a fingerprint of the Pt and Y actually being alloyed.

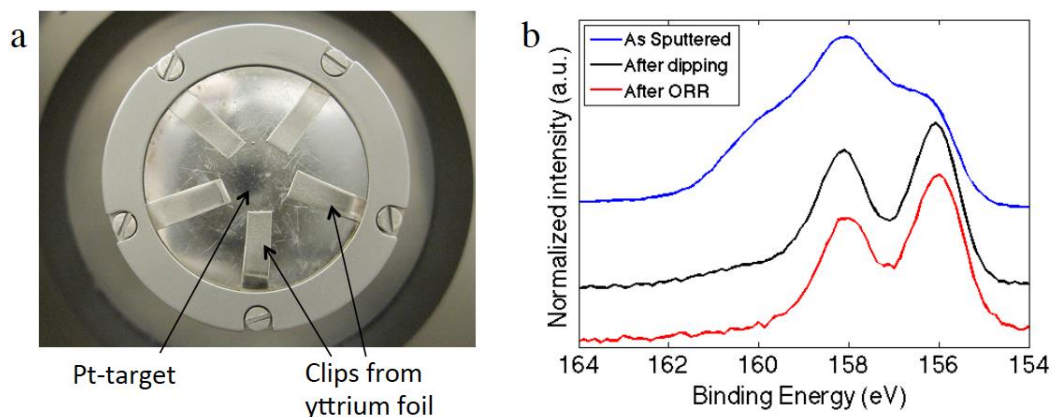


Figure 4. a) Photograph of the Pt-target with attached clips of foil of alloying material used in single target co-sputtering. b) Yttrium spectra from XPS-characterization of as sputtered PtY thin film alloy, after dipping in electrolyte and after electrochemical characterization.

CUT's thin films of PtY have a specific activity 6 times higher than polycrystalline Pt, which is even slightly higher than polycrystalline Pt₃Y. This is the highest specific activity ever reported for as deposited thin films. In addition, after stability tests our thin films retain 80 % of their activity; hence being more stable than nanoparticles of PtNi and PtY. These tests were carried out in collaboration with DTU.

A mass activity (MA) of more than 6 times the MA of PtNPs was obtained for 3 nm thin films of PtY. The company currently driving the development to use sputtering of nanostructured thin films, are in their state-of-the-art MEAs using PtNi thin films with a mass activity 50 % higher than PtNPs. Considering the more than 4 times higher mass activity of PtY thin films, our results should be very interesting for companies involved in manufacturing and use of fuel cells. The developed methods for fabrication of PtY thin films could reduce costs, thus facilitate a commercial breakthrough, of fuel cells. First, non-optimized efforts to transfer the method to the fabrication of MEAs have been carried out in collaboration with Toyota.

CUT also developed a setup in order to simultaneously measure optical and electrochemical signals from the model catalysts (Figure 5), and explored the application of these methods e.g. on the corrosion of Pt thin film catalysts. CUT also fabricated nanostructured model samples both with Pt and PtY alloy thin films for further study at the project partners.

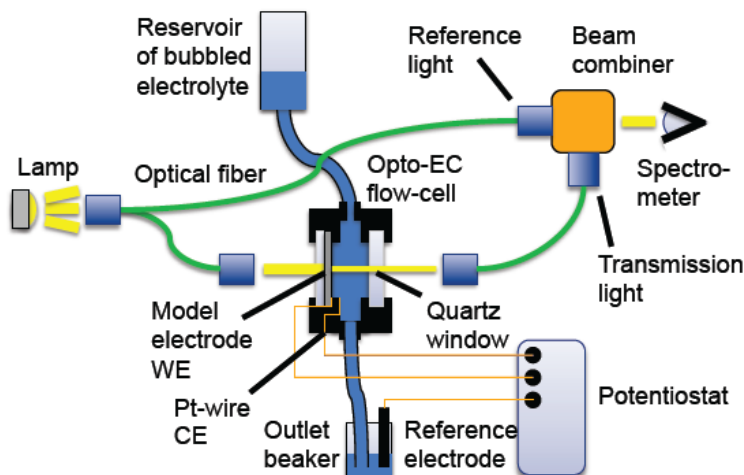


Figure 5. Schematic image of the setup for combining electrochemical and optical characterization and using beam-combiner to in addition obtain a reference signal.

Universita Degli Studi Di Padova (UniPd)

UniPd was mainly active in WP3 and WP4. They have been mainly involved in the preparation of advanced carbon supports modified by ion implantation and chemical doping and in the synthesis of Pt₃Y alloys using reduction deposition methods. In addition they carried out joint studies with DTU on Pd-Ce alloys.

The preparation of advanced support material was originally thought as a model study on HOPG samples to test the idea that the introduction of chemical defects on carbon supports could potentially enhance the stability of the nanoparticles dispersed on the support. TUM and UniPd in collaboration have tested if such benefits were present in the Pd/N-HOPG samples modified by ion implantation. The results of such investigation have been reported in two papers: W. Ju, T. Brülle, M. Favaro, L. Perini, C. Durante, O. Schneider and U. Stimming, *ChemElectroChem*, 2015, 2, 547–558 and W. Ju, M. Favaro, C. Durante, L. Perini, S. Agnoli, O. Schneider, U. Stimming and G. Granozzi, *Electrochim. Acta*, 2014, 141, 89–101. The supported Pd/N-HOPG showed a similar ORR electrocatalytic activity as compared with those supported on pure HOPG. However, the stability of Pd/N-HOPG towards potential cycling decreases strongly due to the existence of Pd²⁺ at the interface, which can accelerate the dissolution of Pd atoms.

A second approach consisted in preparation of innovative chemically doped mesoporous carbon (MC) powders as scalable materials to be employed in electrochemical devices. MC and N-doped MC were at first prepared following an optimized procedure by using mesoporous silica as template, sucrose as carbon precursor, NH₃ as doping agent and H₂SO₄ as catalyst. Pd and Pt NPs were deposited by wet impregnation on both doped and undoped samples, showing that the presence of nitrogen functional groups drives the dimension and the dispersion of metal NPs. Pt nanoparticles supported on N-doped supports showed high activities for the ORR in acidic solutions, with better performances than those of commercial Pt@vulcan (30 wt % Pt on Vulcan

XC-72). Furthermore, Pt NPs loaded on mesoporous carbon seems to possess higher stability with respect to the standard Pt@vulcan. This was rationalized in term of a better confinement effect inside the mesoporous structure. The results of this investigation are summarized in the paper: L. Perini, C. Durante, M. Favaro, V. Perazzolo, S. Agnoli, O. Schneider, G. Granozzi and A. Gennaro, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1170–1179.

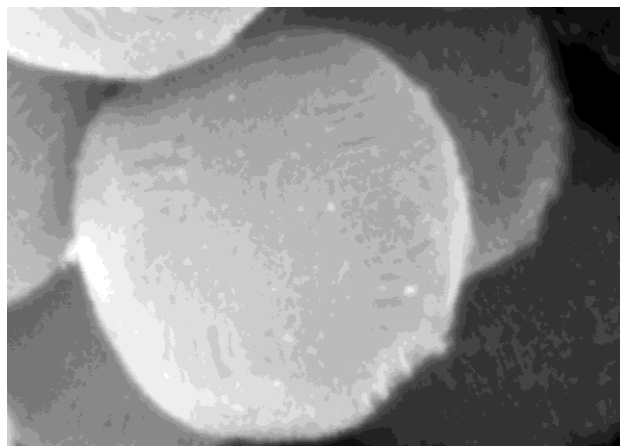


Figure 6. SEM image of the Pt nanoparticles on doped mesoporous carbon

The synthesis of advanced doped material was extended to sulfur doped mesoporous carbon and the results led so far to the two papers: V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G. A. Rizzi, A. Martucci, G. Granozzi and A. Gennaro, *Carbon*, 2015, **95**, 949–963 and Perazzolo, E. Grądzka, C. Durante, R. Pilot, N. Vicentini, G. A. Rizzi, G. Granozzi and A. Gennaro, *Electrochim. Acta*, 2016, doi:10.1016/j.electacta.2016.02.025. Nitrogen doped MCs have superior thermal stability with respect to sulfur doped ones, but lower electrochemical stability. In fact, pyridinic and pyrrolic functional groups resulted less stable during the ADT leading to the formation of oxidized nitrogen groups. On the contrary, N-graphitic and thiophenic groups confirmed their intrinsic thermodynamic stability both in acidic and alkaline electrolytes. The effect of heteroatoms on the catalytic activity of the carbon materials towards ORR was investigated and, notwithstanding the specific nature of the hetero-functional groups, it resulted that when the nitrogen content increases so does the catalytic activity, while the sulfur introduction in the carbon matrix leads to the opposite effect. All the investigated MCs resulted to be active towards H₂O₂ production; in particular N doped materials show high selectivity towards the bielecronic pathway.

Many Pt deposition conditions on doped MC were tested (cf. Figure 6), in order to discover which one produce the best results in terms of Pt nanoparticles diameter, dispersion on MC support and activity towards oxygen reduction reaction. Pt NPs on doped MC showed high catalytic performance for ORR with respect to the commercial Tanaka Pt 50% on Vulcan (50 wt.% Pt/C T-Type catalyst from IonPower®), notwithstanding the halved amount of Pt content.

UniPd has been also intensively working on the preparation of PtY nanoparticles on commercial mesoporous carbon mainly focusing on the reproducibility of the PtY@MC NPs

synthesis conditions, on the validation of the presence of the PtY alloy in the prepared samples and on their ORR characterization. The best Pt₃Y/C alloy sample has been determined and was prepared in sufficient amount for MEA preparation. The so obtained Pt₃Y NPs resulted to be well dispersed on the carbon support and the mean particle size diameter is ca. 2 nm. The activity of the Pt₃Y/C sample towards ORR was evaluated and compared with the commercial Pt/C Tanaka catalyst showing similar current densities than the Tanaka catalyst, better onset potential but containing almost the half amount of Pt. Furthermore, the Pt₃Y/C sample with the highest content of alloy has specific electrochemical active surface area and mass activity values higher than the Tanaka standard.

UNIPD has been also working on the new frontier of metal-less catalysts for ORR. Singly and multiply doped graphene oxide quantum dots have been synthesized and the obtained materials have been characterized by photoemission spectroscopy and scanning tunneling microscopy, in order to get a detailed picture of their chemical and structural properties. The electrochemical activity toward the ORR has been investigated by cyclic voltammetry and rotating disk electrode measurements, showing a clear decrease of the overpotential as a function of the dopant according to the sequence: N ~ B > B,N. Moreover, assisted by density functional calculations of the Gibbs free energy associated with every electron transfer, it has been proved that the selectivity of the reaction is controlled by the oxidation states of the dopants. The results have been published in two papers: M. Favaro, L. Ferrighi, G. Fazio, L. Colazzo, C. Di Valentin, C. Durante, F. Sedona, A. Gennaro, S. Agnoli and G. Granozzi, *ACS Catal.* **2015**, 5, 129–144, and - M. Favaro, M. Cattelan, F. Carraro, L. Colazzo, C. Durante, M. Sambì, A. Gennaro, S. Agnoli and G. Granozzi, *Journal of Materials Chemistry A*, **2015**, 3, 14334-14347

Finally, UNIPD has been strongly collaborating with Prof. Nicolas Alonso-Vante (UP-ICM2MP), by contributing with the surface science analysis of their samples and publishing a total of five papers in collaboration.

Ion Power Inc. (IonP)

Ion Power focused on the preparation of MEAs from benchmark catalysts and from CathCat catalysts. They supported in the selection of the Nafion membrane. In close collaboration with Toyota the optimum formulation for the catalyst ink was evaluated. Toyota and JRC were supplied with MEAs. Due to the in part low amounts of catalyst available Ion Power also successfully modified their experimental procedures to cope with this issue.

Foundation for Research and Technology Hellas - Institute of Chemical Engineering Sciences (FORTH/ICE)

FORTH participated in the WP3, WP5 and WP6, as they were working towards high temperature MEAs with new catalysts.

WP3

Toward the development of new electrocatalysts for the high temperature PEMFCs, FORTH attempted to synthesize a series of Pt alloys, namely Pt₃Co (to be used as reference), Pt₃Y and Pt₃Gd using reduction deposition methods. The methods used were based on the reduction of a Pt and other component salts-precursors in a solution where the carbon based catalyst support is dispersed. The substrates used were oxidized carbon nanotubes (ox.MWCNTs) and the same after functionalization with polar basic pyridine groups (ox.MWCNT)-Py. The latter is specially designed for high temperature electrodes and aims at the increase of the active electrochemical interface through the interactions of the pyridine moieties with the proton conductor, the phosphoric acid. The aim was to understand the effect of the substrate on the Pt, Co or Y deposition, the formation of alloys between the components and the obtained catalyst morphology and activity.

In order to optimize the catalyst synthesis, two methods were examined: (i) Deposition of metals using the polyol synthesis method, which is reduction of precursors in an ethyleneglycol/water EG/H₂O solution. Several parameters were explored like the time of the reaction, the pH of the solution, the EG/H₂O ratio and the precursors used. (ii) Reduction of salts in aqueous solutions using NaBH₄ as the reducing agent. In all cases, the prepared catalysts were physicochemically characterized using conventional techniques like XRD, TEM, ICP and XPS. The deposition of Pt and Co on oxidized nanotubes was successful and led to finely deposited catalyst, with small Pt particle size in the order of 2nm, fine distribution and alloying to a certain extent (shift of the XRD Pt main peak). On the other hand, metal deposition was not successful on the pyridine modified nanotubes. Depending on the method and conditions, the salts were not quantitatively reduced, alloying was not achieved or the obtained dispersion was not optimum. Several trials to adopt the polyol or the NaBH₄ method for the Pt-Y or Pt-Gd catalysts were also made. The synthetic procedures used did not result into a catalyst with the desired characteristics.

WP5

High Temperature (HT) Polymer Electrolyte Fuel Cells (PEMFC) have an operational temperature window of 160-200°C. The electrolyte used was the Advent Technologies high temperature polymer electrolyte, TPS type (aromatic polyethers bearing main and side chain polar pyridine groups, which interact with phosphoric acid, PA). MEAs were prepared using different catalysts at the cathode and different specifications (Pt and acid loading at the electrode) with the aim to understand the effect of the catalyst composition, morphology and substrate on the fuel cell performance. Initially Forth prepared MEAs using commercial Pt/C, as well as homemade Pt₃Co/ox.MWCNTs as benchmark. Thereafter MEAs incorporating Pt/Y₂O₃ deposited on ox.MWCNTs and (ox.MWCNT)-Py (synthesized by the University of Poitiers) were manufactured.

WP6

Forth created the benchmark for high temperature PEMFCs operating at 180°C by gathering in situ electrochemical results from MEAs incorporating commercial 30% Pt/C and homemade Pt or Pt₃Co/ox.MWCNTs. The active electrochemical surface area, ECSA, evaluation using various CO

adsorption based procedures took place in order to result in the optimum method. Moreover, the effect of phosphoric acid amount and platinum loading on the electrodes, as well as the partial pressure of oxygen effect were studied. As the next step, a series of Pt and Pt-Y₂O₃ catalysts prepared by the University of Poitiers using Forth's substrates was evaluated in situ (ECSA measurements with CO stripping, I-V plots and AC impedance spectroscopy) under different operational conditions. Only small differences could be observed when comparing the performance between them, as well as with the benchmark catalysts, which could be rationalized due to the fact that Pt is not an alloy with Y.

Toyota Motor Europe (Toyota)

Toyota actively tested CathCat MEAs. In the beginning of the MEA testing efforts they evaluated several MEAs from Ion Power made with different formulations and identified the best ones for the purpose of the project. They conducted performance and durability tests using both European Harmonized and other test protocols on the benchmark catalysts and the first generation CathCat catalyst. They tested several other MEAs with catalyst materials supplied from different project partners.

Description of the potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and the exploitation of results

In view of the worldwide increasing industrialization and energy consumption, the growing world population and the growing number of automobiles on the road, there is a clear need for electric mobility. It is necessary to save resources, to mitigate the effects of climate change and to reduce pollution. Electric mobility can be based on Li ion batteries, a technology with high efficiency, but also high cost, limited availability of Lithium, and low driving range, at least at reasonable battery weight. The other option are hydrogen fuel cells driven cars, with a better driving range, however also suffering from high cost, limited lifetime and efficiency limitations due to the sluggish oxygen reduction reaction. Another important factor is the refueling infrastructure that has been improved in the past years, but still is way below what is needed. Despite many efforts the high costs of the PEM stacks and the problems with hydrogen infrastructure have prevented up to now the large-scale market introduction of fuel cell vehicles.

The latter aspect was not addressed by the CathCat project. The focus of the CathCat project was on developing better and cheaper catalyst materials for the cathode side of the fuel cell. As described before the starting points was the observation that Pt-rare earth alloys show activity and stability clearly outperforming Pt based catalysts. Therefore the project targeted at further expanding the understanding of the entire portfolio of Pt-rare earth alloys, of finding methods to prepare such alloys in an up-scalable fashion, and to research advanced support materials that even further improve the catalytic activity. Such a new catalyst system was expected to have

significant impact on several levels. As described in the description of work, a significant reduction and/or the replacement of Pt would enable a vast improvement in commercial cost of PEMFCs allowing for commercialization and wide range application in automotive industry. Whilst this is only one component of the fuel cell, the catalyst material contributes significantly to the stack cost (up to 60%). A second aspect was expected by the increased lifetime achieved by the new catalyst/support combinations, leading to an increased total cruising range of the fuel cell during its lifetime and therefore to a reduction in the total costs of the fuel cell system. Such cost reductions would help to enhance the competitiveness of the European fuel cell industry in the medium term, leading to the creation of new jobs and contributing to the well-fare of European Automotive Industry. A widespread commercialisation of fuel cell vehicles would contribute to lower CO₂ emissions, significant improvement in local air quality, and reduction of traffic noise levels, thus enhancing the quality of life. Also, conventional gas stations could be replaced by hydrogen refuelling stations, and the people working at those facilities would remain employed, while battery recharging might be done at home and at fully electronic recharging stations. Apart from these indirect, future consequences of the project there was also an immediate impact: several postdocs and Ph.D. students have worked on the project, gained and expanded their expertise in different branches of science like electrocatalysis, fuel cells, electrochemical testing, surface science methods, and theoretical methods. Several students participating in the project have completed or soon will complete their Pd.D. degree, and several postdoc's careers benefitted from the project.

The project has generated a considerable knowledge output from WP2-4 that will generate a knowledge base for long-term future research in this important area. This concerns the detailed understanding of the Pt-rare earth alloys, their activity and stability and the physical mechanisms behind them (WP2/4), general knowledge about catalytic processes gained in WP2, the preparation of advanced support materials and their electrochemical behaviour when combined with Pt or Pd-based catalysts and also synthetic methods to prepare the Pt-rare earth alloys: several methods have led to promising results that should after further research permit the upscaled preparation of these alloys in a form suitable for MEA testing. This target could not be reached within the CathCat project, other than originally planned, but remains realistic. Also some of the advanced support materials showed excellent performance in combination with Pt in RDE testing, so that within an optimized catalyst layer they should allow the fabrication of improved MEAs. Within the CathCat project there was not enough material available to optimize the catalyst ink composition.

There were extensive dissemination activities within the project. 28 publications have been published in peer-reviewed journals with in part high impact factors, two in conference proceedings and several more are in preparation. Multiple oral and poster presentations were given at international conferences, especially those concerned with electrochemical energy conversion and storage, and in part acknowledged with poster awards. In the final year, the project was presented at two workshops: on the one hand in a dissemination session on several FCH JU funded catalyst project, that took place during the EFCD 2015 conference in La Grande Motte, France, on the other hand

in the actual CathCat dissemination session at the 3degis workshop in Santorini, Greece. All public information about the project has been posted on the website.

The further exploitation of the project foreground will be pursued by the individual partners, who remain owner of their foreground generated. DTU has several patents on Pt-rare earth metals, and continue to do research along those lines. Those partners that are working on the different preparation methods will pursue those in so far as funding will be available either in collaboration with partners in the present consortium, or also within new projects. Similar aspects apply to the advanced support materials. Commercial exploitation requires additional research activities to optimize the preparation methods and MEA performance in preparation to stack integration.

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