Direct ElectroChemical Oxidation Reaction of Ethanol: optimization of the catalyst/support assembly for high temperature operation (DECORE)

FINAL REPORT

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Executive Summary

Recently, an increasing interest in the development of catalyst for Direct Ethanol Fuel Cells (DEFCs) has risen: ethanol (EOH) is an ideal combustible for fuel cells (FCs) due to a high energy density (8 kW/kg), the possibility of being produced from renewable sources and the easy storage and transportation. However, catalysts capable to perform selective and complete oxidation of EOH at the anode side of a DEFC up to carbon dioxide at a high rate are still lacking. In the case of DEFCs, the temperature can play a role in facilitating the C-C breaking, thus enhancing the selectivity toward the complete oxidation. Actually, high temperature PEM-FCs (HT-PEM FC, $T > 90°C$) are considered to be the next generation of PEM-FC technology because they have several advantages over cells operated at low T:
(1) improved reaction kinetics;
(2) higher catalyst tolerance toward contamination;
(3) improved heat rejection capability;
(4) improved water management.
Unfortunately, when PEM-FCs are operated at high temperatures (90-200 °C), catalyst support corrosion is severe, leading to a rapid degradation of the performance. Typically, during long-term HT-PEM-FC operation (> 500 h), the oxidation of the carbon support has clearly been observed, resulting in the separation of catalyst NPs from the carbon support and loss of performance. Therefore, it is necessary to explore alternative materials to replace carbon-based supports in order to improve the durability of PEM-FCs. This point becomes strategic when DEFCs are considered because of the higher operation temperature needed to obtain complete EOH oxidation to carbon dioxide at the anode.
The **DECORE** consortium, composed by seven partners, allied the expertise of five academic, one research agency and one industrial partners from five EU countries (Italy, Germany, Denmark, Spain, Austria) for the development and optimization of innovative catalyst/support assembly for high temperature operation in DEFCs.
Oxycarbidic supports (TiO_xC_y, MO_xC_y, M=Mo,W) were successfully developed as alternative supports for HT-PEM-FCs. In order to reduce the cost of the HT-PEM-FCs, alternative noble metal-free or noble-metal-poor catalysts were also implemented. These materials are based on MO_xC_y carbides (M= Ti, Mo, W) mixed with small amount of noble-metals. The choice of the MC_x was also dictated by the expected good compatibility with the oxycarbidic support.
To tailor the needed materials through a rational design, both the structure and the chemical properties of the support and nano-catalysts were investigated by advanced physico-chemical techniques (e.g. XPS, TEM, SEM, Raman, XRD, AFM, all the electrochemical ones). In addition, innovative tools for determining the electrochemical activity and the degradation mechanisms at *intermediate*-T in half-cells were developed. At the end of the project, a Membrane Electrode Assembly (MEA) was fabricated and tested by the industrial partner and a bench-top single DEFC operating at *intermediate*-T was run in order to develop a conceptual design of an *intermediate*-T DEFC.
The project provided funding for 16 young investigators in the early stage of their career (PhD students and postdocs) who have had the opportunity to visit other partners' labs and obtain valuable scientific and intercultural experiences. This intense exchange is expected to lead cooperation in further collaborative projects in the future.
The project has resulted so far in 20 peer-reviewed publications, 7 PhD/Master theses, 35 presentations in a scientific event, and 10 articles published in the popular press/press releases/WEB pages. A public workshop entitled International Workshop on Ethanol Electro-oxidation has been organized at the end of the project (5-7 December 2016) in Florence (Italy).

Project Context and Objectives

A rapid transition from fossil to more sustainable energy sources is mandatory in the next years. Fuel cells (FCs) represent a promising and flexible technology to convert the chemical energy stored in fuels into electricity with a high efficiency, applicable both in stationary and mobile applications. Hydrogen is often discussed as the energy carrier of choice for use in FCs, and hydrogen based FCs (H-FCs) represent the most efficient and clean FCs, since the exhaust is solely water. However, there are some serious hurdles for the application of H-FCs: hydrogen is not a natural resource and it is normally produced by hydrocarbon steam reforming or by water electrolysis. The latter represents a significant waste of primary energy, only sustainable if electricity from renewable sources is available. Moreover, issues regarding hydrogen storage and distribution need to be solved, especially in the transportation sector. Hence, there is a need for the implementation of alternative energy carriers into FCs. Bioethanol is an attractive alternative energy carrier, especially when it is not produced at the expense of food production, e.g. by fermentation of lignocellulose, which uses crop or wood as precursors. Bioethanol is produced by converting biomass into sugars, which are then fermented to ethanol (EOH). The process of hydrolysis separates most of the water from EOH, leaving an end product that is generally about 95% EOH and 5% water. Such a composition is optimal for the direct use of bioethanol as energy carrier for FCs (to be reminded that in the case that bioethanol is used as a fuel for standard engines, the water has to be removed with the consequent costs). Use of bioethanol results in a neutral carbon footprint, i.e. the carbon dioxide emitted during its use is offset by the absorption from the atmosphere during its growth. It is considered an alternative to petroleum and diesel and its popularity is emerging as a fuel for cars, particularly well established in Brazil. Bioethanol has a number of advantages over conventional fuels. It comes from a renewable and not from a finite resource, such as crops. These crops are specifically grown for energy use and include corn, maize and wheat crops, waste straw, willow and popular trees, sawdust, reed canary grass, cord grasses, Jerusalem artichoke, myscanthus and sorghum plants.

Therefore, development of efficient direct EOH FC (DEFC) FCs exploiting a direct conversion of the chemical energy stored in EOH into electricity would have a tremendous impact on FC technology and commercialization. However, existing catalysts convert EOH into acetic acid and acetaldehyde, a process that releases just a couple of electrons per EOH molecule, hence generates low currents. Breaking down EOH molecules further to produce carbon dioxide would release far more electrons (a total of 12 per molecule) and generate higher currents. For a complete EOH oxidation to carbon dioxide at the anode, the carbon-carbon bond needs to be broken. To address such an issue, appropriate catalysts need to be designed. An alternative route is adopting higher operating temperatures (in the 150- 200°C range, often referenced as *intermediate-T*) to accelerate kinetics.

The main general goal of **DECORE** is to achieve the fundamental knowledge needed for the development of a FC electrode, which can operate efficiently (both in terms of activity and selectivity) as the anode of a DEFC. It is to be reminded that DEFC technology is still lacking in the market. In order to increase the catalyst efficiency, **DECORE** has adopted the strategy of using the temperature range between 150-200 °C (*intermediate*-T). To allow operation in this temperature range, **DECORE** has explored the use of fully innovative supports (based on oxycarbides). The new TiO_xC_y support actually resulted to be more durable than standard carbon supports at the targeted temperature.

Another pivotal point for a widespread FC commercialization relies on reducing (or even avoiding) the noble metal loading in the catalyst without compromising FC performance. State-of-the-art catalysts for both anode- and cathode-side are based on noble metals, especially platinum. Among the components in a PEM-FC, Pt-based electrodes contribute to ca. 55% of the total costs. But even more critical is the fact that the Pt resources are limited and they are confined outside the EU in countries politically not stable. Short supply coupled with an expected increasing demand, is likely to cause prices to rise in the future.

Considering these facts, it is highly strategic to investigate alternative catalyst materials where the precious metal is reduced or completely avoided.

To this end, **DECORE** has explored new nano-catalysts based on group 6 metal carbides (MC_x, M=Mo,W) mixed with small amount of noble-metal. To tailor the needed materials, the active role of the support and nano-catalyst has been studied at atomic level.

DEFC technology is still lacking in the market. The power range for the envisioned application is of the order of hundreds of Watts, i.e. the so called distributed generation, having an impact for devices such as weather stations, medical devices, signal units, auxiliary power units, gas sensors and security cameras.

Project Objectives

The main objectives of **DECORE** were:

-complete electro-oxidation of ethanol (EOR) to carbon dioxide at *intermediate*-T (150-200 °C);

-development of innovative TiO_xC_y and MC_x (M= Mo, W) supports specifically tailored to avoid degradation of the active catalyst and corrosion of the support at *intermediate*-T, and having sufficient electrical conductivity and porosity;

-development of noble-metal-free or noble-metal-poor anode catalysts based on group 6 metal carbides (MC_x, M=Mo,W);

-full characterization of the MC_x/TiO_xC_y assembly;

-development of tools for determining the electrochemical activity at *intermediate*-T in half-cells;

-laboratory-scale validation of the nano-catalyst/support assembly compared to state-of-the-art benchmarks;

-testing the nano-catalyst/support assembly using industrial standards in an existing test rigs of high-T FCs using hydrogen or synthethic reformate as energy carrier at the anode and air at the cathode;

-development and tests of a bench-top single DEFC operating at *intermediate*-T.

Project Results

The original ambitious goals of the project can be summarized as follows:

a) to tailor new nano-materials
    a. which could be used as alternative oxycarbidic supports to be adopted when FCs operating at the *intermediate*-T range (150-200°C) are implemented. These new materials should be more durable than the conventional catalyst support, which typically consist of carbon black (e.g. Vulcan XC-72);
    b. which could be used as noble metal-free catalysts in the form of metal carbides MC_x (M=Mo,W), showing a sufficient catalytic activity towards the Ethanol Oxidation Reaction (EOR) and Hydrogen Oxidation Reaction (HOR) when operated at the anodic side of a FC and run at *intermediate*-T;
b) to test and evaluate the electrochemical properties of the fabricated nano-materials in a half-cell set-up in form of powders;
c) to integrate the new materials in MEAs and to test them under industrial standard-conditions. For these tests, the new materials were introduced at the anode-side of *intermediate*-T MEAs, which were operated at 150°C both with hydrogen/air and with reformate/air.
d) to build a bench-top single DEFC prototype and test it when supplying gaseous ethanol/water to the anode.

With respect to these goals described in the proposal, the original research done in WP2-WP6 has demonstrated that noble metal-free catalysts in the form of MC_x cannot guarantee a sufficient activity towards the EOR. Ethanol adsorbs on the MC_x based materials, which is the first step for the alcohol oxidation reaction, but the half-cell tests up to 70°C demonstrated that these materials are not able to

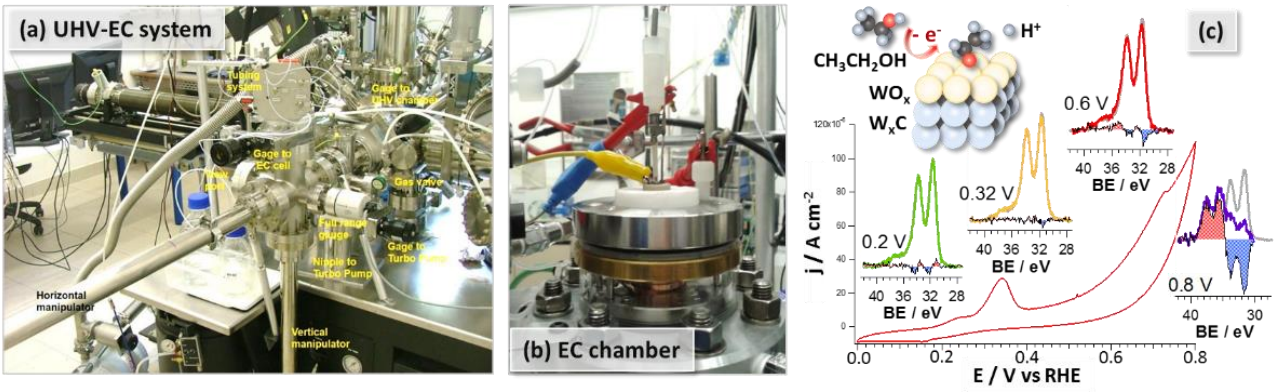
oxidize alcohol at potentials lower than 0.35 V (which was the target of **DECORE**) in this temperature range. For this reason, a contingency plan was undertaken by exploring the incorporation of small amounts of noble metals into the carbides. Several innovative catalysts were prepared and tested. Among them, $PtAuSn/MC_x$ (M=W, Mo) systems were identified as highly promising catalyst materials since the onset for EOR occurs at lower potentials than 0.2 V vs. RHE at 70°C in the half-cell set-up. In addition, Pt_3Sn/TiO_xC_y was found to be a good catalyst for EOR at 70°C. However, the tests at *intermediate*-T made using a gas diffusion electrode (GDE) setup in concentrated 85% phosphoric acid at 150°C did not show the predicted increase in activity due to the increase in temperature. The developed pressurized cell enabled us to demonstrate that this inhibition is also found for the other half-cell reaction, the oxygen reduction reaction, when studied at *intermediate*-T in presence of concentrated phosphoric acid. Therefore, a development of proton exchange membranes suitable for *intermediate*-T which do not contain concentrated phosphoric acid, will be an important step for the exploitation of the new catalysts at intermediate-T DEFCs.
On the other hand, one of the highlights of the project has been the validation of TiO_xC_y as a valid substitute for the standard carbon-based supports. Such a new support has been successfully validated in the reformate oxidation HT-FCs technology, of particular interest for the industrial partner ELCOR. This gives the opportunity for a direct exploitation of the **DECORE** results. In particular, after the *intermediate*-T tests, Pt_3Sn/TiO_xC_y has been identified as possible catalyst for the reformate oxidation in a HT-PEM, with higher efficiency than Pt/TiO_xC_y.

The main achievements of the **DECORE** project in the various scientific work packages are described below.

WP2: Structure/property relationships on TiO_xC_y and MC_x/TiO_xC_y *model* systems

WP2 was focused on the detailed study of the structural, chemical and electrochemical (EC) properties of TiO_xC_y and MC_x/TiO_xC_y *model* systems prepared in UHV and characterized by adopting a surface science based approach.
The team involved in this WP was composed by:

- Prof. G. Granozzi, Professor at UNIPD, in the role of Scientific Supervisor;
- Prof. Stefano Agnoli, Professor at UNIPD, in the role of WP2 leader and Surface Science Supervisor;
- Dr. Christian Durante, Researcher at UNIPD, as Electrochemical Supervisor;
- Dr. Laura Calvillo-Lamana, in the role of active post-doc researcher at UNIPD paid by **DECORE**;
- Prof. Julia Kunze-Liebhäuser, Professor at UIBK, WP4 leader, participating in WP2 in the role of Scientific Supervisor;
- Ms. C. Rüdiger, doctoral student at UIBK, as active researcher for the preparation of the anodic films and participating to surface science measurements.



Experimental set-up for the *in situ* combined XPS and electrochemical measurements (a); *in situ* electrochemical cell (b); and chemical changes induced at different applied potentials on W_xC (c).

The main outcome can be summarized as in the following:
- The study of the carbothermal conversion process of *model* systems (i.e. anodic titania films, deposited catalyst nanoparticles) in UHV proved to be very useful to provide a rational basis to the carbothermal process of the corresponding materials in the form of powders (connection with WP4 and WP5).

- TiO_xC_y is thermally stable up to 550 °C in UHV, which is a much higher temperature than the targeted operational one in *intermediate*-T DEFCs (150 – 200 °C).

- Intrinsic stability of TiO_xC_y and MC_x NPs (M=Mo,W) toward oxidation was determined in UHV, ambient conditions (i.e. in presence of oxygen), as well as under electrochemical conditions (i.e. in aqueous solution). It was clearly demonstrated that, under ambient conditions, it is not possible to have a pure titanium oxycarbide surface, since it tends to oxidize in contact with air leading to the formation of TiO_2 and elemental carbon. Therefore, there will always be a composite system where the outermost surface layers will be formed by TiO_xC_y, TiO_2 and carbon.

- By using the transfer system from UHV to the electrochemical cell (so avoiding the contact with air), it was demonstrated that under electrochemical conditions the surface of the TiO_xC_y film is oxidized leading to the formation of a TiO_2 thin film and a carbon layer on the surface. The TiO_2 film formed is stable and avoids the complete oxidation of the TiO_xC_y film, and its thickness depends on the potential range used for the cycling treatment**.** At the same time, the different stages of the oxidation of the film were determined.

- Studying the deposition of Mo and W at RT in UHV on the TiO_xC_y and TiO_x substrates allowed us to trace the surface reactions occurring among the metals and the substrate. The resulting surfaces are a complex mix of oxides and carbides (i.e. MO_xC_y), which are stable up to 300 °C in UHV. At higher temperatures, volatile oxides (e.g. MoO_3 and WO_3) are formed, which can evaporate in UHV conditions, leading to a significant loss of the metal.

- The procedure to prepare the M_xC/TiO_xC_y (M=Mo,W) assembly in UHV was established. It involves the conversion of the TiO_2 film into TiO_xC_y in $5x10^{-6}$ mbar of C_2H_4 at 550 °C and the subsequent deposition of the M_xC nanoparticles by evaporation of the metal in $5x10^{-6}$ mbar of C_2H_4 at 550 °C. In these conditions, the metal interacts with the carbon and oxygen of the surface of the substrate, forming MO_x and M_xC (or MO_xCy) species, and these species are directly converted into M_xC in the presence of ethylene at high temperature.

- By combining XPS and *in situ* electrochemical measurements, the electrochemical behaviour and the chemical changes caused by the EC work of the M_xC/TiO_xC_y assemblies were studied. For both Mo and W, the main conclusion from this study is that the M_xC film is stable up to 0.6 V vs. RHE due to the formation of a passive film on the surface of the sample. The passive film is a compact thin film that consists mainly of MO_2, $MO(OH)_2$ and M_2O_5. At potentials higher than 0.6 V vs RHE, M_xC starts to dissolve due to the formation of HMO_4^- from MO_3.

- The interaction of TiO_xC_y, Mo_xC and W_xC with different probe molecules was studied by combining TPD and XPS measurements. The results indicate that TiO_xC_y is not active in the decomposition of ethanol in UHV, however, it is an excellent electrocatalyst support since it does not adsorb the CO produced during the oxidation of alcohols that is considered as a poison. On W_xC and Mo_2C, ethanol decomposes under UHV conditions forming acetaldehyde, CO, CH_4 and H_2. Even if the same ethanol decomposition pathways are observed on W_xC and Mo_2C, their performance is very different.

List of published papers:

- L. Calvillo, D. Fittipaldi, C. Rüdiger, S. Agnoli, M. Favaro, C. Valero-Vidal, C. Di Valentin, A. Vittadini, N. Bozzolo, S. Jacomet, L. Gregoratti, J. Kunze-Liebhäuser, G. Pacchioni and G. Granozzi. *Carbothermal transformation of* TiO_2 *into* TiO_xC_y *in UHV: tracking intrinsic chemical stabilities*. **J. Phys. Chem. C 2014, 118, 22601-22610**.

- L. Calvillo, G. García, A. Paduano, O. Guillen-Villafuerte, C. Valero-Vidal, A. Vittadini, M. Bellini, A. Lavacchi, S. Agnoli, A. Martucci, J. Kunze- Liebhäuser, E. Pastor, G. Granozzi. *Electrochemical behaviour of* TiO_xC_y *as catalyst support for direct ethanol fuel cells at intermediate temperature: from planar systems to powders*. ***ACS Appl. Mater. Interfaces*, 2016, *8* (1), pp 716–725.**

- L. Calvillo, C. Valero-Vidal, S. Agnoli, H.Sezen, C. Rüdiger, J. Kunze-Liebhäuser, G. Granozzi. *Combined Photoemission Spectroscopy and Electrochemical Study of a Mixture of (Oxy)carbides as Potential Innovative Supports and Electrocatalysts*. **ACS Appl. Mater. Interfaces, 2016, 8, 19418–19427**.

- C. Rüdiger, M. Favaro, C. Valero-Vidal, L. Calvillo, N. Bozzolo, S. Jacomet, C. Hejny, L. Gregoratti, M. Amati, S. Agnoli, G. Granozzi, J. Kunze-Liebhäuser. *Fabrication of Ti substrate grain dependent C/*TiO_2 *composites through carbothermal treatment of anodic* TiO_2. **Phys. Chem. Chem. Phys., 2016, 18, 9220-9231**.

- C. Rüdiger, M. Favaro, C. Valero-Vidal, L. Calvillo, N. Bozzolo, S. Jacomet, J. Hein, L. Gregoratti, S. Agnoli, G. Granozzi, J. Kunze-Liebhäuse. Substrate grain dependent chemistry of carburized planar anodic TiO2 on polycrystalline Ti, **ACS Omega, 2017**, DOI: 10.1021/acsomega.6b00472

WP3: DFT calculations on TiO_xC_y and MC_x/TiO_xC_y *model* systems

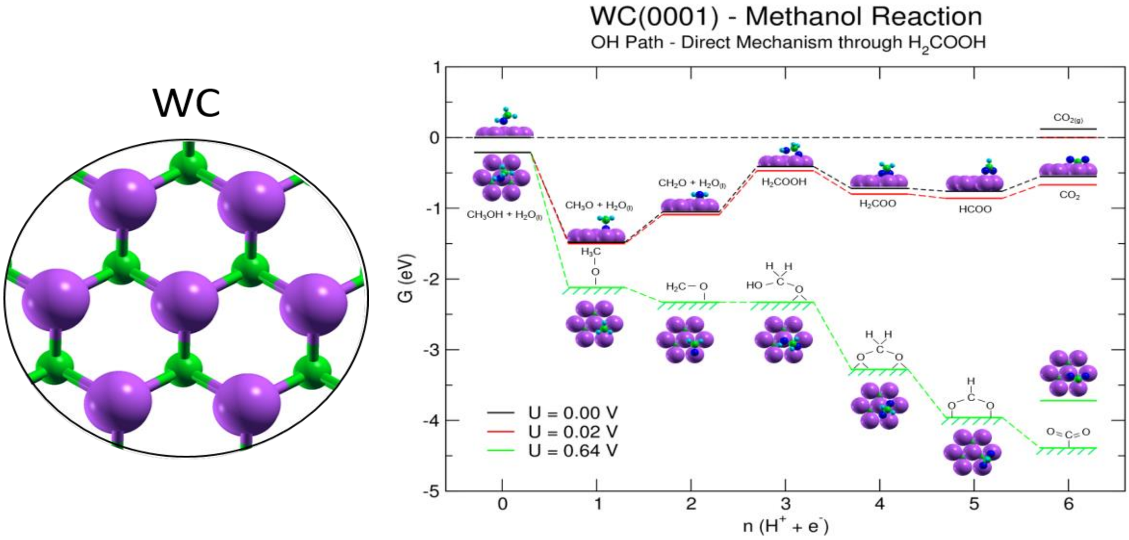
WP3 was the computational WP devoted to the modelling of the systems under study. This activity was performed in direct and constant contact with the WP2. This combination of experimental and computational data led to a rational interpretation of the data, especially as regards the connection between structure and electronic properties.

The following logical steps were involved:

- determine reliable DFT based methods and plausible models to describe TiO_xC_y and WC_x systems;
- determine stable surface models for TiO_xC_y films;
- develop methods to calculate potential/pH Pourbaix-like diagrams for TiO_xC_y systems.

The actual team was composed by:

- Prof. Cristiana Di Valentin, Full Professor of UNIMIB, in the role of WP leader;
- Prof. Gianfranco Pacchioni, Full Professor of UNIMIB, in the role of Scientific Supervisor;
- Prof. G. Granozzi, Professor of UNIPD, in the role of Scientific Supervisor;
- Prof. Maurizio Casarin, Full Professor of UNIPD, in the role of Scientific Supervisor;
- Dr. Andrea Vittadini, CNR Researcher of UNIPD, in the role of Senior Researcher;
- Dr. Diego Fittipaldi, in the role of active researcher paid by **DECORE.**



DFT model of WC(0001) and the study of the path of its methanol Reaction.

The main outcome can be summarized as in the following:

- Studying the TiO_xC_y material by DFT calculations allowed to propose plausible models for the bulk system at varying carbon content.

- Comparison of electronic structure calculations with ultraviolet photoemission spectra provided valuable insight into the possible surface composition of the prepared samples (connection with WP2).

- The calculated values for the work function of the two materials indicate that supporting WC nanoparticles on TiO_xC_y surfaces should induce an electron charging of the catalyst. This is confirmed by the Bader charge analysis and density of states computed for the WC/$TiO_{0.5}C_{0.5}$ interface model.

- The comparison for the onset potential of the MOR on Pt and WC surfaces indicates that WC is an excellent alternative material to Pt as fuel cell anode, especially when enriched by an excess electronic charge, for example by inserting an underlying electron-donating support such as TiO_xC_y.

List of published papers:

- L. Calvillo, D. Fittipaldi, C. Rüdiger, S. Agnoli, M. Favaro, C. Valero-Vidal, C. Di Valentin, A. Vittadini, N. Bozzolo, S. Jacomet, L. Gregoratti, J. Kunze-Liebhäuser, G. Pacchioni and G. Granozzi. *Carbothermal transformation of TiO_2 into TiO_xC_y in UHV: tracking intrinsic chemical stabilities.* **J. Phys. Chem. C 2014, 118, 22601-22610.**

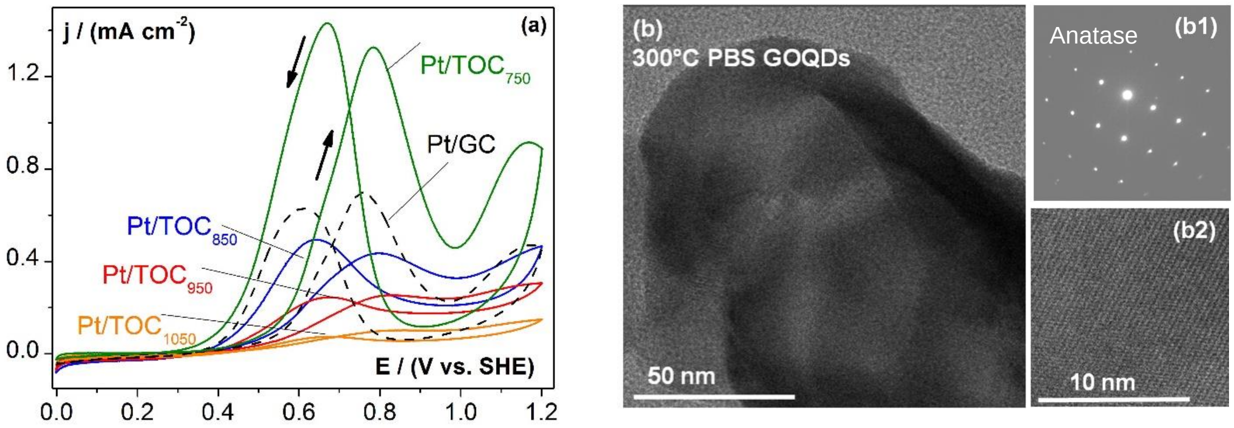
- C. Di Valentin, D. Fittipaldi, G. Pacchioni. *Methanol oxidation reaction on α-tungsten carbide versus platinum (111) surfaces:a DFT electrochemical study.* **ChemCatChem 2015, 7, 3533-3543**.

WP4: Preparation and characterization of high surface area TiO_xC_y supports and MC_x/TiO_xC_y assemblies

WP4 was focused on the production of conductive and electrochemically stable TiO_xC_y materials in the form of powders having sufficient porosity to allow for gas transport when integrated into a MEA (in WP7). In this respect, particular efforts were devoted to the scalability of the preparation procedure. Also titania nanotubes (TNTs), interesting as a proof of concept case, were prepared and characterized to study the role of nanostructuring on advanced supports. Existing knowledge of the conversion of TiO_2 to TiO_xC_y materials from WP2 was used to find the optimum conversion conditions for porous TiO_2 powders. The converted materials were decorated with catalyst NPs (Pt and MC_x, M=Mo, W) to prepare the nano-catalyst/support assembly and electrochemically tested towards benchmark reactions and the Ethanol Oxidation Reaction (EOR) in half-cell experiments up to 70°C.

The actual team was composed by:

- Prof. Julia Kunze-Liebhäuser, Professor at UIBK, WP leader of WP4;
- Dr. C. Valero-Vidal, post-doc at TUM and UIBK paid by **DECORE**;
- Ms. C. Rüdiger, PhD student at TUM and UIBK paid by **DECORE**;
- Mr. Cristoph Traunsteiner, PhD Student at TUM paid by **DECORE**;
- Dr. Niusha Shakibi Nia-Mütterlein, post-doc at UIBK paid by **DECORE**;
- Mr. Christoph Griesser, student at UIBK;
- Mr. Gearoid Manning, exchange student at UIBK;
- Prof. G. Granozzi, Professor at UNIPD, in the role of Scientific Supervisor;
- Prof. Alex Martucci, Associate Professor at UNIPD, in the role of powder preparation Supervisor;
- Mr. Andrea Paduano, PhD student at UNIPD;
- Dr. Markus Nesselberger, post-doc at UCPH paid by **DECORE**.



(a) Ethanol oxidation on TiO_xC_y supported Pt nanoparticles and Pt/GC at room temperature **[ChemCatChem 2013]**; (b) TEM bright field image of TNT-GOQD composites after annealing at 300 °C; (b1, b2) SAED pattern and HRTEM image of TiO_xC_y (Lattice 0.25 nm) **[Adv. Mater. Interfaces 2015]**.

The main outcome can be summarized as in the following:

- TiO_xC_y nanopowders with high porosity have been synthesized via the single step procedure developed by UNIPD. In this procedure, Methylcellulose (MC) was selected as carbon source due to its ease of use in aqueous solutions and its relatively high carbon residual after the thermal treatment.

- A two-step synthesis microwave assisted polyol synthesis proved to be successful to decorate TiO_xC_y with Pt_xSn NPs.

- TNTs were grown in a solution enriched with graphene oxide quantum dots. They were annealed to TiO_xC_y nanotubes in UHV, where the conversion starts at temperatures as low as 300°C. A detailed fundamental study of the conversion was carried out.

- The assembly of MC_x catalyst and the TiO_xC_y support was achieved by physical mixing, which showed to not alter the bulk properties of the precursor materials and to yield well dispersed MC_x (M=W, Mo) materials on the TiO_xC_y support.

- Although chemical surface modifications were observed for the MC_x catalysts and the TiO_xC_y supports, the conductivity of these composite powders remains sufficiently high when chemically and electrochemically tested in 5 M H_3PO_4 at elevated temperatures and up to 1.3 V vs. RHE.

- After initial surface passivation of MC_x and TiO_xC_y, the EC stability window is within the voltage range required for application in a fuel cell.

- According to half-cell tests of pure MC_x (M=W, Mo) towards ethanol electro-oxidation at T< 70 °C, these new metallic carbides showed insufficient activity towards EOR.

- As a consequence, new catalyst materials with small amount of noble metals, e.g. PtAuSn/MC_x (M=W, Mo), (3 wt. % of Pt and Au, 10 wt. % of Sn) were developed (see WP5). PtAuSn/TiO_xC_y showed enhanced catalytic activity in terms of the onset potential towards the EOR and MOR at all temperatures ranging from 20 to 70 °C.

- Pt/TiO_xC_y and Pt_3Sn/TiO_xC_y powders showed a very interesting electrochemical activity towards the EOR and MOR. In particular, the onset potential for EOR with Pt_3Sn/TiO_xC_y powders at 70 °C occurs at potentials as low as 0.2 V vs. SHE (the best result achieved).

List of published papers:

- C. Rüdiger, J. Brumbarov, F. Wiesinger, S. Leonardi, O. Paschos , C. Valero Vidal, J. Kunze-Liebhäuser, *Ethanol oxidation on TiO_xC_y supported Pt nanoparticles,* **ChemCatChem 2013, 5, 3219-3223.**

- A. Zana, C. Rüdiger, J. Kunze-Liebhäuser, G. Granozzi, N.E.A. Reeler, T. Vosch, J.J.K. Kirkensgaard, M. Arenz, *Core-shell TiO2@C: towards alternative supports as replacement for high surface area carbon for PEMFC catalysts,* **Electrochimica Acta, 2014, 139, 21-28.**

-M. Favaro, S. Leonardi, C. Valero-Vidal, S. Nappini, M. Hanzlik, S. Agnoli, J. Kunze-Liebhäuser and G. Granozzi. *In-situ carbon doping of TiO_2 nanotubes via anodization in graphene oxide quantum dot containing electrolyte and carburization to TiO_xC_y nanotubes.* **Adv. Mater. Interfaces 2015, 2, 1400462.**

- Marco Bersani, Andrea Paduano, Marco Favaro, Pramod Koshy, Charles C. Sorrell, Alessandro Martucci, Gaetano Granozzi *Preparation of High-Porosity TiO_xC_y Powders from a Single Templating Carbon Source* **Ceramics International 2016, 42, 7690.**

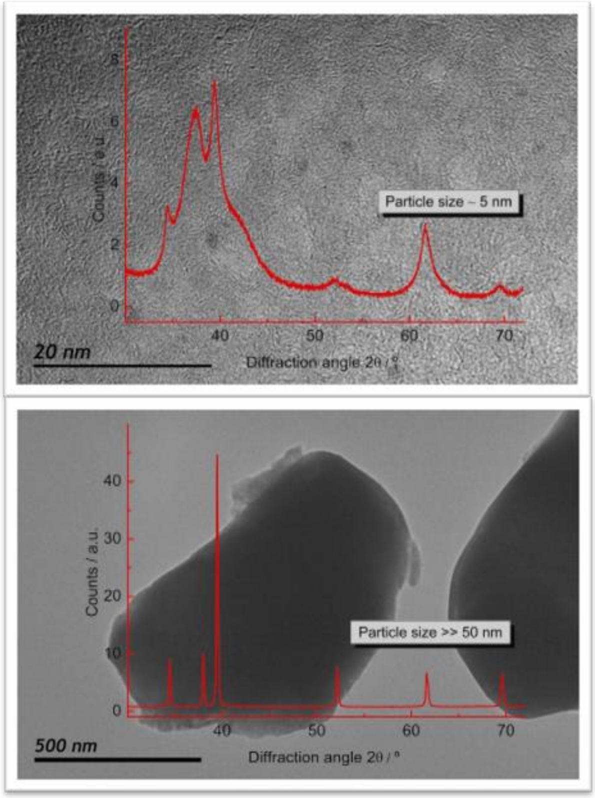
WP5: Preparation and characterization of MC_x (M = Mo, W) catalysts

WP5 was focused on the synthesis and chemical/structural/morphological/EC characterization (up to *70°C*) of MC_x (M = Mo,W) nano-powders with appropriate nanometric size, to be integrated in the MC_x/TiO_xC_y assembly. The conditions for their synthesis were optimized in order to reach the scale needed for their integration into the membrane-electrode assembly (MEA) in WP7.

In WP5 the MC_x nano-powders were tested as *all-in-one* MC_x catalyst/supports. To this end also commercial available powders were studied. To evaluate their EC behavior, MC_x nano-powders were tested towards benchmark reactions (HER/HOR, MOR, CO electro-oxidation) as well as EOR from RT up to 70°C, adopting the tools and procedures developed in WP6. Their stability and chemical/structural changes after the EC work (XPS, UPS, IL-TEM, IL-SEM, STM/AFM) were examined. The activity of the MC_x catalysts in presence of small amounts of noble metals was also investigated as part of the contingency plan initially proposed for the case of insufficient performances of the noble-metal free catalysts.

The research team was composed by:

- Prof. E. Pastor, professor at ULL in the role of WP leader;
- Prof. J.L. Rodríguez, professor at ULL in the role of catalyst preparation supervisor;
- Prof. C. Arévalo, professor at ULL in the role of electrochemistry supervisor;
- Dr. G. García, in the role of active post-doc researcher at ULL paid by **DECORE**;
- Mr. Olmedo Guillén-Villafuerte in the role of Ph.D. student at ULL paid by **DECORE**;
- Mr. Michael Fleige in the role of PhD student at UCPH paid by **DECORE**;
- Prof. G. Granozzi, Professor at UNIPD, in the role of Scientific Supervisor;
- Dr. Laura Calvillo-Lamana, in the role of active post-doc researcher at UNIPD paid by **DECORE**.



TEM images and XRD spectra of synthesized (top panel) and commercial (bottom panel) Mo_2C material.

The main outcome can be summarized as in the following:

- Two synthesis MC_x (M= Mo, W) procedures, carbothermal and urea glass methodologies, were adopted and it turned out that the former is suitable for molybdenum carbide production, whereas the latter is appropriate for tungsten carbide production.

- Several innovative catalysts based on synthetized or commercial carbides (Mo_2C, W_2C and WC) and of small amounts of noble metals (3-5 wt.% of Pt, Au and Rh) or non-noble metals (10-20 wt.% Fe, Ni, Cr and Sn) were successfully synthesized and tested.

- XRD and XPS techniques appear as very important tools for studying the crystalline structure of the bulk and surface chemistry of metallic carbides, respectively. TEM analysis was an essential instrument to confirm the particle size calculated from XRD analysis.

- Differential electrochemical mass spectrometry (DEMS) was adapted for the study of the hydrogen, methanol, carbon monoxide, ethanol and syngas oxidation and hydrogen reduction (HER) on metallic carbides (as well as titanium oxycarbide films and powders) from room temperature up to 70 °C.

- In-situ Fourier transform infrared spectroscopy (FTIRS) was adapted for the study of CO and the ethanol oxidation on metallic carbides and titanium oxycarbide powders.

- Electrochemical studies of benchmark reactions were performed at commercial and synthetized materials (Mo_2C, W_2C and WC) in absence and presence of noble and non-noble metals up to 70 ºC.

- Spectroelectrochemical studies (FTIRS and DEMS) were performed at commercial and synthetized materials (Mo_2C, W_2C and WC) in absence and presence of noble and non-noble metals.

- Electrochemical stability tests for synthesized materials (Mo_2C and W_2C) were performed in different electrolytes (H_2SO_4, $HClO_4$ and H_3PO_4) and working potential ranges.

- n-situ spectroelectrochemical (FTIRS and DEMS) techniques were employed for the electrochemical oxidation of isotope-labeled ethanol ($^{12}CH_3{}^{13}CH_2OH$) on PtAuSn/Mo_2C, PtAuSn/W_2C and PtAuSn/C catalysts.

- A fundamental understanding of the enhanced performance toward the CO and ethanol oxidation reactions at PtAuSn/Mo_2C and PtAuSn/W_2C catalysts in comparison to PtAuSn/C was obtained.

- A full description (including new insights) of the ethanol oxidation reaction in acidic media was reported.

List of published papers:

- M. Roca-Ayats, E. Herreros, G. García, M.A. Peña, M.V. Martínez-Huerta. *Promotion of oxygen reduction and water oxidation at Pt-based electrocatalysts by titanium carbonitride.* **Appl. Catal. B: Environ. 2016, 183, 53–60**.

- O. Guillén-Villafuerte, G. García, J. L. Rodríguez, C. Arévalo, E. Pastor. *New insights on the electrochemical oxidation of ethanol on carbon-supported Pt electrode by a novel electrochemical mass spectrometry configuration.* **Electrochem. Commun. 2016, 63, 48–51.**

- G. García, O. Guillén-Villafuerte, J.L. Rodríguez, C. Arévalo, E. Pastor, *Electrocatalysis on metal carbide materials.* **Int. J. Hydrogen Energy 2016, 41, 19664–19673.**

- G. García, M. Roca-Ayats, O. Guillén-Villafuerte, J.L. Rodríguez, M.C. Arévalo, E. Pastor, *Electrochemical performance of α-Mo2C as catalyst for the hydrogen evolution reaction*. **J. Electroanal. Chem. 2017,** http://dx.doi.org/10.1016/j.jelechem.2017.01.038

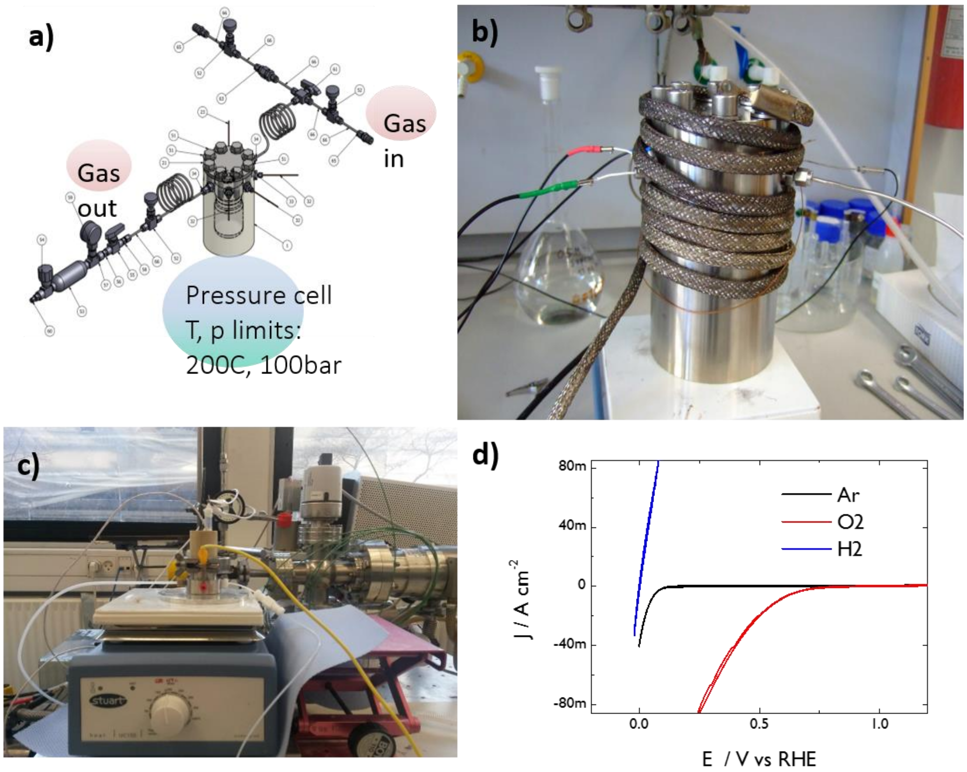
WP6: Lab-scale validation of activity, selectivity and stability at *intermediate*-T of the catalyst/substrate assembly

WP6 was focused on:
- developing standardized *intermediate*-T testing tools in EC half-cell configuration for determining activity, selectivity and stability of non-precious metal catalysts or catalysts with significantly reduced precious metal content
- evaluating the performance of synthesized catalysts for Ethanol Oxidation Reaction (EOR) at *intermediate*-T with standardized tests
- understanding the interaction between ethanol and concentrated phosphoric acid electrolyte
- evaluating the performance of synthesized catalysts for reformate oxidation at *intermediate*-T

Actually, due to the low boiling point of electrolytes and reactants, electrochemical catalyst characterization in half-cells is usually limited to temperatures of about 60-80°C. Higher temperatures are only accessible with specific experimental setups. As such experimental setups are not commercially available, in **DECORE** we needed to design and test specific electrochemical setups that allowed electrochemical characterization at *intermediate*-T, i.e. 150°C. The *design and production* of these setups as well as *their application* to catalyst testing was the focus of WP6.

The research team was composed by:

- Prof. Matthias Arenz, Associate Professor at UCPH, in the role of WP leader;
- Dr. Alessandro Lavacchi, CNR Researcher at ICCOM, in the role of Senior Researcher;
- Michael Fleige, in the role of PhD student at UCPH paid by **DECORE**;
- Dr. Markus Nesselberger, in the role of active researcher at UCPH partially paid by **DECORE**;
- Alessandro Zana, in the role of PhD and Postdoc student at UCPH paid by **DECORE**;
- Kaspar Holst-Olesen, in the role of PhD at UCPH;
- Dr. Francesco Vizza, researcher at ICCOM-CNR in the role of Senior Researcher;
- Dr. Werner Oberhauser, researcher at ICCOM-CNR in the role of Senior Researcher;
- Dr. Lucia Becucci, post-doc at ICCOM-CNR paid by **DECORE**;
- Mr. Carlo Bartoli, technician at ICCOM-CNR;
- Prof. E. Pastor, professor at ULL in the role of WP5 leader;
- Prof. C. Arévalo, professor at ULL in the role of electrochemistry supervisor;
- Dr. G. García, in the role of active post-doc researcher at ULL paid by **DECORE**;
- Dr. Laura Calvillo-Lamana in the role of post-doc researcher at UNIPD paid by **DECORE**;
- Prof. G. Granozzi, Professor at UNIPD, in the role of Scientific Supervisor.
- Dr. Niusha Shakibi Nia-Mütterlein, post-doc researcher at UIBK.



Design of the High Temperature and High Pressure vessel for EtOH electrooxidation. b) High Temperature and High Pressure vessel for EtOH electrooxidation. c) GDE set up designed for high T and high Mass transport Operation. c) polarization curves and proof of concept of the GDE set-up presented in c).

The main outcome can be summarized as in the following:
- In the first part of WP6 we developed several EC half-cells test tools, which are operable at *intermediate*-T in acidic conditions. We first developed a pressurized electrochemical half-cell suitable to pressures up to above 100 bar and ca. 200°C. One of the main challenges that was achieved within **DECORE**, was the development of a proper reference electrode, which is essential for reliable electrochemical testing. Several suitable designs were achieved within **DECORE**, see publications for details. In addition to the initial development of the pressurized setup, we included the option of controlled mass transport, which is essential for many electrocatalytic measurements. Successively, we designed an advancement that allows the application of external reference electrodes. As catalyst testing in electrochemical half-cells often involves screening of many materials, we also developed a Gas Diffusion Electrode (GDE) setup, specifically applicable for the testing of EtOH oxidation catalysts at *intermediate*-T in concentrated phosphoric acid. This setup can be operated non-pressurized and is only limited by the "stability" of the phosphoric acid, i.e. the oligomerization and polymerization of the orthophosphoric acid.

- Based on studies of the ethanol-electrolyte interaction, materials suitable for a reference electrode, the dispersion of the catalyst, and the electrochemical behavior of the catalyst powders, a standardized protocol for EC half-cell tests at *intermediate-T* was developed.

- With IL-SEM a suitable an atomic scale methodology for mechanistic degradation studies at *intermediate-T* was developed. A review paper concerning identical location microscopy has been accepted and is in print.

- In the second part of WP6 we applied these techniques to the catalyst developed within the **DECORE** project. For this, we defined a standardized, fast and reliable protocol for evaluating the performance of electrocatalysts at *intermediate*-T. Testing the electrocatalysts synthesized within DECORE with respect to their ethanol oxidation activity at *intermediate*-T in concentrated phosphoric acid, it turned out that (as expected) catalyst stability is a major challenge. Catalyst systems that showed promising performance at temperatures below 100°C in diluted acid electrolytes proved instable at the harsh *intermediate*-T conditions in concentrated acid. As heating up the setups takes a certain time, it was not feasible to determine initial activities of instable catalysts.

- M_2C/TiO_xC_y (M=Mo, W) based catalyst assemblies were not sufficient stable at *intermediate*-T conditions.

- The most promising catalyst systems identified in WP6 were based on small amounts of precious metals supported on TiO_xC_y. We tested several Pt and PtSn based catalysts. The most promising system we identified was a Pt_xSn/TiO_xC_y system. PtSn is also known to be active for EtOH oxidation at low temperatures, but it must be highlighted that the precious metal contend of our catalyst is significantly reduced as compared to reported low temperature catalysts.

In addition to EtOH oxidation, we also tested the catalysts developed by **DECORE** for reformate oxidation as alternative to direct ethanol feed. Also in these tests the same catalyst of the Pt_xSn/TiO_xC_y system showed the best performance.

- An important challenge of HT-PEMFCs, independent of if operated in direct ethanol cell or reformate mode, is the electrolyte, i.e. concentrated phosphoric acid. Initially it was assumed, and also reported by other research groups, that the interaction of ethanol with hot phosphoric acid is a major detrimental effect. It is also known that gas solubillity is significantly reduced in concentrated phosphoric acid, thus inhibiting the performance. However, in studies investigating second half-cell process, the oxygen reduction reaction, we could show that the kinetic reaction rate (specific activity) of benchmark catalysts in concentrated phosphoric acid at *intermediate*-T is also significantly inhibited at high pressure (10 bar). It is roughly the same as in diluted acid at room temperature. As under these conditions gas solubility is not a limiting factor, this result shows that there is an additional inhibition mechanism of concentrated phosphoric acid. This inhibiting mechanism is most likely not limited to a simple blocking effect, which is often discussed, but more to an interface transport barrier.

List of published papers:

- G. K. H. Wiberg, M. Fleige and M. Arenz, *Design and test of a flexible electrochemical setup for measurements in aqueous electrolyte solutions at elevated temperature and pressure*, **Review of Scientific Instruments 2014, 85, 85105.**

- G. K. H. Wiberg, M. Fleige and M. Arenz, *Gas Diffusion Electrode Cell for High Surface Area Catalyst Testing in Concentrated Phosphoric Acid at Elevated Temperatures*, **Review of Scientific Instruments 2015, 86, 24102.**

- M. Fleige, G. K. H. Wiberg, and M. Arenz, *Rotating disk electrode system for elevated pressures and temperatures*, **Review of Scientific Instruments 2015, 86, 64101.**

- M. J. Fleige, K. Holst-Olesen, G. K.H. Wiberg, and M. Arenz. *Evaluation of temperature and electrolyte concentration dependent oxygen solubility and diffusivity in phosphoric acid*, **Electrochimica Acta 2016, 209, 399.**

- A. Zana, C. Rüdiger, J. Kunze-Liebhäuser, G. Granozzi, N.E.A. Reeler, T. Vosch, J.J.K. Kirkensgaard, M. Arenz, *Core-shell TiO_2@C: towards alternative supports as replacement for high surface area carbon for PEMFC catalysts*, **Electrochimica Acta, 2014, 139, 21.**

- Y. X. Chen , A. Lavacchi , H. A. Miller , M. Bevilacqua , J. Filippi, M. Innocenti, A. Marchionni , W. Oberhauser , L. Wang , F. Vizza, *Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis*, **Nature Communications 2014, 5, 4036.**

WP7: Activity/durability industrial standard tests and assembling of a bench top DEFC single cell

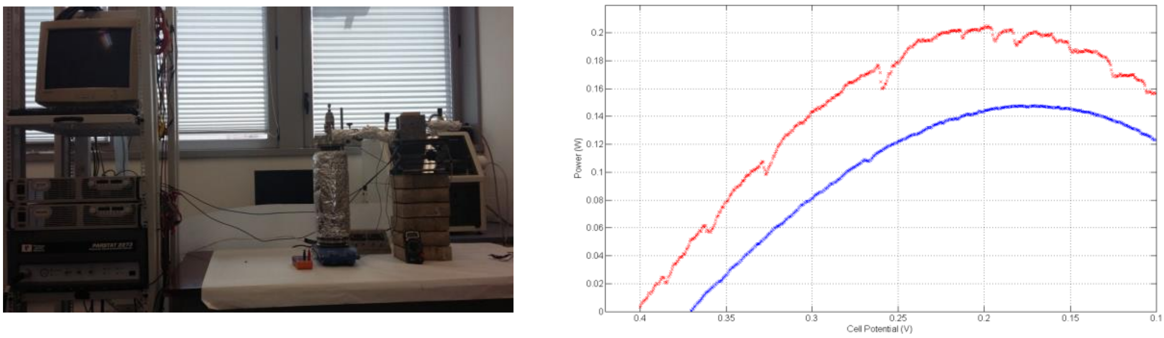
WP7 focused on integrating the materials validated in WP6 in a PBI MEA by the industrial partner ELCOR. According to the outcomes of WP2, WP4 and WP5, it turned out that TiO_xC_y is a valid alternative to standard carbon support to operate at *intermediate*-T. One of the goal of WP7 was then to validate this system in test rigs of HT-PEM cells using H_2 or synthetic reformate as energy carrier at the anode and air at the cathode. This allowed to follow industrial procedures to test the stability and activity of the innovative support. On the contrary, the activities of the investigated MC_x (see WP5) were not sufficiently high to use them as catalysts. Therefore, such MC_x carbides were also tested as further possible innovative supports.

The MEA developed by ELCOR and based on Pt/TiO_xC_y at the anode side was transferred to ICCOM, where a bench-top *intermediate*-T DEFC single-cell was developed and tested. This allowed to test the efficiency of the *intermediate*-T DEFC. Based on the results of these tests a concept of an ethanol fuel cell system was developed.

The research team was composed by:

- Dr. Martin Batzer, Leader of the elcore-testfield at ELCOR
- Dr. Markus Perchthaler, project manager at ELCOR
- Marina Welsch, development engineer at ELCOR
- Robert Csaky, Student at ELCOR
- Marinko Bilanzija, testing personnel at ELCOR

- Steffen Seyda, testing personnel at ELCOR
- Dr. Alessandro Lavacchi, CNR Researcher at ICCOM, in the role of Senior Researcher;
- Dr. Francesco Vizza, researcher at ICCOM-CNR in the role of Senior Researcher;
- Dr. Werner Oberhauser, researcher at ICCOM-CNR in the role of Senior Researcher;
- Dr. Lucia Becucci, post-doc at ICCOM-CNR paid by **DECORE**;
- Mr. Carlo Bartoli, technician at ICCOM-CNR;
- Dr. Hamish Miller, Staff Researcher at ICCOM-CNR
- Dr. Jonathan Filippi, Temporary Contract Researcher at ICCOM-CNR
- Dr. Marco Bellini, Post Doc at ICCOM-CNR
- Mrs. Maria Folliero, Ph.D. Student at ICCOM-CNR



Experimental set-up for the *intermediate T direct ethanol fuel cell (left)* and power density curves acquired on the system at 150° (blue) and 160 (red).

The main outcome can be summarized as in the following:

- A method for preparing stable inks was delivered. Both Mo_2C and W_2C powders led to inks which expressed a high sedimentation rate. By increasing the thickener-content in the ink, the sedimentation rate was lowered so that the ink was sufficiently homogeneous for a few minutes, which allowed it to be processed at lab-scale.

- A complete procedure for the manufacturing of TiO_xC_y powder was delivered. The procedure required the addition of a milling step to reduce the size of the TiO_xC_y particles. This procedure was required to achieve a double goal: i) making the catalyst layer homogeneous in order to avoid difformity of the resistance along the MEA and hence the formation of hot spots; ii) increasing the surface area to better distribute Pt nanoparticles.

- Only TiO_xC_y membranes were tested in the MEAs as both Mo_2C and W_2C showed limited electrocatalytic activity. Once assembled into the MEA, even the systems with TiO_xC_y showed poor performance leading to an OCV potential of only 230 mV. According to this we switched to the addition of a limited amount of Pt nanoparticles (0.5 mg cm^{-2}). While delivering promising performance, this system did not compare well with the commercial ELCOR system for reformate oxidation. Therefore, an optimization of the MEA fabrication parameters would be necessary for these kind of materials.

- The same MEAs were tested in the direct ethanol fuel cell that was assembled at ICCOM in WP7. We achieved very good activity at a platinum loading of 0.5 mg cm^{-2} which is much lower than analogous systems reported in the literature, that usually operate with loadings well exceeding 1 mg cm^{-2}. We found that ethanol oxidation requires the supply of water at the anode and that the $EtOH/H_2O$ ratio that delivers the best performance is 1:4. Under these conditions the cell delivered 45 mW cm^{-2} at 150 °C. We observed that slightly increasing the temperature to 160 and 180 °C produced a dramatic improvement in the power density, delivering respectively 63 and 93 mW cm^{-2}. 40% selectivity toward CO_2 production was also found.

- The use of commercial bioethanol (0.8-1 Eur/L) did not produce any significant change in the performance, showing that robustness of the catalyst toward the use of large-scale production ethanol from biomass.

- On the basis of WP7 findings we delivered the concept of a small power system based on a direct Ethanol Fuel Cell. As system capable of delivering 100 W. An important element of the concept we delivered is that a water management system must be included in the cell. This is for the fact that the anodic oxidation of ethanol requires large amount of water. This water must be captured from the cathode side rather being supplied from an external source. This is because water evaporation is very costly in energetic terms and the absence of a recovery system would make any *intermediate*-T direct ethanol fuel cell unpractical.

Potential Impact and main dissemination activities and exploitation results

At the end of the project, the main outcomes which can potentially be exploited are the following:
- Efficient new and synergistically active supports (TiO_xC_y and MC_x (M=W, Mo)) apt for *intermediate*-T set-ups have been synthesized, characterized and validated;
- Experimental tools for studies at *intermediate*-T have been developed and disseminated to the scientific community;
- An efficient new catalyst for EOR (PtAuSn) has been supported on synergistically active support materials (TiO_xC_y and MC_x (M=W, Mo)) and validated at 70°C in a half-cell set-up. The catalyst performance is excellent with the lowest onset potentials reported to date for the EOR due to high C-C bond splitting activity. The activity decreases upon operation in media with water shortage as it was the case during operation at *intermediate*-T in a GDE charged with concentrated phosphoric acid;
- A promising catalyst (Pt_3Sn/TiO_xC_y) for reformate oxidation has been prepared with a new method and validated at *intermediate*-T which has the potential to be adopted in HT-PEM technology;
- At ICCOM, a bench-top single DEFC, based on a MEA developed by ELCOR, was built and run, and this allowed to discuss a conceptual design of a DEFC operating at intermediate-T. It was shown that the maximum power density of the devices is in the range between ca. 50 and 80 mW cm^{-2} at 150-180°C. While significantly above of the state-of-the-art values, such values are not yet good enough to justify an exploitation of the technology for power demanding applications.

DECORE has led to a significant innovation in the concept of the MEAs for *intermediate*-T FCs. The main outcome is the demonstration that it is possible to have alternatives to carbon as catalyst support. **DECORE** technology has been demonstrated to have the potential to impact on the market of reformate HT-PEM-FCs, a technology that is already deployed into the market and that is still asking for large innovation for cutting costs and increasing performance. **DECORE** has shown that the new proposed MEAs, based on titanium oxycarbides and tiny addition of Pt, have a large potential in HT-PEM-FCs. To come to a full commercial exploitation in reformate HT-PEM-FCs, two aspects have clearly identified that still need to be worked out to produce systems capable of generating a net advantage on the market. In particular, we still require to act on two major issues: i) the improvement of the dispersion of the support of the catalyst and ii) the reduction of the specific resistance of the support. It is worth mentioning that there are no principle limitations to the achievement of such targets with additional efforts in the optimization of the composition and the synthesis of the materials. We believe that with these additional efforts we would be able to overcome the performance of the conventional catalyst based on carbon supported nanoparticles, reducing the production cost by cutting the platinum content in the FCs.

In the case of DEFCs, where devices are not yet in the market, **DECORE** had significant breakthroughs, but a commercial exploitation is still difficult to imagine and the activity has been more focused on the dissemination of scientific results. **DECORE** consortium has come to the conclusion that patenting, at this stage, is premature.
To explore exploitation, **DECORE** was not limited to the production of the materials, but also focused on the production process. Particularly, materials have been produced with processes that can use commercial devices that are well known in the powder and FCs industries. Once the materials will be fully optimized the scale-up of the production will be easy to implement.

Dissemination by scientific peer-reviewed publications
The project has resulted so far in 20 peer-reviewed publications, 8 PhD/Master theses, 38 presentations in a scientific event, 10 articles published in the popular press/press releases/WEB pages.

A public workshop was organized at the end of the project, having the title:
International Workshop on Ethanol Electro-oxidation held in Florence (Italy) from 5 to 7 December 2016.

Hereafter the main numbers of this workshop:
- number of participants: 51
- source nationality: 11 (Italy, Spain, Austria, Germany, Brazil, Canada, China, Thailand, Denmark, Switzerland, United Kingdom)
- Sponsorships (consortium members, ERIC, INSTM International association of Hyrogen energy, International Journal of Hydrogen Energy, International Society of Electrochemistry, Divisione di elettrochimica della Società Chimica Italiana)
- Number of Sessions: 6
- Location: Palazzo Incontri, Sala Verde (1st floor) -Via de Pucci, 1 Florence and Conference CNR Research Area, Via Madonna del Piano, 10 Sesto Fiorentino Building F, Conference Hall
- Number of Abstracts: 39 (26 Oral, 13 Poster)
- Keynotes speakers : 6
- Invited speakers: 9