Novel catalyst materials for the cathode side of MEAs suitable for transportation applications				
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Deliverable **D1.11**	WP1	**Coordination and Project Management**		
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Project Context and 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. In addition, 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 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. For Pd that 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 following Multiannual Implementation Plan (MAIP) and Annual Implementation Plan (AIP) targets were addressed:

- 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 g/kW, BoL > 55% efficiency, BoL Power density at nominal power : > 1 W/cm2 at 1.5 A/cm2, Lifetime (EoL) > 5,000h at dynamic operation (car)* applying typical load profiles (accelerated life tests), Maximum EoL degradation < 10% in rated power density, Power density > 0.9 W/cm2 at 1.4 A/cm2 at EoL, operation temperature: up to 130 °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 Pt_3Ni or Pt_3Co, 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 Pt_3Y and Pt_3Sc [2], later also including Pt_5Gd [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 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.

Summary of Project Results

In the CathCat project, a complete understanding of the catalytic behavior of Pt-RE alloys was achieved using DFT calculations and experimental studies on model alloys and nanoparticles at DTU. 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. At DTU-CINF, studies on polycrystalline Pt-RE alloys were carried out. ORR RDE measurements of sputter-cleaned Pt_5Gd showed a 5-fold increase in activity relative to Pt at 0.9 V in 0.1 M $HClO_4$, and Pt_5La and Pt_5Ce more than a 3-fold enhancement. Depth profiles of Pt_5La and Pt_5Ce after electrochemistry exhibited the formation of a thick Pt overlayer, as previously observed for Pt_5Gd. Also alloys with Sm, Tb, Dy, and Tm were studied. Depth profiles of the alloys after electrochemistry exhibited the formation of a thick Pt overlayer. 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 Pt_5Gd, which 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, a maximum mass activity for particle sizes of around 8 nm, and thus a good stability. Also Pd_5Ce was studied theoretically at DTU and experimentally at UniPd.

Large efforts went into the preparation of nanoparticles and thin films from such materials, which was highly challenging due to the large reactivity and low standard potentials of the RE metals. Efforts regarding the synthesis of Pt-rare earth alloys included solution-based methods (carbonyl method, water-in-oil route, alkalide reduction applied at Université de Poitiers (UP), polyol synthesis at FORTH), sputter-based techniques at CUT, electrochemical methods at TUM and gas phase reduction of precursors at elevated temperatures at University of Padova (UniPd). The water-in-oil route led to Y-/Gd-oxide modified Pt nanoparticles that showed an increased catalytic activity at 0.9 V. 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. At TUM experiments in non-aqueous media on the electrodeposition of Pt, Y, La and Gd were carried out. While the deposition of Pt was successful, the deposition of the RE elements was harder. The deposition of La was accomplished from several media.
UniPd prepared PtY nanoparticles on commercial mesoporous carbon using their solvent-free method. The best Pt_3Y/C alloy sample has been determined and was prepared in sufficient amount for MEA preparation. In RDE tests the catalyst surpassed the benchmark catalysts. FORTH attempted the polyol synthesis method but failed. At FORTH, a modified polyol process was also applied for the preparation of Pt-Co catalyst. Depending on the exact nature of the carbon nanotube supports used, formation of a Pt_3Co alloy was observed or not. CUT successfully prepared Pt-Y and Pt-Tb thin films with very high activity that were also tested in MEA.

Further work focused onto advanced support materials: At UP-IC2MP, mixed electron- and cation conducting transition metal oxides were investigated in order to exploit the strong metal-support interaction ($Ti_{0.7}M_{0.3}O_2$; 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. Improvements in activity were achieved and one sample was up-scaled for MEA testing. In addition at UP-IC2MP Pt-CeO_x/C electrocatalyst and PdCu nanorods were prepared using a MOF route. At UniPd advanced carbon supports were studied. TUM and UniPd tested if Pd/N-HOPG samples modified by ion implantation showed improved catalytic performance. As this was not the case, UniPd focused on innovative chemically doped mesoporous carbon (MC) powders (N- and S-doped) and deposited Pd and Pt NP thereon. For these materials improved activity was found both for Pd and Pt NP deposited. A sample type with high activity was up-scaled for MEA fabrication and tested in MEA.

Model substrate and catalyst/support materials were characterized for their structural, electrochemical and catalytic properties using in-situ and ex-situ techniques. Model alloys were fabricated also using lithographic methods at CUT and tested at TUM using STM and

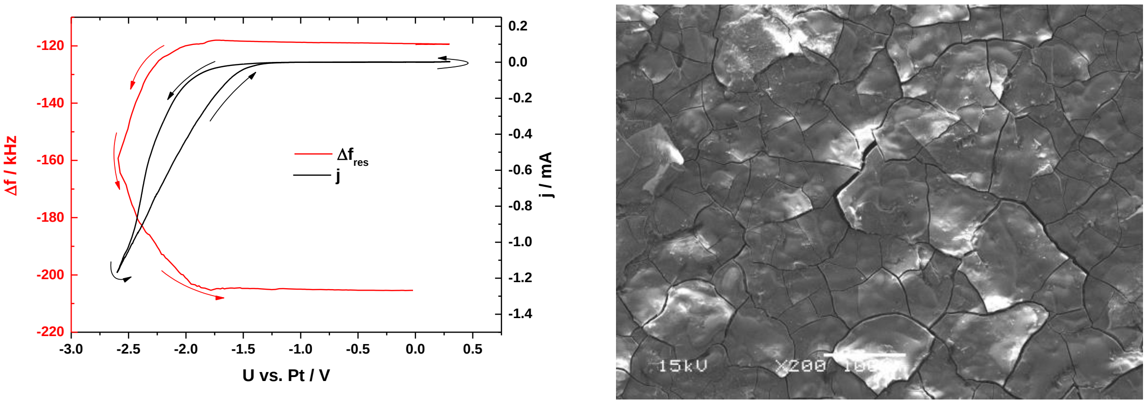
AFM. RDE testing of benchmark and new catalysts were carried out, and experiments to improve the technique carried out. Optical methods were optimized and applied at CUT to study catalyst performance and degradation.

FORTH prepared and tested Pt_3Co catalysts on carbon nanotubes in high temperature PEMFCs. They also studied Pt/Y_2O_3 catalysts from UP-IC2MP in their MEAs. Ion Power prepared benchmark MEAs and MEAs from catalyst materials provided by CathCat partners. These were tested in part and JRC and extensively at Toyota for performance and durability. Unfortunately, none of the MEAs with new catalysts exceeded the benchmark performance.

Details of Research

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), 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 1). Experimental techniques included the electrochemical quartz crystal microbalance, scanning probe microscopy techniques, SEM, EDX and other.



a) **b)**

Figure 1. 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 2). Several catalysts provided by Ion Power and by UniPd were then tested with these methods.

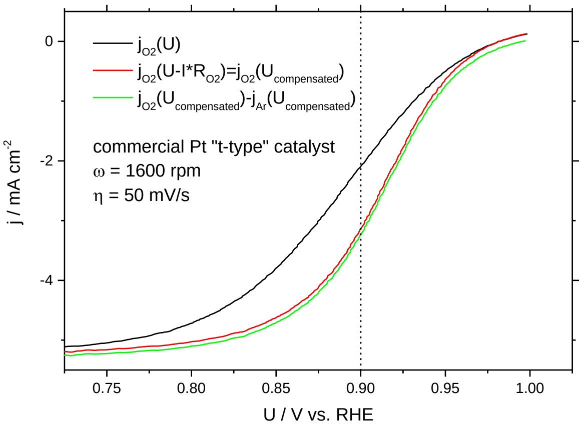


Figure 2. Characterization of Catalyst Material with the rotating disc electrode technique as measured (black curve) and after correction for uncompensated resistance (red) and background current correction (green).

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-Y_2O_3 and Pt-Gd_2O_3 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 Pt_5Gd showed a 5-fold increase in activity relative to Pt at 0.9 V in 0.1 M $HClO_4$, and Pt_5La and Pt_5Ce 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 Pt_5Gd. 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 Pt_5Gd. The initially most active alloy was Pt_5Tb that however showed larger activity losses during cycling. Therefore the Pt_5Gd 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 Hoegskola 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 3a. 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 3b). This is a fingerprint of the Pt and Y actually being alloyed.

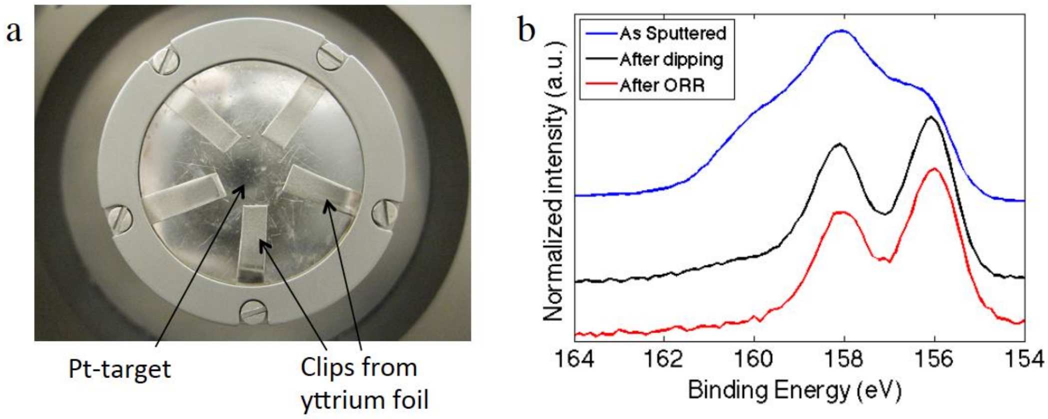


Figure 3. a) Photograph of the Pt-target with attached clips of foil of alloying material used in single target co-sputtering. b) Yttrium spectra from XPS-characterization of as sputtered PtY thin film alloy, after dipping in electrolyte and after electrochemical characterization.

CUT's thin films of PtY have a specific activity 6 times higher than polycrystalline Pt, which is even slightly higher than polycrystalline Pt_3Y. 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 4), 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.

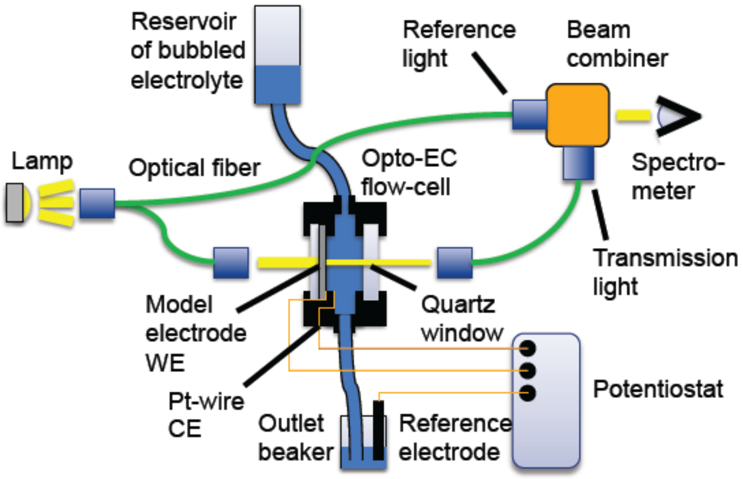


Figure 4. Schematic image of the setup for combining electrochemical and optical characterization and using beam-combiner to in addition obtain a reference signal.

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 Pt_3Y 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 Pd^{2+} 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, NH_3 as doping agent and H_2SO_4 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.

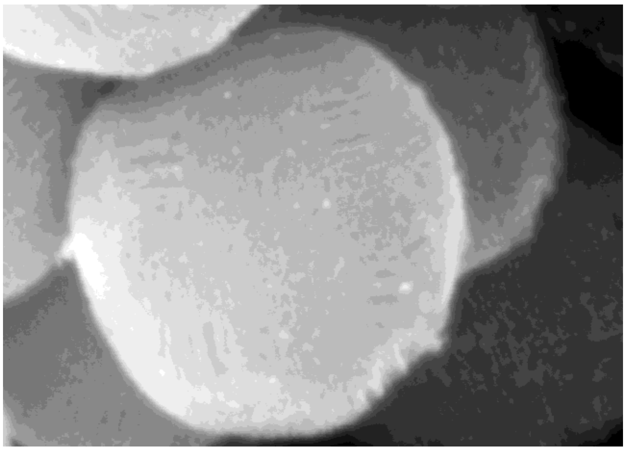


Figure 5. SEM image of the Pt nanoparticles on doped mesoporous carbon

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 H_2O_2 production; in particular N doped materials show high selectivity towards the bielectronic pathway.

Many Pt deposition conditions on doped MC were tested (cf. Figure 5), 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 Pt_3Y/C alloy sample has been determined and was prepared in sufficient amount for MEA preparation. The so obtained Pt_3Y NPs resulted to be well dispersed on the carbon support and the mean particle size diameter is ca. 2 nm. The activity of the Pt_3Y/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 Pt_3Y/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. Sambi, 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 Pt_3Co (to be used as reference), Pt_3Y and Pt_3Gd 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/H_2O solution. Several parameters were explored like the time of the reaction, the pH of the solution, the EG/H_2O ratio and the precursors used. (ii) Reduction of salts in aqueous solutions using $NaBH_4$ 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 $NaBH_4$ 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^{o}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 Pt_3Co/ox.MWCNTs as benchmark. Thereafter MEAs incorporating Pt/Y_2O_3 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^{o}C by gathering in situ electrochemical results from MEAs incorporating commercial 30% Pt/C and homemade Pt or Pt_3Co/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-Y_2O_3 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.

Publications

1. Jiwei Ma, Aurélien Habrioux, and Nicolas Alonso-Vante; **The Effect of Substrates at Cathodes in Fuel Cells**, ChemElectroChem, 1 (2014) 37-46.
2. S. Mokrane-Soualah, A.S. Gago, A. Habrioux, N. Alonso-Vante, **Mixed-oxide $Ti_{1-x}W_xO_2$ as support for (photo)-electrochemical processes**, Applied Catalysis B: Environmental, 147 (2014) 756-763.
3. S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E.A. Paoli, R. Frydendal, T.W. Hansen, I. Chorkendorff, I.E.L. Stephens, J. Rossmeisl, **Enabling direct H_2O_2 production through rational electrocatalyst design**, Nature Materials, 12 (2013) 1137-1143.
4. L. Perini, C. Durante, M. Favaro, S. Agnoli, G. Granozzi, A. Gennaro, **Electrocatalysis at palladium nanoparticles: Effect of the support nitrogen doping on the catalytic activation of carbon halogen bond** , Applied Catalysis B: Environmental, 144 (2014) 300-307.
5. P. Malacrida, M. Escudero-Escribano, A. Verdaguer-Casadevall, I.E.L. Stephens, I. Chorkendorff, **Enhanced activity and stability of Pt-La and Pt-Ce alloys for oxygen electroreduction: the elucidation of the active surface phase** , Journal of Materials Chemistry A, 2 (2014) 4234-4243.
6. Y. Luo, A. Habrioux, L. Calvillo, G. Granozzi, N. Alonso-Vante, **Yttrium Oxide/Gadolinium Oxide-Modified Platinum Nanoparticles as Cathodes for the Oxygen Reduction Reaction**, Chemphyschem, 15 (2014) 2136–2144.
7. Wenbo Ju, Marco Favaro, Christian Durante, Lorenzo Perini, Stefano Agnoli, Oliver Schneider, Ulrich Stimming and Gaetano Granozzi, **Pd Nanoparticles deposited on nitrogen-doped HOPG: New Insights into the Pd-catalyzed Oxygen Reduction Reaction** , Electrochimica Acta, 141 (2014) 89-101.
8. T.P. Johansson, E.T. Ulrikkeholm, P. Hernandez-Fernandez, M. Escudero-Escribano, P. Malacrida, I.E.L. Stephens, I. Chorkendorff, **Towards the elucidation of the high oxygen electroreduction activity of Pt_xY: surface science and electrochemical studies of Y/Pt(111)**, Physical Chemistry Chemical Physics, 16 (2014) 13718-13725.
9. Marco Favaro, Lara Ferrighi, Gianluca Fazio, Luciano Colazzo, Cristiana Di Valentin,Christian Durante, Francesco Sedona, Armando Gennaro, Stefano Agnoli, and Gaetano Granozzi, **Single and Multiple Doping in Graphene Quantum Dots: Unraveling the Origin of Selectivity in the Oxygen Reduction Reaction**, ACS Catalysis, 5 (2015) 129-144.

10. Wenbo Ju, Tine Brülle, Marco Favaro, Lorenzo Perini, Christian Durante, Oliver Schneider, Ulrich Stimming, Palladium Nanoparticles Supported on HOPG: Preparation, Reactivity and Stability, ChemElectroChem, 2 (2015) 547-558.
11. Lorenzo Perini, Christian Durante, Marco Favaro, Valentina Perazzolo, Stefano Agnoli, Oliver Schneider, Gaetano Granozzi, and Armando Gennaro, Metal–Support Interaction in Platinum and Palladium Nanoparticles Loaded on Nitrogen-Doped Mesoporous Carbon for Oxygen Reduction Reaction, ACS Appl. Mater. Interfaces, 7 (2015) 1170-1179.
12. C.M. Pedersen, M. Escudero-Escribano, A. Velázquez-Palenzuela, L.H. Christensen, I. Chorkendorff, and I.E.L. Stephens, Benchmarking Pt-based electrocatalysts for low temperature fuel cell reactions with the rotating disk electrode: oxygen reduction and hydrogen oxidation in the presence of CO, Electrochimica Acta, 179 (2015) 647–657.
13. J. Ma, A. Habrioux, Y. Luo, G. Ramos Sanchez, L. Calvillo, G. Granozzi, P.B. Balbuena, and N. Alonso-Vante, Electronic Interaction between Platinum Nanoparticles and Nitrogen-doped Reduced Graphene Oxide: Effect on the Oxygen Reduction Reaction, Journal of Materials Chemistry A, 3 (2015) 11891-11904.
14. Y. Luo, A. Habrioux, L. Calvillo, G. Granozzi, and N. Alonso-Vante, Thermally Induced Strains on the Catalytic Activity and Stability of Pt–M_2O_3/C (M=Y or Gd) Catalysts towards Oxygen Reduction Reaction, ChemCatChem, 7 (2015) 1573–1582.
15. Y. Luo and N. Alonso-Vante, The Effect of Support on Advanced Pt-based Cathodes towards the Oxygen Reduction Reaction. State of the Art, Electrochimica Acta, 179 (2015) 647–657.
16. M. Favaro, F. Carraro, M. Cattelan, L. Colazzo, C. Durante, M. Sambi, A. Gennaro, S. Agnoli, and G. Granozzi, Multiple doping of graphene oxide foams and quantum dots: new switchable systems for oxygen reduction and water remediation, Journal of Materials Chemistry A, 3 (2015) 14334-14347.
17. Amado Velázquez-Palenzuela, Federico Masini, Anders F. Pedersen, María Escudero-Escribano, Davide Deiana, Paolo Malacrida, Thomas W. Hansen, Daniel Friebel, Anders Nilsson, Ifan E.L. Stephens, Ib Chorkendorff, The enhanced activity of mass-selected Pt_xGd nanoparticles for oxygen electroreduction, Journal of Catalysis, 328 (2015) 297-307.
18. V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G.A. Rizzi, A. Martucci, G. Granozzi, A. Gennaro, Nitrogen and sulfur doped mesoporous carbon as metal-free electrocatalysts for the in situ production of hydrogen peroxide, Carbon, 95 (2015) 949-963.
19. Y. Luo, J.M. Mora-Hernández, L.A. Estudillo-Wong, E.M. Arce-Estrada, N. Alonso-Vante, Nanostructured palladium tailored via carbonyl chemical route towards oxygen reduction reaction, Electrochimica Acta, 173 (2015) 771–778.
20. B. Wickman, M. Fredriksson, L. Feng, N. Lindahl, J. Hagberg, C. Langhammer, Depth probing of the hydride formation process in thin Pd films by combined electrochemistry and fiber optics-based in situ UV/vis spectroscopy,, Physical Chemistry Chemical Physics, 17 (2015) 18953-18960.
21. M. Favaro, G.A. Rizzi, S. Nappini, E. Magnano, F. Bondino, S. Agnoli and G. Granozzi, A synchrotron-based spectroscopic study of the electronic structure of N-doped HOPG and PdY/N-doped HOPG, Surface Science, 646 (2016) 132-139.
22. V. Tripkovic, J. Zheng, G.A. Rizzi, C. Marega, C. Durante, J. Rossmeisl, G. Granozzi, Comparison between the Oxygen Reduction Reaction Activity of Pd_5Ce and Pt_5Ce: The Importance of Crystal Structure, ACS Catalysis, 5 (2015) 6032-6040.
23. W. Ju, R. Valiollahi, R. Ojani, O. Schneider , U. Stimming, The Electrooxidation of Formic Acid on Pd Nanoparticles: an Investigation of Size-Dependent Performance, Electrocatalysis, 7 (2016) 149-158.

24. V. Perazzolo, E. Grądzka, C. Durante, R. Pilot, N. Vicentini, G.A. Rizzi, G. Granozzi, A. Gennaro, **Chemical and Electrochemical Stability of Nitrogen and Sulphur Doped Mesoporous Carbons**, Electrochimica Acta, 197 (2016) 251-262.
25. L.A. Estudillo-Wong, Y. Luo, J.A. Díaz-Real, N. Alonso-Vante, **Enhanced oxygen reduction reaction stability on platinum nanoparticles photo-deposited onto oxide-carbon composites**, Applied Catalysis B: Environmental, 187 (2016) 291-300.
26. Y. Luo, L. Calvillo, C. Daiguebonne, M.K. Daletou, G. Granozzi, N. Alonso-Vante **A highly efficient and stable oxygen reduction reaction on Pt/CeO_x/C electrocatalyst obtained via a sacrificial precursor based on a metal-organic framework**, Applied Catalysis B: Environmental, 189 (2016) 39-50.
27. Y. Luo, L. A. Estudillo-Wong, L. Cavillo, G. Granozzi, N. Alonso-Vante **An easy and cheap chemical route using a MOF precursor to prepare Pd–Cu electrocatalyst for efficient energy conversion cathodes**, Journal of Catalysis, 338 (2016) 135–142.
28. M. Escudero-Escribano, P. Malacrida, M.H. Hansen, U.G. Vej-Hansen, A. Velázquez-Palenzuela, V. Tripkovic, J. Schiøtz, J. Rossmeisl, I.E.L. Stephens, I. Chorkendorff **Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction**, Science, 352 (2016) 73-76.
29. J. Ma, L. Seidl, W. Ju, E. Mostafa, L. Asen, S. Martens, U. Stimming and O. Schneider, **Applications of Ionic Liquids in Electrochemical Energy Conversion and Storage**, ECS Transactions, 64(4) (2014) 407-423.
30. M.U. Sreekuttan, J.M. Mora-Hernandez, Y. Luo, and N. Alonso-Vante, **Substrate Effects on the Catalytic Center of $CoSe_2$ for Oxygen Reduction Reaction**, ECS Transactions, 64(36) (2015) 1-9.

Further publications have been submitted or are in preparation.

References

[1] V. Tripković, E. Skúlason, S. Siahrostami, J. K. Nørskov, J. Rossmeisl, *Electrochimica Acta* **2010**, *55*, 7975-7981.

[2] J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Nørskov, *Nature Chemistry* **2009**, *1*, 552-556.

[3] J. Rossmeisl, J. K. Nørskov, *Surface Science* **2008**, *602*, 2337–2338.

[4] V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, J. K. Nørskov, *Angewandte Chemie-International Edition* **2006**, *45*, 2897 – 2901.

[5] J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, *Journal of Physical Chemistry B* **2004**, *108*, 17886-17892.

[6] M. Escudero-Escribano, A. Verdaguer-Casadevall, P. Malacrida, U. Grønbjerg, B. P. Knudsen, A. K. Jepsen, J. Rossmeisl, I. E. L. Stephens, I. Chorkendorff, *Journal of the American Chemical Society* **2012**, *134*, 16476-16479.

[7] I. E. L. Stephens, A. S. Bondarenko, U. Gronbjerg, J. Rossmeisl, I. Chorkendorff, *Energy & Environmental Science* **2012**, *5*, 6744-6762.

[8] M. Mavrikakis, B. Hammer, J. K. Nørskov, *Physical Review Letters* **1998**, *81*, 2819-2822.

[9] T. Bligaard, J. K. Nørskov, *Electrochimica Acta* **2007**, *52*, 5512-5516.