





## **BOOK OF ABSTRACTS**

Edited by: P. Brault, D. Jones, L. Boillot & M. Mikikian



GREMI



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## FOREWORD

The goals of our "European Fuel Cell Car Workshop" are to establish recent advances made in Europe in the fuel cells and hydrogen sector and how they contribute towards achieving the COP21 objectives for transport and sustainable mobility. With 8 plenary lectures, 40 presentations (oral and poster) and a round table discussion on research and innovation, EFCW2017 is bringing together more than 80 researchers dedicated to realising the potential of fuel cell electric vehicles. Major European industrial groups (Toyota, Daimler, BMW, VW, Audi, Johnson Matthey Fuel Cells), European and French SMEs (Anleg, Borit, NelHydrogen, Symbio, STEP) are amongst the delegates. These lectures and presentations, chosen for their innovative content, will explain the recent advances of the whole hydrogen value chain from the particle to the vehicle.

EFCW2017 is organized by the CNRS and the SMARTCat project co-financed by the Fuel Cell and Hydrogen - Joint Undertaking. The SMARTCat project aims at developing innovative catalysts for fuel cell cars. The workshop will give the audience new insights into what is happening in the fuel cells and hydrogen field for automotive applications: fuel cell and hydrogen storage components, systems and powertrain, and the approach of European automobile manufacturers in the deployment of fuel cell electric vehicles.

EFCW2017 gratefully acknowledges the FCH2-JU, the Région Centre Val de Loire, the Conseil Départemental du Loiret, and the city of Orléans for strong support in funding and welcoming the workshop.

We wish you an enjoyable time in Orléans for working, exchanging ideas and test driving the fuel cell cars, and visiting the City of Joan of Arc.

Pascal Brault

Deborah Jones

Lionel Boillot

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## TOPICS

- 1. Recent advances in Fuel Cell materials/components
- 2. Recent advances in H<sub>2</sub> storage components
- 3. Recent advances in stack components and developments
- 4. Recent advances in FC powertrain system, H<sub>2</sub> storage/distribution
- 5. Recent advances in the FC electric automotive industry

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# Identification and optimisation of active electrocatalytic sites for fuel cell applications

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Keywords: Oxygen reduction reaction, electrocatalysis, active catalytic sites.

According to the existing paradigms of heterogeneous catalysis, the first steps in the design of new catalysts consist of two procedures: identification of the nature of so-called active sites (after H.S. Taylor, 1925) and their optimization, so that they bind reaction intermediates optimally (P. Sabatier, 1911). In contrast to homogeneous catalysis, where the methodology of elucidating the active sites is rather developed, heterogeneous (electro)catalysis suffers from the absence of well-established means to find them at the surface. Namely the lack of understanding of the nature of the catalytic centers largely hinders further optimization of their electronic properties and hence their activity, selectivity and stability. In the presentation, several experimental and joint theoretical/experimental approaches will be presented in order to identify active sites and design new better materials for the fuel cell applications. One example is illustrated in Figure 1, where theoretical analysis and experiments with model "stepped" single crystals explain the high activities of the "concave" nanoparticles towards the oxygen reduction reaction (ORR).



Figure 1: Joint theoretical and experimental identification of the nature of active catalytic sites helps in rational design of improved nanostructured electrocatalysts [1]. For instance, the most active towards the oxygen reduction reaction sites of Pt materials are located at the "concave" sites [2]. Adapted from [2].

#### Acknowledgements

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## Recent Advances and Remaining Challenges for Automotive PEM Fuel Cell Membrane Electrode Assemblies and Components

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Keywords: membrane electrode assembly, catalyst development, performance, robustness, cost

PEM fuel cell systems employed as the primary power source for automotive applications provide the most challenging demands for the membrane electrode assembly (MEA) and its constituent components. Targets for performance, lifetime and cost for widespread adoption of the technology are well-established [1-2]. MEA power density performance is crucial but current targets of 1.0 Wcm<sup>-2</sup> are now being attained at cell and stack demonstration level through a combination of advanced components, such as the use of very thin (<20  $\mu$ m) reinforced and highly conducting low equivalent weight (<800EW) perfluorosulphonic acid membranes, and elevated pressure operation. OEMs are now pushing to extend peak power density out towards 1.5 Wcm<sup>-2</sup> at >0.6 V. At the same time costs need to be reduced, and in particular platinum loadings per cell need to be reduced from current practical levels of around 0.4 – 0.5 mgcm<sup>-2</sup> down to around 0.15 - 0.2 mgcm<sup>-2</sup>, to meet the target of around 10g Pt for a PEMFC-powered vehicle. Improved cathode (oxygen reduction) catalysts are required that are some four-times more active on a mass basis (>0.44 Amg<sup>-1</sup>Pt) than conventional carbon black supported nano-particulate platinum catalysts [3] to meet these targets.

Several catalyst design approaches have recently been reported to have kinetic mass activities in the range of  $0.5 - 1.0 \text{ Amg}^{-1}\text{Pt}$  - significantly higher than the established target. However, these catalysts have typically either been synthesized as model materials in tiny quantities and evaluated in the RDE, or at best prepared in a more practical form as a dispersed supported catalyst in very low quantities and evaluated in low area single cells. As yet none of these exciting new materials have found their way into practical MEAs. It is now of the utmost importance to move forward from a materials invention activity to exploiting these new catalysts in the real-world practical environment. Project INSPIRE, initiated in 2016 and funded by the FCH JU, has the challenging objective of taking several world-leading catalyst design developments, many funded by earlier FCH JU projects, and determining how best to incorporate these into catalyst layer structures that can deliver on their potential by operating at high current densities with minimal mass transport losses, and additionally scaling the best materials to sufficient quantities to provide material for MEA manufacture for multiple full-size stack demonstrations. Progress in INSPIRE on the further development of proven high activity materials, including nano-particulate Pt/alloy catalysts, de-alloyed Pt/Ni catalysts and extended thin film Pt and Pt/Ni core-shell catalysts, will be presented.

To meet the stack lifetime requirements of 6,000 hours operation with <10% peak power degradation over an operationally-relevant drive cycle, the MEA has to be robust to real-life situations, in particular to cell reversal, extensive start up/shut down cycles, operation over a wide range of temperature and relative humidity, rapid freeze-start and trace levels of carbon monoxide in the hydrogen fuel. Recent progress in MEA design to address these issues, through the use of more corrosion resistant catalyst supports, the incorporation of oxygen evolution reaction catalysts into the catalyst layers and improved catalyst layer and GDL design, will also be presented.

#### Acknowledgements

The work on new catalyst developments has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under Grant Agreement No. 700127 INSPIRE. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation Programme.

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## **Recent Advances in H2 storage components**

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Keywords: hydrogen storage, compressed, gaseous, hydrides, cryogenic, composite, pressure, vessel

This presentation will first provide a snapshot of the on-going activities in the field including some research or demonstration programs, technological achievements, hot R&D topics along with some of the remaining limitations or bottlenecks. Examples from past and/or current projects like H2E (FR-Bpi), COPERNIC (FCH-JU) and HYPACTOR (FCH-JU) will be highlighted.

Then specific perspectives will be presented and discussed to tackle the most expected issues.



Figure 1: CEA (Monts, F-37260) Robot assisted filament winding unit.

#### Acknowledgements

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- 3. HYPACTOR, F. Nony et al., COPV resistance to mechanical impact FCH JU 2014-2017, WHEC 2016



## Copernic: On Tank Valve with integrated pressure regulator

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## AutoStack-CORE: Second Generation PEM-Fuel Cell Stack for Automotive Applications

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Keywords: automotive PEM fuel cell stack, performance, cost

Car manufacturers such as Toyota, Honda and Hyundai have started market introduction of fuel cell vehicles in regions with existing hydrogen refueling infrastructure. Other OEMs such as Daimler have announced launch plans in 2017 or will follow in a not too distant future. Europe has a strong position in fuel cell component development and manufacturing, as well as in system integration yet competence in automotive stack technology needs to be strengthened.

AutoStack-CORE is a European project started in 2013 joining forces of automotive OEMs, the component supply industry and research organizations with the objective to develop best of its class automotive stack technology using industrially manufactured components while meeting the cost constraints for market introduction.

In this project, two stack generations were developed and tested. A power density of ~  $4kW\cdot I^{-1}$  was reached while meeting cost targets. Performance and endurance was assessed by short stack and full sized stack tests. A benchmark analysis showed that the second stack evolution favorably compares to state of the art stack technology and can be considered best of class concerning power density.



Figure 1: BoL performance evolution of AutoStack-CORE

#### Acknowledgements

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## Metalic Bipolar plate Manufacturing

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Keywords: bipolar plates, forming, cutting, welding

Borit developed the technology to produce metallic bipolar plates, which is next to the MEA, one of the basic components of a fuel cell. Borit offers a one-stop-shop solution by combining co-engineering in a direct interaction with the customer with a cost efficient and high quality manufacturing chain. Metallic bipolar plates are a low cost alternative for the graphite plates, required to achieve the fuel cell cost targets set by fuel cell manufacturers. Typical material thickness for bipolar plates is 0.075 up to 0.25 mm.

Borit starts producing the bipolar plates from a standard coil of metal (mainly stainless steel types).

- Based on the customers drawings, Borit designs dedicated tools for forming, cutting, welding and leak testing of the bipolar plates.
- The metal is fed from the coil into the Borit Hydrogate press <sup>[1]</sup> and positioned under the forming die. The 2 halfs of the bipolar plate are then formed using hydraulic pressure (up to 2000 bar), washed, dried, cut in sheets.
- In a next step, the sheets containing the plate halves are pre-cut.
- The 2 half plates are welded together using a fiber laser source. This is a very critical production step, since the welded bipolar plates must be leak tight.
- The plates are also laser marked with an individual number.
- After welding, the bipolar plates are 100% tested for leaks; 3 channels have to be tested : air, fuel and cooling channel.
- In a next step, the plates are cleaned and coated
- Optionally seals are applied to the bipolar plates before shipment to the customers for stack assembly



Figure 1: Hydrogate press line.

#### Acknowledgements

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## **Ongoing research on fuel cell powertrains**

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Keywords: components, energy management, diagnostic, prognostic, durability

Continuous depletion of the crude oil and gradual increase in the oil price have emphasized the need of a suitable alternative to our century-old oil-based economy. A clean and efficient power supply device based on a renewable energy source has to be available to face this issue. Among the different technological alternatives, fuel cell power generation becomes a more and more interesting and promising solution for both automotive industry and stationary power plants. However, many technological hurdles have still to be overcome before seeing the development of industrial and competitive products in these fields.

Among them and focusing on automotive applications, different issues must be solved regarding development of specific components (e.g. air compressors, high efficient power electronics, ...), new on-line energy management strategies for fuel cell hybridized systems, efficient diagnostic and state-of-health estimation methodologies, able also to operate in real-time and with limited number of additional physical sensors. Moreover, regarding the increase of the durability and of the reliability of those powertrains, prognostic algorithms able to estimate the remaining useful lifetime of the fuel cell system under actual operating conditions are requested. The proposed presentation will provide a state-of-art on these different items.



Fig. 1: Mobypost vehicles – First fleet of FCV in France (FC powertrain integrated @ FCLAB / UTBM)

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## Hydrogen – Green and zero emission fuel for the transport sector

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The future transport solutions will be dominated by zero-emission technology to reduce local environment and global climate impact. Green and zero-emission solutions will increasingly also become the most cost-effective sustainable solution.

The dominating energy source for transportation fuels have been based on fossil fuels the last 100 years. The massive penetration of diesel and gasoline vehicles have significant impact on environment and climate. In addition security of supply is threatened on longer term.

The UN and national strategies lead to complete transition by 2050 to renewables in all sectors. In the power sector good progress has been achieved and some countries now get more than 50% of electricity from renewable sources. This has been achived through deployment of massive solar and wind power plants. This trend is now the dominating trend and more than 50% of investments in the power sector is in renewables. The cost have come down and is now able to compete with fossil sources and the penetration will continue. The development leads to significant emission reduction from the sector, but also a significant change in the price structure of the power market.

Spot market prices are lower than in the last 3 decades and the variable production leads to longer periods with overproduction of power. This new source of cheap power can be utilized for green fuel in the transport sector.

Hydrogen is an ideal energy carrier for renewable energy. By coordinating the hydrogen production through water electrolysis with the wind and solar production the power green power is converted and can be used in the transport sector. Energy density of hydrogen is 2-3 times higher than diesel and 100 times higher than batteries.

Storing hydrogen in large quantities can be done in caverns similar to natural gas and offer seasonal storage capacities at very low cost.

Hydrogen production through water electrolysis is a mature technology, which is still advancing through higher current density and improved stack design and materials leading to higher conversion efficiency and lower cost. Also fueling equipment is now being produced in series production with a high level of functional safety. This sector is still in early market, so much advancement is still to come, establishing Hydrogen as a competitive fuel for the transport sector.

I will present the current state within green hydrogen production and fueling technology and come with our recommendations.



## Toyota fuel cell technology

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Keywords: fuel cell stack,

Hydrogen Fuel Cell Vehicles are zero-emissions vehicles that represent a viable solution to energy and climate change issues; hydrogen can be in fact generated by different energy sources. Toyota started the development of fuel cell technologies in 1992; after several model changes and 'limited market' introduction experience, in December 2014 Toyota launched a hydrogen fuel cell vehicle (Mirai) that in addition to a very attractive drivability features a cruising range of more than 500km, a cold-start capability at -30degC and about 3 minutes refuelling time.

The system uses in-house made components such as the fuel cell stack, the fuel cell boost converter and the high-pressure hydrogen tanks.

With a maximum power of 114 kW the Toyota fuel cell stack achieves a volumetric power density of 3.1 kW/L thanks to the design and manufacturing of a unique separator consisting of 3D fine mesh flow channels and an internal water circulation system that eliminate the use of any external humidifiers.

A new more compact, high-efficiency, high-capacity converter has been developed to boost the generated power to 650 volts, thereby downsizing the fuel cell stack and reducing the system costs.

High pressure Hydrogen vessels with a three-layer structure made of carbon fibre-reinforced plastic are used to store hydrogen at 70 MPa at a world-leading 5.7 wt% hydrogen storage capacity (mass of stored hydrogen / mass of empty tank).

Toyota is now looking at the future planning to increase the production of the fuel cell vehicle in line with the high vehicle demand and solve the next technology challenges to be able to enter a mass scale production market at the advancement of a widespread hydrogen infrastructure.

## Fuel Cell cars, the market issues

Jst \_ Ard

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Keywords: Market development, H2 clusters, car fleets, economies of scales, car TCO, European Programs

Our lecture aims at presenting the market drivers and prerequisites to a successful Fuel Cell Electric Vehicle market development.

We can observe a recent acceleration of electric vehicles penetration in the market. This not only due to the consequences of the so-called "dieselgate", or to the rise of the consumer awareness for "green" solutions. Policy makers are now taking actions, and car OEMs are rolling out new models and more competitive solutions. Currently, this trend mainly benefit to BEVs, not much to FCEV yet. As a matter of fact, the battery world which has accumulated enormous amount of research and industrial investments for decades, is now coming to maturity, entering mass production cycle.

Despite a long history, the Fuel Cell world is just starting to seriously invest, comparatively, and is still far from mass production to reach economies of scales. However, there is practical and viable path for this electric vehicle solution, which is partly competing with BEV, but seem to have a much broader range of transportation applications, covering bikes, cars, utilities, trucks, special engines, buses, ships, trains and even aeronautics. Furthermore, hydrogen energy is not only a convenient electric storage solution for mobility, it can also bring great services to the global energy system, enabling and accelerating the energy transition towards a more distributed, more efficient, more flexible and more sustainable electric grid.

This lecture identifies the challenges, the drivers, and the key milestones to reach for making FCEV a successful and viable solution. In particular it addresses the critical importance for hydrogen cars to reach an acceptable TCO (total cost of ownership) that is close to diesel ICE, as well as securing the ROI (Return On Investment) for the refueling infrastructure in order to motivate both private and public entities to invest, and get a better leverage on financial resources. Initially, the role of the national and European funding programs remains absolutely key to deploy successful demonstrators proving the case for this solution.

The lecture will also explain what strategy the French ecosystem has been developing to tackle the issues and make a successful market kick-off for FCEV mobility. In essence, the strategy relies on the initial role of vehicle fleets to trigger further infrastructure investments and development, and the need to solve the "chicken and egg" dilemma through comprehensive, self-contained and profitable local hydrogen ecosystems.

Simultaneously, energy providers and utilities have started to understand the key role that hydrogen could play in the energy system since electrolysers producing green hydrogen will contribute to provide flexibility to the electric network, adapt to local power needs, improves the ROI of intermittent renewable electricity production infrastructure thanks to storable hydrogen; and finally, offer more possibilities to get a better value for renewable electricity outside the electricity grid, notably through mobility. These two converging developments could drive the successful deployment of FEVs.



Kangoo ZE H2 from Symbio



## Hydrogen Strategy Basis for the Oslo Region

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Keywords: fleet, hydrogen, battery, zero-emission vehicle, Norway

While the main focus of fuel cell technology has historically been the car market, many other applications of fuel cells are being developed or deployed, both automotive and stationary. The case of Akershus County (the region surrounding Oslo) in Norway is special in several regards:

- It has a large density of battery cars, by far the largest in the world;
- No natural gas network is present;
- Electric power prices are reliably low;
- Legislation grants privileges (no tax, free parking, use of bus lanes) to electric cars, both battery and hydrogen.

At the time of writing, the county of Akershus and Oslo are the site of all Norwegian hydrogen refuelling stations, and authorities have been consistently positive towards hydrogen for a long time.

The sales of battery vehicles in Norway took off with the arrival of mass-produced battery cars from major producers, such as Mitsubishi, Tesla, Nissan, BMW and more. Most owners charge their cars at home, and a country-wide network of fast chargers has been deployed and is being extended.

Therefore, this market for zero-emission vehicles is very competitive for hydrogen cars, and the presence of only a handful of hydrogen refuelling stations (all concentrated around Oslo) is a major handicap. Most consumers will not consider buying a hydrogen vehicle before a country-wide refuelling network is in place, which is difficult in Norway due to the large area to cover compared to e.g. Denmark, which has a similar population and a complete hydrogen network.

To bypass the well-known chicken-and-egg problem, we propose focusing the promotion of hydrogen mobility on *fleets*. Fleet owners can make an economic case for owning a dedicated refuelling station for their vehicles, providing therefore "chicken and egg" at the same time. With some form for financial support from the government, the fleet owners can make their station available to the public, thereby adding a station to the public network at a minimal cost for the public. The continued usage of the station by fleet owners would guarantee continued maintenance, and would assure consumers that the station will not be closed after a short time, as demonstration projects often are.

Some fleets can be deployed with current technology and available infrastructure: for Akershus county, we identified the possibility of hydrogen taxis in and around Oslo, forklifts in logistic companies, and material handling vehicles at Oslo Airport Gardermoen.

Deploying hydrogen buses in Oslo has already started years ago with the CHIC project, but experiences are mixed due to the low availability that was experienced.

In a longer perspective, the Akershus region can support the development of hydrogen-fuelled industrial vehicles (trucks, dumpers, etc.) and maritime applications, such as ferries and ships: each of these applications could result in one or more hydrogen stations made available to the public.

The market for private hydrogen vehicles will not start growing significantly until a large, country-wide network of refuelling stations will be established, and is likely going to be one of the last markets for hydrogen technology to achieve full market penetration.

#### Acknowledgements

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## New methods and new catalysts for the ORR: Surface science applied to CoO<sub>x</sub>/Pd(100) ultrathin films.

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Keywords: CoO<sub>x</sub>, Pd@CoO<sub>x</sub>, electron tunneling, oxygen reduction, methanol, catalytic species

A great deal of efforts is currently taken for the development of innovative electroactive materials. A little travelled road to reach the target envisages the used of ultrathin metal oxide thin films supported on metal substrate. As a matter of fact, these hybrid systems exhibit unprecedented structural and chemical properties and a wide gamut of special phenomena such as interfacial electronic hybridization and easy electron tunneling that can be exploited for a rational design of highly active catalysts. However, the subtle physics and chemistry ruling these systems require a sophisticated methodological approach for their study. With this aim, a rather unique home-lab set-up (see Fig.1), which allows combining X-ray photoelectron spectroscopy (XPS) and electrochemical measurements, has been used. We have prepared highly controlled CoO<sub>x</sub>/Pd(100) model systems in UHV conditions, with atomic scale precision in order to study the activity of different prototypical cobalt oxide nanometric films (CoO and Co<sub>3</sub>O<sub>4</sub> from nm to bulk dimension) and the influence of the Pd substrate on their chemical properties. Composition/structure/activity relationships have been established through a systematic study of their electrochemical behavior and the chemical/structural changes induced under working conditions. The combination of cobalt oxide with palladium allowed to obtain a very active material, with an activity comparable to pure palladium, but maintaining a higher poisoning tolerance due to the presence of the oxide. Moreover, thanks to the exploitation of an in situ technique we were able to identify the real active phase involved in ORR conditions. Such study demonstrates how the use of ultrathin hybrid films and in situ techniques can pave the way toward the development and comprehension of radically new electrode materials.



Figure 1: Experimental set-up for the in situ combined XPS and electrochemical measurements (left); LSV in  $O_2$ saturated 0.1M KOH and number of transferred electrons for the CoOx/Pd(100) systems studied (middle); and Co  $2p_{1/2}$ region for the CoO and Co<sub>3</sub>O<sub>4</sub> systems at different potentials in  $O_2$ -saturated 0.1M KOH.

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## Innovative Corrosion Resistant Catalysts and Supports For Proton-Exchange Membrane Fuel Cell Cathodes

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Keywords: Proton-Exchange Membrane Fuel Cell, Metal Oxides, Hollow Nanoparticles

The ever-increasing energy consumption from developed and developing countries endangers our future supply of energy and releases greenhouse gases in the atmosphere. As a response, more efficient and diversified power generation systems are required, in particular based on renewables. In this context, electrochemical storage and conversion systems such as electrolysers and fuel cells will be major actors. They can store electrical energy into chemical energy via water electrolysis (for example into the H-H bond of the H<sub>2</sub> molecule), and convert back this chemical energy into electrical energy via fuel cells when needed [1]. A major challenge in these systems is however to find highly active and stable materials, to sustainably catalyse the electrochemical reactions [1].

This contribution first shortly presents the degradation mechanisms of proton-exchange membrane fuel cell materials in model and real PEMFC operating conditions. Then, innovative strategies towards more active and more stable electrocatalysts will be emphasized, in particular using alternative supports (graphitic carbon and metal-oxides)[2, 3] and catalysts (hollow Pt-based nanoparticles)[4, 5] investigated at LEPMI.



Figure 1: (a) Scanning electron microscopy image of antimony-doped tin dioxide aerogel and (b) transmission electron microscopy image of hollow PtNi/C nanoparticles used as PEMFC cathode support and catalyst, respectively.

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## **Carbon gel-supported catalysts for PEM fuel cell catalytic layers**

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Keywords: nanostructured carbons, carbon gels, catalysts, platinum, alloys

In an attempt to replace carbon blacks with a catalyst support with tunable (surface) chemical composition and adequate pore texture, which both impact the performance of PEMFC catalytic layers [1], the synthesis of carbon-xerogel (CX) supported Pt [2] and PtCo catalysts has been studied and optimized. Pt catalysts with excellent dispersion (particle size ~3-4 nm, Fig. 1a) and high mass fractions (up to at least 40% wt.) supported on texture-tailored carbon materials (pore size from 20 to 500 nm) were prepared using very simple impregnation-reduction processes in liquid phase. The obtained catalysts display excellent intrinsic catalytic activities and can be used to prepare Membrane-Electrode Assemblies (MEAs) with interesting mass transport properties compared to those elaborated from carbon black supported catalysts.



Figure 1: TEM pictures of (a) a Pt/CX catalyst (40% wt.) prepared by impregnation-reduction process and (b) hollow PtCo/C nanoparticles.

The same type of nanostructured carbon can be used to support hollow PtCo nanoparticles (Fig. 1b). These catalysts were thoroughly characterized using physico-chemical and electrochemical techniques, including accelerated stress tests on rotating disk electrodes. The hollow PtCo/CX catalysts display much better stability than Pt/CX and Pt/carbon black samples. PtCo/CX catalysts were also tested in MEA configuration for at least 50 h of accelerated stress tests, which allowed comparing the overall stability of the samples. Finally, current research goes towards the modification of the carbon surface properties, for instance by nitrogen doping *via* plasma treatments. The goal is to improve the nanoparticle stability and increase the catalyst lifetime.

#### Acknowledgements

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## Use of Carbone Nanotube as catalyst support in PEMFC

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Keywords: Carbone Nanotube, catalyst nanostructuration, core-shell, ageing tets.

The corrosion of the active of the membrane electrode assembly (MEA) is one a factor which impact the durability of the PEMFC. The more commonly used catalysts are based on Platinum nanoparticles supported on Vulcan types carbon (Pt/C). But those catalysts which give high beginning of life performance surfer from both carbon corrosion by releasing  $CO_2$  or CO (which a poison for the catalyst), and Pt corrosion which lead to Pt leaching and finally loss of ECSA.

To address that issue, carbone nanotube (CNT) has been used as catalyst support. In order to obtain a catalyst matching with the PEMFC specifications (high ECSA, high support and catalyst stability, scalability, integration in MEA) both the CNT support and the catalyst preparation have been optimized. Both catalysts have been developed to address either the anode (fig 1) or the cathode side.

The presentation is reporting the *ex situ* and *in situ* characterization of the catalyst (electrochemical, TEM, SEM) as well as tolerance toward degradation test performed in 25 cm<sup>2</sup> single cell (fig 2). An emphasis will be put on the anodic active layer degradation. Indeed the integration of Pt/NTC at the anode side showed a better tolerance toward loss of electrochemical surface area (ECSA) of that electrode and more specifically for bus application.



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## One-step flame synthesis of cathode catalyst nanoparticles supported on stable oxide material – example of Pt on ATO

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Keywords: Cathode catalyst, Pt on ATO, Nanoparticles, Flame spray pyrolysis

In the present work one-step flame spray pyrolysis (FSP) is applied to produce Pt nanoparticles supported on Sb-/Nb-doped tin-based oxide materials. This synthesis procedure and the prepared materials is then evaluated for the potential application for production of and use as cathode catalysts in PEMFCs, offering high electrochemical stability and corrosion resistance for this application as compared to carbon [1-3]. Flame spray pyrolysis (FSP) is an excellent tool for pioneering development of complex nanomaterials for various applications, recently applied by e.g. SINTEF, for the synthesis of electrode materials for electrochemical applications [4]. The method is a reproducible and scalable process already being investigated by commercial powder producers [5]. The catalyst performance is evaluated both ex-situ and in-situ. In addition, PEMFC operation is carried out at different RH of gases, using electrochemical characterizations techniques, e.g. cyclic voltammetry and EIS. Finally, the durability towards start-up and shutdown operation of the Pt/ATO based catalyst coated membranes (CCM) is also investigated. The work shows that the one-step FSP Pt/ATO catalyst is highly active for the ORR. However, they still underperform in comparison to state-of-the-art Pt/C catalysts. Efforts on improving the electrode conductivity and transport properties are also carried out and show that Pt/ATO+C composites electrodes may improve the high current densities performance of the fuel cell compared to Pt/ATO alone. Pt/ATO based CCMs also show improved stability towards high voltage operation compared to conventional Pt/C catalysts.



Figure 1: HAADF STEM image of ~1 nm Pt particles dispersed on ATO support prepared by one-step flame synthesis.

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# PGM free Electrocatalyst based on $\text{Fe-N}_x$ modified Mesoporous Carbon for Oxygen Reduction Reaction

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Keywords: Non PGM, fuel cell, ORR,

The scarcity and high cost of platinum, as well as the low durability of platinum-based catalysts, are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR.<sup>1,2</sup> In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyse the  $O_2$  reduction to  $H_2O$  at overpotentials comparable to that of the most active Pt catalyst.<sup>3</sup>

In this paper, nitrogen doped mesoporous carbons containing small amount of Fe and/or Co (M@N-MC,) were prepared from several types of polysaccharides including agarose. The first step is the formation of a hydrogel embedding an iron or cobalt metalorganic complex. After the freeze-drying of the gel, the material is subjected to a first thermal treatment to obtain a crude product, which is ball milled and further activated at high temperature. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe–N<sub>x</sub> bond at 708.6 eV (Fig. 1a). Beside Fe-N<sub>x</sub> not visible from TEM analysis, iron is present as big core shell NPs with iron oxide core and carbon shell.

The catalytic performances of catalyst ink prepared from M@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M HClO<sub>4</sub> attesting that  $O_2$  is reduced following an almost 4e<sup>-</sup> pathway at very positive potentials (0.6 V vs RHE) (Fig. 1b).



Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals. (b) Example of RRDE measurement on Co@N-MC in 0.1 M HClO<sub>4</sub> at 1600 rpm and v = 5 mV/s.

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## Local *in-operando* measurement of the protonic resistance of PEMFC electrodes and membranes

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**Keywords:** PEMFC, self-humidification, humidity catalyst layer, electrochemical impedance spectroscopy, segmented cell

This work focuses on the development of electrochemical impedance spectroscopy (EIS) methods to measure the protonic resistance of PEMFC active layers. Experimental spectra of a cathode fed with nitrogen  $(H_2/N_2)$  are fitted to a volumetric electrode impedance model [1], [2] to yield the protonic resistance of the electrode and that of the membrane in controlled humidity conditions.

In addition, EIS measurements are performed on a cathode fed with oxygen  $(H_2/O_2)$ , delivering current and producing water. The protonic resistances of the membrane and of the electrode are obtained in several conditions of gas stoichiometry and of current density. The effective humidity within the membrane and within the electrode are estimated using the calibration obtained in controlled humidity conditions.

As an illustration of the validity of the technique, the case of a cell operated with dry oxygen at the cathode is studied. Thus, the monitoring of a MEA self-humidification is achieved with spatial resolution using a segmented cell designed in our lab. It is compared to the cases of fully humidified gases and of partially humidified gases. In all tested conditions, the effective humidity is higher within the cathode than within the membrane. In dry oxygen conditions, most of the cathode is fully hydrated, except for the segments located close to the air inlet.

This work paves the way for a better understanding of water management. It is to the best of our knowledge one of the first attempts to measure the effective humidity within the catalytic layer, and within the membrane *in-operando*.



Figure 1: Profiles of effective humidity within the cathode catalyst layer (a) and within the membrane (b). Measurement performed with a linear segmented fuel cell with 50%RH  $H_2$  and 8%RH  $O_2$ stoichiometries 2/10 respectively T=80°C, P=1.5bar.

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## Unique Behaviour of Shaped Palladium Nanoparticles in Electrochemical Hydrogen Adsorption and Absorption

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Keywords: Palladium, Nanoparticles, Hydrogen, Adsorption, Absorption, Hydrogen Evolution

Palladium (Pd) is an excellent hydrogen (H) host and find application inhydrogen storage systems and anodes in rechargeable nickel–metal hydride [Ni-M(H)] batteries. The charge and discharge kinetics of Ni-M(H) batteries are limited by the slow H diffusion in solids and pulverization of host materials. This kinetic limitation can be overcome through the use of nanoparticles (NPs) that can be quickly charged and discharged, due to their dimensions leading to high surface-to-volume ratio. Pd is capable of both adsorbing and absorbing H, and in the case of bulk materials, the amount of adsorbed H (H<sub>ads</sub>) is tiny as compared to the amount of H<sub>abs</sub>. H adsorption and absorption can be accomplished under gas-phase and electrochemical conditions, but the respective mechanisms are different owing to the nature of the H precursor.

In the present communication, Pd-NPs with controlled size and shape distributions (nano-spheres, nanocubes and nano-octahedrons) are synthesized using a method based on chemicalreduction of  $K_2PdCl_4$  in ultrapure water with polyvinylpyrrolidoneas surfactant and with ascorbic / citric acid as reducing and surface agents.The Pd-H interactionsare examined using electrochemical techniques.The potential range in which H electro-adsorption, electro-absorption, and evolution reaction occur is examined in an acidicmedium using cyclic-voltammetry (CV). The three processes give rise to unique features CV profiles and are observed in distinct potential ranges (Figure 1). This behavior isnot observed for bulk Pd materials and arises due to the nanoscopic nature of the Pd materials.In the case of octahedral Pd-NPs the H loading is as high as  $0.9^1$ .On the basis of thermodynamic analysis of H adsorption and absorption as well as through the application of the surface stressmodel in the analysis of H absorption mechanism, it is proposed that the octahedral Pd-NPs develop a core-shell-skin structure<sup>2</sup>.



Figure 1: CV profile for octahedral Pd-NPs acquired in 0.5Maqueous  $H_2SO_4$ solution at T=296 K and s=1.0 mVs<sup>-1</sup> in the range of -0.05 to 0.40 V. The purple and red transients refer to UPD H (shown in detail in the inset), the green and blue transients refer to H absorption and  $H_{abs}$  desorption, and the black transient refers to HER.

#### Acknowledgements

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# Computational prediction of nano-electrode structures by using highly ordered ionomers for statistical morphology analysis

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Keywords: highly ordered ionomer structure, catalyst utilization, nano morphology, statistical analysis

New concepts of nano-electrode structures for advanced electrochemical energy application are proposed by using highly ordered ionomer structures. Catalyst utilization of the highly ordered ionomer catalyst layers is predicted by statistical morphology analysis [1, 2] and compared with both conventional and VACNT catalyst layers. For the detailed morphological analysis, a series of multi-component distributions at a 95% confidence level are randomly generated to deduce the statistical variations of effective transport paths of ternary catalyst components. In the highly ordered ionomer catalyst layers, all of the ionomers are successfully interconnected and therefore, all ionomers can be utilized as ionic current paths. Numerical results reveal that despite the relatively poor interconnections of the electric and mass transport paths (49.3% and 86.1%, respectively), the statistical average catalyst utilization of highly ordered ionomer catalyst layers is significantly improved when compared to conventional catalyst layers. For the conventional electrodes of 30 vol.% Pt/C, 33 vol.% ionomer, and corresponding porosity of 37%, the average effective catalyst utilization is estimated to be 27.5%. However, for the highly ordered ionomers, the average effective catalyst utilization is predicted to be 34.7%, which is remarkably higher than that of the conventional catalyst layers with the same catalyst composition. It is also found that the ionomer volume fraction of the ordered ionomer catalyst layers can be considered as a catalyst utilization determining factor and a moderate amount of ionomers are necessary to enhance electrochemical performance.



Figure 1: Schematic diagram and three-dimensional morphological structures of VACNT and ordered ionomer catalyst layers

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#### A review of PEM URFCs and hydrogen compressors

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Polymer Electrolyte Membrane (PEM) technology is usually used for fuel cell [1] and water electrolysis [2] applications. The same concept of PEM cell can also be used for other applications such as Unitized Regenerative Fuel Cells (URFCs) or hvdrogen purification/compression cells. A URFC [3] is a reversible electrolyzer-H<sub>2</sub>/O<sub>2</sub> fuel cell system. Such electrochemical device can be alternatively operated in water electrolysis or  $H_2/O_2$  fuel cell modes. Whereas PEM water electrolysis and PEM H<sub>2</sub>/O<sub>2</sub> fuel cell technologies are individually well-established, optimized and efficient technologies, it is still a challenging task to develop efficient URFCs, that can sustain repeated operation cycles with the same level of electrochemical performances than their individual counterparts. The PEM cell can also be used for hydrogen purification (selective electrochemical extraction of hydrogen from various gas mixtures) and for hydrogen electrochemical compression (a DC power source is used for hydrogen compression) [4,5]. Alternatively, the hydrogen purification and compression devices can be merged into a single device that achieves both functions and delivers purified and compressed hydrogen.

The purpose of this communication is to provide a brief review of the state-of-the-art in these fields, including recent developments. The discussion will cover main aspects such as general principles (thermodynamics and kinetics), material science (electrocatalysis, polymer electrolytes), cell design (cell components and cell geometry), electrochemical engineering (cell stacking), electrochemical performance and efficiency, SWOT analysis, and economic aspects.

#### Acknowledgement

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## Reliable optimization of the PEMFC stack efficiency for automotive application

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Keywords: stack efficiency, performance optimization, stack test procedures

The operating conditions essentially determine the performance and the efficiency of a polymer electrolyte membrane fuel cell (PEMFC) stack in an automotive system. Due to space and weight limitations in such systems, an optimization is mandatory to assure high power output and fuel utilization. Typically, the operating conditions are defined in a system by look-up tables and are not adapted over stack lifetime. But the best operating conditions can vary over the lifetime due to the presence of different degradation phenomena, e.g. resulting in changes of the electrode structure, the electrode hydrophobicity, and the catalyst activity. Predefined tables cannot cover this behavior and the use of optimization algorithms is highly favorable to facilitate optimal stack operation during entire lifetime.

In the presented work,  $\eta^*_{\text{stack}}$  is defined to represent the stack efficiency in a system because the commonly used stack electrical- and fuel efficiencies do not consider the operating conditions [1]. This new efficiency covers all power losses based on the applied conditions including theoretical losses for stack feed stream conditioning. An example is given which power losses are relevant and dominant for automotive application. The performance and efficiency determining conditions are characterized by the stack temperature as well as the stoichiometric values, the relative humidity, and the pressures of the reactants. Their effect is non-linear and synergistic. A separate optimization of the parameters is not meaningful. Therefore, a direct-search algorithm, the Nelder-Mead simplex, was used for the simultaneous optimization of all parameters [2]. The algorithm was realized using harmonized test procedures elaborated in the Stack-Test project to assure reliable and reproducible parameter optimization [3]. The optimization process and the used test procedures are explained in detail and presented results demonstrate that the efficiency can be improved in a running PEMFC stack by up to 4 % only by optimizing the operating conditions in an automotive system (Figure 1).



Figure 1: efficiency optimization process for a PEMFC stack operating at 0.75 A/cm<sup>2</sup>.

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## **EU Harmornised Test Protocols for Automotive Applications**

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Keywords: Harmonisation, Testing, Protocols, Automotive

The European Union's transport sector is the second largest energy consumer in Europe being responsible for 33% of the total energy consumption and about 25% of the total European greenhouse gas emissions (GHG) emissions. The European Union is committed to transforming its transport and energy sector as part of a future low carbon economy. It is recognised that Fuel Cell and hydrogen technologies hold great promise for energy and transport applications from the perspective of meeting Europe's energy, environmental and economic goals and are part of the Strategic Energy Technologies (SET) Plan - , which was adopted by the European Union in 2008.

Proton Exchange Fuel Cells due to their high energy density, low operating temperature and high efficiency are considered to be very suitable for vehicle propulsion. In such applications, fuel cells could encounter operating conditions which are severe to the materials involved.

The objective of this paper is to present a set of harmonised operating conditions, testing protocols and procedures for assessing both performance and durability of Polymer Electrolyte or Proton Exchange Membrane Fuel Cells (PEMFCs) in Single Cell configuration for automotive applications to allow fair comparison of test results from various projects and laboratories.

The paper presents a set of reference operating conditions such as temperature, pressure, humidification, gas flow and composition at the fuel and oxidant inlet representative for future automotive applications. A methodology is established to examining the relative influence that the individual operating parameters exert on the MEA performance in single cell configuration.

Fuel cell durability is evaluated through endurance testing by applying a repetitive load profile to the cell and measuring performance degradation in terms of cell voltage decrease as function of operating hours. To assess the cell degradation rate a dynamic load cycle for endurance testing is proposed. The Fuel Cell Dynamic Load Cycle, (FC-DLC) is used in this document and is derived from the New European Driving Cycle (NEDC) modified for fuel cell applications.

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## Hydrogen Mobility Europe (H2ME) – Creating the European Vision for Hydrogen Transportation

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Keywords: FCEVs, Hydrogen Refuelling Stations, Energy Security, Hydrogen, Demonstration, Europe

The European Commission [1] has identified Hydrogen Fuel Cell Electric Vehicles as a key technology needed for Europe to meet its ambitious target of reducing GHG emissions from the transport sector by 60% by 2050 [2]. Hydrogen refuelling technology has progressed significantly since the first demonstration and funding programmes began, but a number of market barriers persist preventing its widespread uptake within European markets [3].

H2ME combines Europe's four leading initiatives on hydrogen mobility (in Germany, France, The Netherlands and the UK [4]), removing market barriers to create a truly European hydrogen network and a united deployment strategy. The project will provide a unique opportunity for these major initiatives to harmonise their strategies for the first time and significantly expand Europe's hydrogen vehicle and station network. H2ME is the largest demonstration project to date, testing different strategies and the latest technology from leading car OEMs of the sector (Daimler, Symbio FCell, Honda, Hyundai and Toyota). H2ME has launched 49 stations and more than 1400 vehicles across 10 countries throughout the five year duration of the project.



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## HYACINTH: HYdrogen ACceptance IN the Transition pHase Public and stakeholder acceptance of Fuel Cell Electric Vehicle (FCEV) in Europe.

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Keywords: hydrogen, FCEV, acceptance, attitude, general public, stakeholders, toolbox.

The overall purpose of HYACINTH is to gain deeper understanding of social acceptance of  $H_2$  technologies across Europe and to develop a communication / management toolbox for ongoing or future activities introducing  $H_2$  into mobility, stationary and power supply systems.

The central methodologies used in HYACINTH to collect the necessary information to understand the acceptance process and develop the management toolbox have been: 1. Analysis of the visibility of hydrogen energy and FCH technologies in society (desktop research and expert interviews). 2. Interviews on awareness of FCH technologies in the general public (qualitative interviews). 3. Interviews on acceptance of hydrogen energy in the general public (qualitative and quantitative interviews). 4. Interviews on hydrogen energy and FCH technology acceptance at selected stakeholders.

The social research on awareness and acceptance of hydrogen energy and FCH technologies have been based upon interviews with up to 7,000 European citizens and up to 455 selected stakeholders. The evaluation of the interviews generates the knowledge on the state of awareness and acceptance as well as on the influencing factors to the acceptance process that are transferred to the applied knowledge of the management toolbox to be developed in HYACINTH. The toolbox can support future projects (stakeholders, regions and organizations) in setting up their projects under consideration of the acceptance processes influenced by their activities. The project started in September 2014 and is expected to finish around mid-2017.

The results of the surveys and interviews will enable the hydrogen community to set up communication measure that supports the acceptance process of FCEV and its deployment. The first results obtained shown that around 45% of respondents have heard a little bit about FCEV and even a 15% reports knowing a few things about fuel cell cars. Once the participants were informed on FCEV (benefits and features), in all the countries surveyed we find that the majority of the population rates the technology as a good option (percentages vary between 44% and 56%), followed by those who rate it as acceptable (between 23% and 37%). The majority of participants in the seven studied populations would be happy to have a hydrogen fuel cell car in the future. More than 60% in the full sample would like to buy a FCEV in the future. Besides, stakeholders' recommendations have been collected during the interviews that would be used for the development of the HYACINTH management toolbox.

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## Oxygen reduction reaction at binary and ternary nanocatalysts based on Pt, Ni,

Cu, Co and Au

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Keywords: Cobalt, Copper, Gold, Platinum, Alloys, oxygen reduction reaction

Improving design and/or reducing noble metal content in electrocatalysts for fuel cellelectrodes while maintaining and/or increasing proton exchange membrane fuel cell (PEMFC)performance in terms of durability and power density are crucial challenges for PEMFC massmarket applications. A possible way consists in combining noble metals (Pt, Pd, Au ...)and non-noble metals for preparing binary and ternary nanocatalysts. The formation of platinum alloys with transition metals such as Ni, Co, Fe, Cr represents a promising way for improving the activity of Pt-based catalysts [1-3].Pt based alloys have indeed often demonstrated higher electrocatalytic activity towards ORR than pure platinum.However, while non-noblemetals are interesting from a cost reduction point of view, their presence may involve lower stability of the catalyst than that of pure platinum due to their dissolution [4.5], which leads to a loss of performances in PEMFC. Au addition was proposed toimprove durability of the nanocatalysts [6-9].On the other hand, the atomic structure andmorphology [10] also play very important roles in the electrocatalytic efficiency for ORR.

In this context, the present study aims at systematically comparing the catalytic activity and the selectivity towards the ORR of binary and ternary catalysts based on Pt, Ni, Co, Cu and Au in order to determine the best atomic ratio for this reaction, in terms of kinetics current density and of number of exchanged electrons per oxygen molecule reduced. For this purpose, monometallic (Pt/C), binary (Pt<sub>x</sub>Ni<sub>10-x</sub>/C, Pt<sub>x</sub>Co<sub>10-x</sub>/C, Pt<sub>x</sub>Cu<sub>10-x</sub>/C) and ternary (Pt<sub>x</sub>Au<sub>y</sub>Ni<sub>z</sub>/C, Pt<sub>x</sub>Au<sub>y</sub>Cu<sub>z</sub>/C, Pt<sub>x</sub>Au<sub>y</sub>Cu<sub>z</sub>/C) nanocatalysts supported on carbon Vulcan XC-72 have been first synthesized by a wet chemical method and comprehensively characterized. The morphologies, compositions and structures of the particles were characterized by physical methods (transmission electron microscopy, X-ray diffraction and atomic absorption), whereas metal loadings on the carbon support was determined by thermogravimetric analysis. Electrochemical active surface areas and surface compositions were estimated by cyclic voltammetry. Electrocatalytic activity, selectivity and durability of catalysts were studied by the rotating discand rotating ring disc electrodes.

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## Boosting Oxygen Reduction Catalysts through Preventing Active Sites Poisoning by Using Hydrophobic Ionic Liquids

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Keywords: oxygen reduction, ionic liquids, hydrophobicity, nonreactive oxygenated species, supported catalysts

Developing low-cost, efficient and durable electrocatalysts for cathodic oxygen reduction reaction (ORR) is a prerequisite for the broad market penetration of low temperature fuel cells. A major barrier is stemming from the poisoning of surface active sites by non-reactive oxygenated species (e.g.,  $OH_{ad}$ ) and the slow ORR kinetics on Pt catalysts. Herein, we disclose a facile approach to accelerating ORR kinetics on Pt through a surface modification using hydrophobic ionic liquid (IL). It is demonstrated that introduction of a common and inexpensive IL as  $[C_4C_1im][NTf_2]$  to the carbon-supported Pt electrocatalyst (Pt/C) can efficiently reduce the overpotential of ORR and bring in a remarkable 3 times enhancement in activity. We discovered that the origin of accelerated ORR kinetics on IL-modified Pt catalysts lay in the higher accessibility of surface Pt sites preserved by the hydrophobic IL, as evidenced by voltammetry, Tafel plot and CO-stripping. (Figure 1).

We found that the ORR performance is highly sensitive to the nature of cations (Figure 1). The molecular variation reveals that the alkyl chain length of the imidazolium shows a pronounced influence on the intrinsic activity, and accessible electrochemically active surface area (EAS). The best performing IL [Bmim][NTf<sub>2</sub>] results in a nearly 3 times higher activity than the pristine Pt/C in terms of both intrinsic and mass activity, which is substantially beyond the US Department of Energy activity target for 2017-2020. Furthermore, the enhanced performance can be stabilized after the repeated potential scanning up to 30000 cycles between 0.4 and 1.1 V in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solution.



Figure 1. a) Tafel plots. The inset shows the activity comparison of the Pt/C before and after IL modification. b) Comparison of Pt activity for ORR. c) Scheme illustrating that the IL would help protect Pt sites from being oxidized by repelling water.

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## New evidences of platinum-yttrium alloyed nanoparticles formation on carbon support and catalytic activity for oxygen reduction reaction

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**Keywords:** Pt catalyst, Pt<sub>x</sub>Y alloy, half cell test, stability test.

In the past years, intensive research activities have been conducted for searching active Pt structures to reach the DOE targets, which led to the development of many different types of alloys, often identified as skinlayer, core-shell, and thin film electrocatalysts. Among many, Nørskov and coworkers identified by a density functional theory (DFT) computational screening a skin-type Pt<sub>x</sub>Y catalyst as a very promising cathode material for the ORR [1]. In this paper  $Pt_x Y$  NPs, where *ca* 41% of the Y atoms are alloyed with the Pt, were synthesized via a solid state method involving the chemical reduction of Pt(acac)<sub>2</sub> and  $Y(NO_3)_3 \cdot 6H_2O$  salt precursors by  $H_2/N_2$  flow at high temperature [2]. Temperature and time exposure to the reducing environment play a pivotal role in obtaining the alloy and a narrow size NPs dispersion. The best performing sample is actually the one containing the maximum amount of alloved Y atoms Pt<sub>x</sub>Y600h5, which gives 2 and 3-fold enhancements in specific and mass activity for the ORR, respectively, when compared to the standard Pt/C Tanaka catalyst with 50% Pt loading. In the adopted experimental condition, the specific activity and the mass activity determined for  $Pt_xY600h5$  are 1.570 mA/cm<sup>2</sup><sub>Pt</sub> and 0.586 A/mg<sub>Pt</sub>, which are very good values for the 2015-2017 DOE Stack Targets (0.860 mA/cm<sup>2</sup><sub>Pt</sub> and 0.44 A/mg<sub>Pt</sub>, respectively). Furthermore, 60% of the initial specific activity measured at E = 0.90 V vs. RHE is retained after an accelerated stress test composed of 10000 potential cycles between 0.60 and 1.05 V vs. RHE. The effect of different carbon (Vulcan XC72, nitrogen doped mesoporous carbon, multiwall carbon nanotubes) support will be also discussed.



Figure 1: a) TEM images of  $Pt_xY@MC$  samples obtained from  $Pt(acac)_2$  and  $Y(NO_3)_3$  at 600 °C for 5 h, b) percentage of metallic Y, Y carbide and Y oxide in  $Pt_xY$  samples prepared at different temperatures and determined from the multicomponent fits of the Y 3d XPS peaks.

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## Distribution of Relaxation Times as a Diagnosis Tool for Polymer Electrolyte Fuel Cells

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**Keywords:** PEFC, EIS, impedance spectroscopy, DRT, electrochemical characterization, polarization processes, diagnosis

Electrochemical impedance spectroscopy (EIS) has proven its applicability for the characterization of electrochemical systems such as fuel cells. In general, physico-chemical processes with different time constants can be distinguished in the EIS spectra. However, the deconvolution of different processes overlapping in the frequency domain and the identification of the underlying physicochemical mechanisms remains challenging. Systematic and comprehensive parameter variations combined with high resolution deconvolution techniques are required to resolve the polarization processes and set up physicochemical meaningful models. The distribution of relaxation times (DRT) [1] has been established as a valuable diagnosis tool giving direct access to the quantities of interest in the measurement data by providing a higher resolution in the frequency domain. The benefits of this approach have been successfully demonstrated for high temperature fuel cells and lithium-ion batteries [2, 3].

For the first time, we will present this approach for PEFCs. Impedance measurements in a wide frequency range (10 mHz to 1 MHz) have been conducted on 1 cm<sup>2</sup> commercial MEAs (Greenerity H500EL2). The impedance data quality was ensured by an improved Kramers-Kronig validity test [4]. The combination of small active electrode areas (1 cm<sup>2</sup>) and high gas flow rates (250 ml/min) eliminates lateral gradients in temperature, gas composition and current density. Hence, we trigger a homogenous operational state over the entire cell area during one measurement, sharpening the peaks in the DRT and increasing the resolvability of individual processes in the impedance spectrum.

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# Understanding ternary PEMFC nanocatalyst atomic arrangement during growth and annealing: a Molecular Dynamics approach.

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**Keywords:** nanocatalyst growth, molecular dynamics simulations, plasma sputtering deposition, PEMFC electrodes

On one hand, Pt based ternary alloys are known to improve the activity and stability of PEMFC's catalysts. [1-2]. On the other hand, magnetron sputtering deposition has already demonstrated its ability for the fabrication of efficient PEMFC electrodes with high Pt utilization rate [3]. In the present study, MD simulations on  $Pt_xM_yN_z$  (M; N, being less noble or common metals) deposition and growth are carried out for studying the preferred morphology and structure (size, geometry, atomic arrangements ...) of such clusters.

As the nanoparticle growth by sputtering methods is atomic by nature, simulations at the molecular level are expected to be relevant for understanding basic mechanisms of this deposition method. Indeed, molecular dynamics (MD) as being able to exactly calculating the trajectory of atomic systems is a suitable method for addressing this topic, especially in the context of plasma sputtering [4, 5]. Very recently, it has been shown that MD simulations allowed confirming and predicting the morphology and structure of Pt nanocatalysts [6,7] as well as for Pt<sub>x</sub>Pd<sub>y</sub>Au<sub>z</sub> [8]. For the latter, a comparison is provided between sputtering and chemical synthesis methods.

Initial conditions of MD simulations are selected for matching experimental chemical and physical methods. Ternary catalyst  $Pt_xPd_yAu_z$ ,  $Pt_xNi_yAu_z$ ,  $Pt_xCu_yAu_z$  and  $Pt_xNi_yCu_z$  supported on porous carbon mimicking gas diffusion layers are studied. Radial distribution functions and X-Ray Diffraction pattern are systematically computed for enabling direct comparison with experiments.

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## Patterned Gas diffusion media for Polymer Electrolyte Membrane Fuel Cells

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**Keywords:** polymer electrolyte fuel cells, hydrophobicity, gas diffusion media, polytetrafluoroethylene, laser modification

Polymer electrolyte membrane fuel cells with their high gravimetric energy density face a water balance problem especially under variable loads, e.g. in automotive operation. The excess product water needs to be removed from the fuel cell while maintaining a humidified membrane.

The gas diffusion layer (GDL), which also provides contact to the electrochemically active components, is responsible for the internal passive water management of the cell. They typically consist of a conductive medium, a carbon based powder in the microporous layer (MPL) or carbon felt/fibres/cloth in the macroporous backing, and a hydrophobicity impregnation agent like polytetrafluoroethylene (PTFE). The ratio determines the overall hydrophobicity and a fine adjustment is crucial for performance and stable operation.

In the presented work, the MPLs were modified with laser irradiation to form a structured, nonuniform hydrophobicity, thus introducing more hydrophilic evasion pathways for water while maintaining more hydrophobic areas to assure sufficient gas transport to the catalyst. The effect of the modification is mostly due to a local removal of PTFE.

Appropriate modifications can result in considerable performance improvement, in particular under high loads, and more homogeneous current density.



Figure 1: SEM image of a laser patterned microporous layer (~ 600x800 µm).

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### Comparison of Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilising Rotating Disk and Floating Electrodes with those from Membrane Electrode Assemblies

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# **Keywords:** Rotating disk electrode, Floating electrode, Membrane electrode assembly, Pt/C and PtNi/C catalysts

Comparison of electrochemical surface area and mass activity results for the oxygen reduction reaction, derived from experiments using the rotating disk electrode technique (RDE) between different laboratories, and between in situ and ex situ measurements is considered beset with pitfalls, and recent studies have attempted to identify sources of error and non-reproducibility<sup>1-4</sup>. That such comparison should be possible is nevertheless extremely important to new fuel cell catalyst development. Therefore, within the framework of project INSPIRE, we have developed a protocol for RDE testing and applied it to a reference Pt/C catalyst and to a developmental PtNi/C catalyst, and compared the results with those obtained using the floating electrode (FE) technique<sup>5</sup>, and with those obtained from complete membrane electrode assembly (MEA) testing within a full single fuel cell, both with regard to initial properties and those after accelerated ageing induced by voltage cycling.

For RDE measurements, a detailed testing protocol was developed to enhance the accuracy and comparability of the method, and was validated by experimental investigations. Comparable results for the activities of the Pt/C catalysts between the different laboratories were achieved. The kinetic activity of the PtNi/C catalyst was higher than that of the Pt/C catalyst, but the scatter of the data was larger in RDE measurements. Based on the results of MEA degradation studies, a modified procedure for accelerated aging in RDE measurements was developed, that was able to induce activity losses in the supported Pt catalyst without being unduly harsh for the Pt alloy catalysts. The floating electrode technique delivered similar kinetic current densities at 0.9 V as measured in the RDE, but did not require a mass transport correction, as the limiting currents were several orders of magnitude larger. In this case also mass activities at much lower potentials more representative of actual fuel cell applications were determined, namely at 0.65 V vs. RHE. Measurements of the same catalysts in small and large size MEAs provided further data. Overall, very good agreement was found for the Pt/C catalyst between data derived from RDE, FE and MEA.

#### Acknowledgements

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# Co-based nanospinels as earth-abundant catalysts for ORR and OER in alkaline medium

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One of the challenges to overcome for the large-scale development of regenerative fuel cells concerns the development of highly stable reversible air electrodes which are able to catalyze efficiently both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Recently, numerous studies were dedicated to the activation of ORR and/or OER in alkaline medium on heteroatom-doped graphene supported transition metal oxides (TMO) [1-4]. Identification of the active sites, understanding of reaction mechanisms, and that of the interaction between oxide nanoparticles and carbon-based substrate in this type of catalyst are of upmost interest in improving catalysts design. The development of such electrode materials, free from precious group metals and capable of decreasing overpotentials in fuel cells and water electrolyzer, requires stable supporting and conducting substrates in order to deposit low metal oxide loadings (ca. 30 wt.%). This challenging approach led us to prepare Co3O4materials on graphene-based composites more stable than the commonly used electrode support (Vulcan carbon). Co3O4 particles synthesized from a solvothermal method were thereby deposited onto reduced graphene oxide (RGO) and N-doped reduced graphene oxide (NRGO) prepared from the Hummers method (Figure 1A). The structural properties and surface composition of the different materials characterized by X-ray induced photoelectron spectroscopy measurements were combined to cyclic voltammetry experiments for revealing the charge transfer from cobalt to nitrogen, which greatly affects the charge acceptance of the surface Co atoms. Changes in electron density on surface Co atoms are responsible for enhancing catalytic performances of the composite catalysts towards the ORR and OER. For the first time, a work focused on the investigation of oxide-carbon heterointerface, allows highlighting the importance of nitrogen doping in the graphene substrate. With only 30 wt. % of metal oxide, the difference between the charge and discharge voltages ( $\Delta E$ ) due to the ORR and OER is 810 mV, as shown in Figure 1B.



Figure 1: A) Facile two-step synthesis of  $Co_3O_4/NRGO$  material B) Polarization curves obtained with  $Co_3O_4/NRGO$ electrode in an  $O_2$ -saturated electrolyte (0.1 mol  $L^{-1}KOH$ ) at 1600 rpm.

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### **Electrodeposition of Pt - Rare Earth Alloys as ORR Catalysts for Fuel Cells**

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There is a strong need for improved catalysts for the cathode side of PEM fuel cells. With pure Pt, overpotentials of several hundred mV arise due to the sluggish kinetics of the oxygen reduction reaction (ORR). The high amount of Pt catalyst therefore required to power hydrogen fuel cell driven electric vehicles leads to costs too high for widespread market introduction. Polycrystalline Platinum - rare-earth metal (RE) alloys, on the other hand, show very promising catalytic properties for ORR, *e.g.* an increase in the kinetic current density by a factor of 3-5 compared to pure Pt [1-3], and a good stability [2]. Also for Pt-RE nanoparticles prepared in a cluster source, an enhanced mass activity was found [4].

Because of the low standard potentials of the RE metals and their high sensitivity to moisture and air it is a challenge to synthesize such nanoparticles with a scalable method, but this is mandatory in order to provide material for MEA fabrication and –later- industrial production. In this study, electrochemical deposition from ionic liquids (ILs) was selected as scalable method. ILs offer a wide electrochemical potential window and in literature successful deposition of selected pure rare-earth metals has been reported [5]. However, there are also reports showing fundamental obstacles for deposition of RE metals from some ionic liquids [6].

In this work, in preparation of alloy deposition, the electrochemical processes in ionic liquid based electrolytes containing Gadolinium salts were studied. Several ionic liquids and Gd precursors were investigated. As the transport properties in ionic liquids are strongly enhanced at elevated temperatures, also the influence of the temperature was researched. Applied methods comprise electrochemical techniques, partially in combination with the electrochemical quartz crystal microbalance (EQCM) technique, and exsitu characterization of deposited layers by electron microscopy / EDS.

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## Design and Optimization of Hollow PtNi Nanostructures for the Oxygen Reduction Reaction

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Keywords: Proton-exchange membrane fuel cell, hollow nanoparticles, nanoscale Kirkendall Effect.

During the United Nations Conference on Climate Change held in Paris in 2015, agreement was reached by 195 states to limit the global average temperature increase to 1.5 °C above pre-industrial level. To achieve this ambitious objective, increasing the efficiency of conventional energy systems and developing renewable energy sources is required. Proton exchange membrane fuel cells (PEMFC) have the potential to power future portable, automotive or stationary devices, however kinetic, stability and cost limitations remain on the cathode side where the oxygen reduction reaction (ORR) takes place.

In this contribution, we report our most recent findings on the synthesis, ORR activity and stability of porous hollow PtNi/C nanoparticles developed at LEPMI. We firstly shed fundamental light on their mechanism of formation, then focus on their electrocatalytic activity for the ORR and their stability in simulated PEMFC operating conditions. The enhancement in mass and specific activity for the ORR is 6-fold and 10-fold on the best porous hollow PtNi/C nanocatalyst (Ni content 15 at. %) relative to standard solid Pt/C nanocrystallites of the same size, respectively. After 5,000 potential cycles between 0.60 and 1.00 V *vs.* RHE at  $T = 80^{\circ}$ C, combined physical, chemical and electrochemical results show that losses in ORR activity are related to weakening of strain and ligand effects associated with the dissolution of Ni atoms. However, the initial catalytic advantage of hollow over solid PtNi/C nanoparticles is maintained during the accelerated stress test. Investigations on various PtNi nanostructures indicate that implementing structural disorder in ORR nanocatalysts is a new direction to look at to improve sustainably the ORR kinetics.



Fig. 1: Specific activity for the ORR determined from steady-state I-E curves in O<sub>2</sub>-saturated 0.1M HClO<sub>4</sub>.

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# Water management in the Gas Diffusion Layer of PEM fuel cells: dynamic breakthrough effects on porous media liquid water saturation

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Keywords: Gas Diffusion Layer, water management, liquid saturation, porous media, dynamic breakthrough

Polymer Electrolyte Membrane (PEM) fuel cells are just beginning to reach the market place. They are being used in backup power applications as well as in the transportation sector. Worldwide, major automotive manufacturers, such as Toyota [1], Nissan, Hyundai and Volkswagen, are developing fuel cell vehicles that will extend the range of battery-only electric vehicle and drastically reduced the refueling time.

However, the widespread adoption of fuel cell technologies has been hindered by high costs and limited durability – to which insufficient water management is a key contributor. PEM fuel cells are fed with hydrogen and oxygen gas from air to produce electricity with water and heat as the only by-products, and porous materials (termed the gas diffusion layers (GDLs)) are used to evenly distribute the reactant gases. A small portion of the water produced by the electrochemical reaction is actually required to humidify the polymer membrane minimizing the ionic resistance. However, in practice, an excess of liquid water tends to accumulate in the GDL and block the pathways that are needed for the reactants to reach the catalytic sites. This excess liquid water can lead to flooding, uneven power generation, and irreversible material damage. With the physical barriers of excess liquid water removed, the power density and affordability of fuel cells for transportation will reach the targets needed for commercial success.

Liquid water flow inside a GDL is intrinsically unsteady. Whatever is the way the water enters the GDL, i.e. under vapor or liquid state, most part of the water travels through the porous media to the gas channel under discontinuous form. Manke et al. [2] observed the dynamic breakthrough of liquid water in an operating fuel cell using X-ray radiography. They noticed that the liquid saturation at a given location fluctuates, not only inside the GDL but also in the channel. The liquid water breakthrough at the channel/GDL interface induces strong transient pressure variations inside the liquid phase. The pressure fluctuation can affect the local liquid saturation and may explain the change in breakthrough location, that is not predicted by classical invasion-percolation methods used to compute the two-phase flow inside the GDL.

In this communication, a droplet growth model in a two-pore network will be presented to clarify the flow interaction between two neighbouring pores. This work is based on a recently published "one-drop" model [3]. The model takes into account both viscous and capillary effects dominating the fluid transport in porous media. Results obtained with this model show that, as the viscous effects get predominant over capillary effects, a change in the preferential location of droplet emission is revealed. The model is validated using experimental visualizations of the droplet formations at the tip of two connected capillaries. Furthermore, a simple capillary network is realized in a microfluidic device. With this basic network, the change in preferential paths for liquid water invasion is confirmed. It clearly highlights the modification of the network saturation as the flow regime is varied from the capillary to the viscous regime.

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# About fuel starvation: characterization of the mechanism of degradation and mitigation strategies

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Keywords: fuel starvation, degradation, mitigation strategies

Fuel starvation occurs when the anode surface is not entirely fed by hydrogen. This situation can be the consequence of local flooding by liquid water or nitrogen [1] and is always encountered during the start-up (shut-down) procedure [2] when hydrogen (air) is flowing in an air (hydrogen) filled anodic compartment. This local lack of hydrogen allows a local increase of the oxygen concentration on the anode due to permeation through the membrane and a substantial increase of the local anodic potential. As a result, the local potential of the opposite cathode can reach values as high as 1.5V depending of cell potential. This phenomenon is thus responsible for carbon oxidation and catalyst dissolution of the cathode electrode.

This presentation is dedicated to the characterization of fuel starvation events using a segmented cell with reference electrodes along the active area [1,2]. An example of operation with a dead-end anode is shown in figure 1. Some mitigation strategies will be suggested.



*Figure 1:* Time evolution of local current density (2.a, fuel cell average current density set to 0.33 A/cm2), local anode (2.b) and cathode (2.c) potentials and CO2 emissions (2.d) at the cathode exhaust between two successive purges. The cell was fed with dry hydrogen (at 1.3 bar) and the anode outlet remained closed as long as the fuel cell voltage was higher than 0.5 V. In Fig. 2(abc) the segments in blue are located near the hydrogen outlet (i.e., close to segment #1) and the red ones near the hydrogen inlet (i.e., close to segment #20).

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### How to design catalytic nanocluster by magnetron-sputter gas-aggregation?

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Keywords: gas-aggregation, gas-condensation, magnetron sputtering, design, catalyst, nanoclusters

Physical processes are able to produce multifunctional nanoparticles (NPs) from individual atoms. Due to the fast kinetics and the non-equilibrium mechanisms occurring in this process, the NPs properties are not controlled anymore by thermodynamic. Unconventional pathways of NPs formation are possible which can lead to complex and sophisticated NPs with various functionalities for different applications, such as magnetic, plasmonic, catalytic, gas-sensing,..

This study is focused on magnetron-sputter gas-aggregation, in which the nanoparticle synthesis is decomposed into four stages, i.e. aggregation, mass-filtration, and deposition. By combining the gas-aggregation source with a conventional magnetron deposition process, we have demonstrated that it is possible to form the core-shell PdPt@Pt catalyst on proton exchange membrane. The atomic composition and the size of the core NPs were measured by Rutherford Backscattering Spectroscopy (RBS) and transmission electron microcopy (TEM). The crystal structure were studied on the SixS line of the Sun synchrotron using grazing incidence X-ray diffraction (GIXD) and central grazing incidence X-ray diffraction (GISAXS). Integrated into a PEMFC, such core-shell NPs allows the reduction of the time necessary to obtain the fuel cell nominal power.

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### Surface structuration of proton exchange membrane for low Pt loaded fuel cell in the frame of the LAVOISIER project

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This study aimed to structure the surface of proton exchange membranes by creating regular and ordered micrometric (sometimes nanometric) patterns associated with Pt nanoclusters synthesized by magnetron sputtering. The membranes were hot pressed against molds previously structured by two laser micromaching [1] (pulsed Ti-sapphire femtosecond laser) or by plasma etching through a patterned polymeric mask, in order to form wavelets, bumps, pillars and cylindrical holes on their surface. Once pressed, the thickness of the Nafion NRE 211 membrane is lightly decreased and is no longer constant over the entire surface. At the top of the bumps, pillars or holes, the thickness increases, while in the valleys, the thickness drops. The figure shows the SEM (scanning electron microscopy) micrographs of the two membranes after pressing. These membranes were associated with thin catalyst layers (25  $g_{Pt}cm^{-2}$ ) performed by plasma sputtering, inserted into fuel cells, tested in operation at different temperatures and H<sub>2</sub>/O<sub>2</sub> pressures and compared to pristine membrane. Whatever the structuration process, the fuel cell with structured membranes are more efficient than fuel cell with pristine coated membrane. Moreover, the achieved power densities seem to be very dependent on the size of the patterns for both architecture. In all case the improvement appears to be (mainly) due to an increase of the exchange current density and of the membrane conductivity, thanks to the specific surface area increase. In addition to the size, the shape of the patterns is also a determining parameter. Indeed, the membrane with the pillars induces a better fuel cell operation. The origin of this result is still discussed. In summary, this study showed that the structuration of the membrane made it possible to increase the low Pt loaded fuel cell performances and that the shape/size of the patterns and the location of the Pt catalyst directly influenced the fuel cell operation.



Figure : SEM micrograph of two membrane surface with pillars (a) and cilindrical holes (b)

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## DFT Studies of the ORR Activity of Carbon Encapsulated Fe<sub>3</sub>C

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Keywords: Oxygen Reduction Reaction, Density Functional Theory

CarbonbasedcatalystscontainingFe-N<sub>4</sub>C<sub>N</sub> active sites have shownactivity for the oxygenreductionreaction (ORR) comparable to platinum in acidelectrolytesatlowcurrentdensities.<sup>[1-3]</sup>Thesecatalysts, however, require highloading to achieve the current densities desired for fuel cell applications. Improvements in volumetricactivity are therefore needed to the reducemass transport limitations of the thick catalyst layer. Furthermore, long-termstability and suppression of H<sub>2</sub>O<sub>2</sub>selectivity need to be addressed. Graphite encapsulated Fe<sub>3</sub>C was recently suggested to be a durable ORR catalyst without nitrogen containing active sites.<sup>[2]</sup>

Here, we use atomic-scaledensity functional theory to investigate the pathway for  $O_2$  reduction to  $H_2O_2$  and  $H_2O$ on extended model surfaces of a Fe<sub>3</sub>C-graphite catalyst in order to elucidate effects of catalyst doping, strain, thickness and quality of the encapsulating graphitic layers.

We find  $Fe_3C$  significantly increase the activity of graphite zigzag edges, whereas the activity of nitrogen free graphite basal planes is comparatively unaffected by the presence of  $Fe_3C$ .

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### Molybdenum disulfide as new catalyst for electrolysers

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There is a growing interest in alternative catalysts as a cost efficient alternative to noble metals for heterogeneous catalysis applications. Particularly for PEM fuel cells and electrolysers for hydrogen production the catalyst costs are a decisive factor for a broader use. Recently, inorganic materials, like  $MoS_2$  and mixed Fe-oxides, came into focus again. While most bulk minerals are rather inert, strongly increased reactivity is found for nanopowders or nanostructured materials. This effect arises from a complex interplay of structural, electronic and dynamical effects of material and support, and is not fully understood, yet.

Using a combination analytical techniques directly or indirectly sensitive to hydrogen (neutron spin-echo (NSE), neutron diffraction (ND), low energy electron diffraction (LEED), nuclear reaction analysis (NRA), X-ray photoelectron spectroscopy (XPS)) the reactivities of two types of samples, natural crystals (SPI) and commercially available nanopower (Sigma-Aldrich), towards hydrogen have been investigated.

Diffraction experiments with neutrons and electrons reveal that both types of samples (single crystal and nanopowder) are well defined and show activity also in crystalline form, which allows drawing fundamental mechanistical conclusions. There is a striking similarity of the single crystal and nanopowder signals, both showing a diffraction peak around  $Q = 1 \text{ Å}^{-1}$  and, in addition, the nanopowder showing stronger small angle scattering.

By nuclear reaction analysis (NRA) using the reaction  ${}^{1}H({}^{15}N,\alpha\gamma){}^{12}C$  on single crystals we could show that a considerable percentage of hydrogen is absorbed into the bulk. The time dependence of the NRA curves reveals diffusion of surface hydrogen into the bulk. The powder is considerably more reactive towards H<sub>2</sub>, as can be concluded from neutron spin-echo spectroscopy evidencing fast conversion of ortho- to para-H<sub>2</sub> (several minutes) at low temperatures and reinstating hydrogen uptake above room temperature. With the same technique, over the whole accessible temperature range between 20 and 500 K unusually fast incoherent hydrogen motion was found. The observed dynamical processes also show a strong dependence on crystal direction.

On single crystals, which have been loaded with hydrogen electrochemically and heated afterwards, a cycle of surface reduction and oxidation is observed by photoelectron spectroscopy. This temperature dependence, however, is not reflected in the diffusional or vibrational dynamics.

#### Acknowledgements

J. Küchle acknowledges support by the ILL student internship program. Photoelectron spectroscopy has been carried out at the Helmholtz Center Berlin (HZB) synchrotron facility, Germany.



# Recent development on gadolinia doped ceria barrier layer to reduce the degradation rate on high temperature electrolysis systems

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Keywords: High temperature electrolysis, Cell manufacturing, Gadolinia doped ceria, Magnetron sputtering

Hydrogen is an abundant resource on earth available in water, hydrocarbons and biomass. Thanks to fuel cell, hydrogen can be used to produce electricity and heat for stationary or mobile applications. Hydrogen can also be directly used as combustible (i.e. in space shuttle main engine). Among the lifecycle of hydrogen (production, transport, storage, use), one of the main step concerns the production of pure hydrogen.

Hydrogen can be produced by steam reforming from fossil energy, electrolysis thanks to electricity and gasification from biomass. Among those technologies, direct production from biomass is still under development. Even if a lower cost can be obtained, production through reforming generates carbon dioxide. Electrolysis system is a more environmentally friendly solution (especially when electricity is produced via renewable or nuclear energy). Systems operating at higher temperature (about 800°C), presenting the more interesting energetic ratio are developed. However the lifetime of electrolysis cells and more generally the systems durability must be improved. To reach this goal, deleterious interfacial reactions between YSZ (yttria stabilized zirconia) electrolyte and LSCF (doped-lanthanum cobaltite) electrode must be avoided.

In this work, a focus is made on the deposition of GDC (gadolinia doped ceria) barrier layer to limit the degradation rate due to interfacial reactions between electrolyte and electrodes. Recent development for thin GDC layer (below 500 nm) manufactured by magnetron sputtering will be presented. The thin oxide layers were characterized and the cells performances were measured in HTE (high temperature electrolysis) and SOFC (solid oxide fuel cell) modes. To evaluate the influence of the GDC layer characteristics, the performances were compared with a similar cell manufactured with a 2  $\mu$ m thick GDC barrier layer manufactured by screen printing.



## **Rejuvenation of Fuel Cells**

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Keywords: fuel cells, degradation, rejuvenation, stationary, automotive

During the execution of baseline tests on two  $\mu$ CHP units in the Sapphire project, malfunctions in the logging system caused a series of unscheduled shutdowns due to the crash of the computers controlling the systems; the  $\mu$ CHP systems experienced repeated emergency stops, after each of which laboratory personnel restarted them after some hours.

After over 3000 hours of testing, data logs indicated that stack voltages, while erratic, experienced a long-term recovery correlated with the frequency of emergency stops. Data analysis with techniques developed within Sapphire indicates that this recovery was due to an increase in catalytic activity, most likely on the cathodic side [1]. A second 3000-hour test campaign on both systems confirmed the ability of emergency stops to rejuvenate the fuel cells.

The results were surprising, since start/stops are usually associated to severe voltage degradation [2], but the data indicates that appropriately executed shutdowns can be beneficial for cell performance. The exact mechanism of the rejuvenation process is not identified yet, but the two  $\mu$ CHP systems investigated in Sapphire showed respectively record-low degradation rates (-0.2  $\mu$ V/h) and sustained rejuvenation rates (4  $\mu$ V/h) over 3000 hours, as shown in Figure 1.

The potential of cell rejuvenation for the automotive sector will be investigated in project Giantleap, which focuses on fuel-cell buses with a high degree of hybridisation with batteries. This high hybridisation gives a significant freedom to the control system to implement rejuvenation cycles on the fuel cells. A major concern is whether the rejuvenation cycles can be implemented in an automotive setting, and whether they could promote other secondary degradation mechanisms, e.g. membrane degradation.



Figure 1 Stack voltage of two  $\mu$ CHP systems subject to repeated shutdowns over two 3000-hour test runs. The first run showed a degradation rate of -0.2  $\mu$ V/h (system 2, orange) and a rejuvenation rate of 4  $\mu$ V/h (system 1, blue). The second run confirmed the phenomenon with periods of repeated shutdowns and periods of steady operation.

#### Acknowledgements

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## Volume manufacturing of PEMFC stacks for transportation and in-line quality assurance – project VOLUMETRIQ

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**Keywords:** Membrane scale-up, Cell and stack component manufacture, European automotive stack manufacture, Quality assurance

VOLUMETRIQ, funded under the topic "Cell and stack components, stack and system manufacturing technologies and quality assurance" of the 2014 annual working plan, has the ambitious objectives of simultaneously achieving the scale-up of a novel reinforced membrane, based on an electrospun polymer nanofibre reinforcement, first developed in MAESTRO, with at-scale downstream manufacture of catalystcoated membranes, alongside the volume production of bipolar plates and the manufacture of automotive stacks reaching 2020 cost and power targets. It thus has every potential to provide a European automotive stack platform integrating European cell and stack components. In the first 12 months (of the 42 month duration), reference membrane electrode assemblies have demonstrated a beginning of life current density of 2.0 A/cm<sup>2</sup> at 0.6 V in single cell testing, while first improved MEAs incorporating project reinforced membranes have given 1.29 W/cm<sup>2</sup>, which represents an encouraging improvement in power density over the reference, and shows real promise of reaching the final target of  $1.5 \text{ W/cm}^2$  at 0.6 V. At materials development level, good progress has been made in low equivalent weight ionomer development both for the membrane and the catalyst layer, and the design of the membrane reinforcement has been fixed. At the manufacturing level, advances have been made in the upscale of the novel membrane reinforcement and a continuous membrane casting line has been used to produce VOLUMETRIQ membranes at scale. Bipolar plate design optimisation for the high power stack demand has begun, and tooling is being prepared for volume manufacture of the plates and for the fully automated line for production of the ElringKlinger liquidcooled automotive NM5 stack, having a final stack power density of >3.5 kW/L. Fuel cell stack requirements, and corresponding test protocols for use in generating membrane, MEA and stack performance data have been agreed and validated. This poster will describe the current status of VOLUMETRIQ cell and stack components and of the VOLUMETRIQ stack.



Figure 1: MEA using a membrane with electrospun reinforcement demonstrates higher performance than the project reference MEA using a membrane with conventional reinforcement

#### Acknowledgements

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## Advanced Metrology Developments applied to Proton Exchange Membrane Fuel Cell

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Keywords: Metrology, electrode temperature, ENA, Power spectral analysis, Diagnosis, PEMFC

In the background of the energy demand, primarily based on hydrocarbons, that irreparably increases; hydrogen, if it produced in a safe and renewable way, appears as a viable energy source for the future. Combined with the proton exchange membrane fuel cell (PEMFC), it can provide electricity and heat energy without local greenhouse gas emissions. Although PEM fuel cells are currently being marketed, many scientific and technological aspects should be clarified and optimized to achieve a sustainable development. The two biggest barriers are durability and cost.

To improve the cost and durability as well as the performance of a multiphysic system such as PEMFC, we have developed experimental metrology and methodology to understand mechanism within the fuel cell system. We combined fluid, thermal and electric metrology within the assembly of a PEMFC to provide rich descriptors of the physical transfers to diagnose, monitoring and improve the fuel cell operation. Tests have been performed with an adequate use of a fluidic (water balance) and thermal (platinum microwires inserted at the electrode) metrology. These simultaneous measurements have revealed the influence of temperature gradients on the water transport within the stack [1].





Figure 1: Water transport by thermal gradient in a fuel cell

Figure 2: ENA of fuel cell for different humidities

Electrical metrology development based on high speed voltage fluctuations measurements (electrochemical noise analysis - ENA) have been developed to provide accurate descriptors for the diagnosis and prognosis of a PEMFC single cell and stack. ENA was applied to study the aging of an 8 cells hydrogen PEMFC stack in an automotive application.

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### **Evaluation of tri-metalic catalysts in metallic bipolar plate stack**

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Keywords: tri-metallic catalysts, automatic manufacturing, PEMFC stack.

The cost of fuel cell system and particularly of stack remains an important issue before their massive deployment in automotive applications. To decrease cost, two key drivers must be optimized. On the one hand, it will be necessary to increase the stack power density in order to decrease the number of components to reach the targeted power. On the other hand, it will be mandatory to decrease the overall cost of catalyst by decreasing the platinum loading (in g/kW).

In the frame of SMART-CAT project, tri-metallic catalysts have been developed based on gold, platinum and nickel alloys showing interesting electro-catalytic activities regarding oxygen reaction reduction. According to initial results obtained using rotating disc electrode and 25 cm<sup>2</sup> single cells, it was decided in the project to manufacture 220 cm<sup>2</sup> MEA to be tested in a stack based on metallic bipolar plate technology. First, catalyst layers were manufactured using classical screen printing techniques. Catalyst prepared by IC2MP was used to prepared ink at CEA facilities. The ink was then used to prepare Gas Diffusion Electrode (GDE). Secondly, PVD technique was used to prepare GDE with low platinum loadings. GDE were used to manufacture high surface MEA (220 cm<sup>2</sup>) using an automatic device located at CEA.

Both stacks were characterized using electrochemical techniques (polarization curves, impedance spectroscopy, cyclic voltammetry,...).Performances and robustness obtained in representative conditions of automotive applications using a new catalyst prepared by classical route or by PVD) were compared to performances obtained with classical MEA manufactured with pure platinum.



Figure 1: Polarization curves obtained with 10 cells stacks containing SMART-CAT MEA in automotive European conditions.

#### Acknowledgements

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## Toward a New PEMFC Stack Design for Controlled Water Management

Jorksk

March, 1<sup>st</sup> - 3<sup>rd</sup> 2017.

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Water management remains one of the most important issues for optimal performances and lifetime of PEMFC. In this context, an experimental approach was developed in order to study the influence of the temperature field on water transport in a single cell. The experiments consisted in creating various thermal configurations by imposing a temperature difference between the two bipolar plates and in measuring, at the anode and at the cathode, the average temperature of the electrodes and water fluxes by means of water balance. The results obtained for three thermal configurations put forward a strong influence of the temperature profile on the water transport. On the whole, water fluxes were directed as the heat fluxes which depend on the temperature difference between the MEA and the plates [1]. These results show that water transport in the cell can be managed by a control of the temperature difference between the anode plate and the cathode plate, which is possible for a single cell but not for all the cells in a stack with standard configuration. Therefore a new stack design (prototype presented in figure 1) was proposed in order to make possible a differentiate thermal control of the anode plate and of the cathode plate [2]. Internal water management through thermal control also allows reducing hydrogen starvation when the fuel cell operates in dead end mode at the anode. Indeed, if the temperature at the anode is higher than at the cathode, the water produced by the electrochemical reaction mainly flows through the cathode side: the water content in the hydrogen channel is then reduced and the channel can remain closed during a longer period. As a consequence, hydrogen consumption decreases as well as the occurrence of the conditions giving rise to electrodes materials degradations [3].



Figure 1. New stack design prototype

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### Hybrid Fuel Cell, Photovoltaic Autonomous system

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Keywords: Fuel Cell, Renewable energy, Hybrid Systems.

The SAPAC Project, aims to realize different devices coupling a fuel cell to renewable energy sources (for the time being: photovoltaic) offering a competitive alternative to batteries to power different autonomous systems.

The strength of such a storage system is linked to the hydrogen advantages: high autonomy per unit of mass and volume, seasonal storage...

A prototype has been achieved, it can power 250W with a storage of 2.5kWh. As designed. hydrogen tanks can easily be added to reach 17kWh with a weight of 180kg vs. almost 1000kg for lead batteries.

This "Hydrogen battery" can now replace a lead battery in an autonomous system thanks to its integrated energy management which take into account different factors (light energy available, hydrogen storage level...). This energy management is also monitored throw a web interface which can give all information needed for maintenance: water level, hydrogen level, pressure, autonomy...

#### Acknowledgments

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Figure 1: Flowsheet of the system



# Methodology for optimizing the subsidy policy in hydrogen refueling stations deployment. Application to Spanish case.

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**Keywords:** stackelberg equilibrium, hydrogen refueling station, fuel cell electric vehicles, location model, subsidies policy.

The use of Alternative Fuel Vehicles (AFV) to replace vehicles powered by internal combustion, is an alternative form of road transport that may provide, in the long term, security in energy supply, reduction in greenhouse gas emissions and improvement in air quality in cities [1], [2].

Location models are intended to accelerate market acceptance of AFV, making efficient decisions about infrastructure design. One of the main problems which must be addressed in the roll-out of the necessary infrastructure for the use of alternative fuels in transport is the so-called chicken and egg problem [2]. Infrastructure (supply) leads to demand, but in order for the infrastructure to be economically viable, there must already exist a given level of demand. Figure 1 shows the essential elements of this vicious circle involving supply and demand.



Figure 1: Simplified representation of the elements in the supply, demand and market process of AFV

This problem requires public-private partnerships to overcome the initial stage in the AFV market. A temporary policy of government subsidies can change this situation. This work proposes a Stackelberg equilibrium model for the optimal design of temporary subsidy policies for the deployment of alternative fuel infrastructure. At the upper level, the government provides dynamic incentivization policies for alternative fuel station owners. The behaviour of hydrogen station owners in a competitive environment, the alternative fuel user behaviour (buying of Alternative Fuel Vehicles, making trips and choice of routes) and the availability of alternative fuel are accounted for at the lower level. The model determines the optimum subsidies, which allow a given level of coverage by infrastructure in a certain year. Moreover, the model imposes as a constraint the successful transition of the energy market from the point of view of the infrastructure, i.e the sustainability of the infrastructure without subsidies.

With an annual investment per person between 0.35 and  $1.29 \in$  in the 30 years of the study, it can have hydrogen as an alternative fuel in the graph study. A numerical example with a simplified Spanish road network illustrates the proposed model.

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