Description of main S & T results/foregrounds

WP 1: New materials and novel reactor concepts

The synthesis of the different doped carbon catalysts, i.e. N-, P- and B- doped either in a powder form and supported on a macroscopic host structure, has been completely achieved, both by in-situ and ex-situ doping methods along with their in-depth characterization, after each stage (after synthesis, after purification, after functionalization, and after catalytic tests) by numerous techniques available within the consortium.

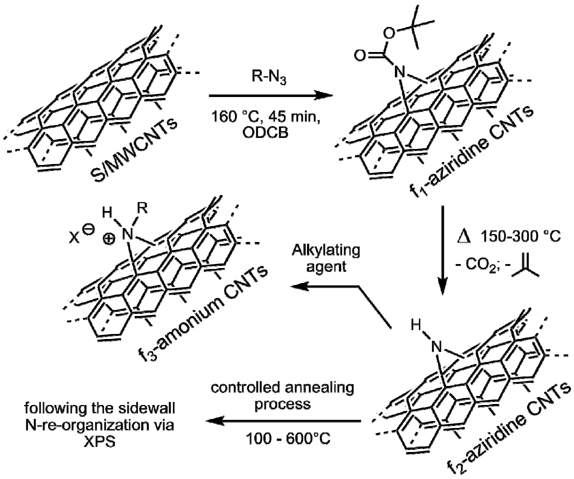
The doping dispersion has been greatly improved by controlling the synthesis parameters, especially the synthesis temperature, in order to produce doped carbon-based materials with as small as possible diameter which will provide high effective surface area for the subsequent catalytic applications. Characterization results have also evidenced the extremely homogeneous coverage of the layer of the N-doped carbon nanotubes/nanofibers on the surface of the macroscopic host structures which is fully in line with the first objective of the WP.

The synthesis of hetero-doped nanomaterials has been greatly improved by the development of a new method in place of those developed above, i.e. CVD and organic functionalization, starting with an aqueous solution containing raw materials from food residues, i.e. dextrose, ammonium carbonate and citric acid, to deposit a thin and homogeneous layer of the nitrogen-doped carbon active phase onto different supports (powder, grains, pellets, foams and monolith). The as-synthesized metal-free catalysts deposited on different supports are thoroughly characterized after different stages of preparation regarding the optimization process. According to the characterization results the N@C film is well dispersed on the support surface with an extremely high density of exposed active sites available for catalysis. Such predominant localization is of extreme importance as it allows the fruitful use of the active phase whereas for the case of in-situ N-doped carbon nanotubes and nanofibers part of the nitrogen localized underneath the surface is not accessible for the reaction. In addition, the mechanical strength of the composite is significantly improved compared to that of the supported N-CNTs/N-CNFs synthesized by the CVD method. The homogeneous interface between the N@C layer and the support also enhances the heat and mass transfer during the catalytic processes as well. These results are fully in line with the main objectives of the WP.

The last development carried out within WP1 concerns the use of the N@C as solid glue for the anchorage of the N-CNTs obtained by the ball-milling process onto the SiC foam surface for subsequent use in the AOP processes. The presence of the N@C as solid glue significantly improves the mechanical anchorage of the ball-milled N-CNTs with outstanding catalytic performance for the AOP processes.

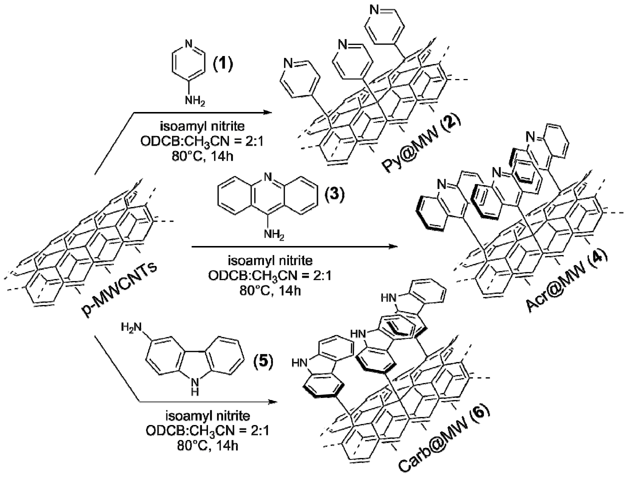
A series of N/P/B-CNT samples were prepared by *ex-situ* exohedral functionalization/doping approach and tested as metal-free catalysts. Particular attention has been paid to the control of the nature of the dopant, *i.e*. nature and basicity of the nitrogen species, role of the neighboring atoms/groups and their influence on the final catalytic performance. The *ex-situ* doping of carbon nanomaterials with light hetero-elements has been accomplished through four main synthetic protocols:

1) a [2+1] cycloaddition of nitrenes (Scheme1) to MWCNT sidewalls and tips capable to bring the N-containing functionalities as close as possible to the Csp^2 network (see deliverable D1.4).



Scheme 1

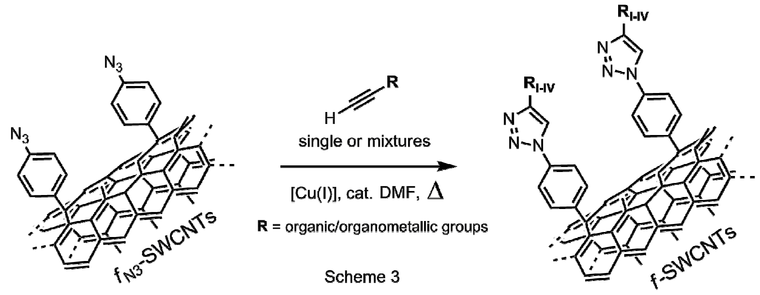
2) well established literature approaches like: a) the classical Tour protocol (Scheme 2), *via* aryldiazonium salt, that allows to bring at the CNTs surface selected N-containing groups. b) the 1,3-dipolar cycloaddition reaction of azomethine ylides for the formation of a pyrrolidine ring fused with the CNTs sp^2 network.



Scheme 2

3) a thermal treatment of MWCNTs in presence of N/B/P-containing organic compounds under inert atmosphere; to this purpose, aromatic molecules were selected in order to facilitate the formation of a strong π-π interaction with the CNTs sp^2 network

4) an original functionalization protocol for the decoration of CNTs *via* "click" chemistry (Scheme 3) that allows to bring at the nanomaterial surface selected groups or mixture thereof



Scheme 3

The listed *ex-situ* decoration protocols have provided fundamental insight to the complex structure-reactivity relationship of N-doped carbon nanomaterials in catalysis (and in particular in ORR) and the methodology described has evidenced a number of remarkable advantages respect to the state-of-the-art: 1) mild reaction conditions required to N-decorate the CNTs surface (energy saving process); 2) easy tailoring of the N-containing functional groups, 3) full exposure (atom saving) of the active sites to the nanomaterial outer side where the catalytic process takes place; 4) outstanding catalytic activity and long-term stability of selected N-doped metal-free samples for ORR in basic medium as well as for advanced oxidation processes. The unprecedented *ex-situ* decoration strategies adopted in the study have allowed, for the first time, to highlight the role of each doping functionality/group on the final catalytic performance of complex metal-free carbon nanomaterials thus paving the way to the rational design of catalysts with improved efficiencies.

For the synthesis of macroscopically shaped supports coated with N-CNTs a similar synthesis protocol for the synthesis of powdery N-CNTs was used whereas some development has been done by SICAT in order to produce the SiC foams according the sizes and dimensions requested by the partners. At low N-CNTs loading the macroscopic shape of the host matrix is completely retained while at high N-CNTs loading (> 30 wt.%) the macroscopic structure becomes fragile during transport and handling. Representative digital photos of the SiC foam, before and after N-CNTs (21 wt %) deposition, are presented in Fig. 1-2A and B. SEM analysis indicates that the SiC surface is completely covered with a dense layer of N-CNTs with an extremely homogeneous diameter centered at 70±10 nm (Fig. 1-2C and D). TEM analysis indicates that the microstructure of the supported N-CNTs remains similar to that of the bulky N-CNTs. The samples obtained were sent to the different partners of the project for catalytic testing, i.e. ORR and AOP processes

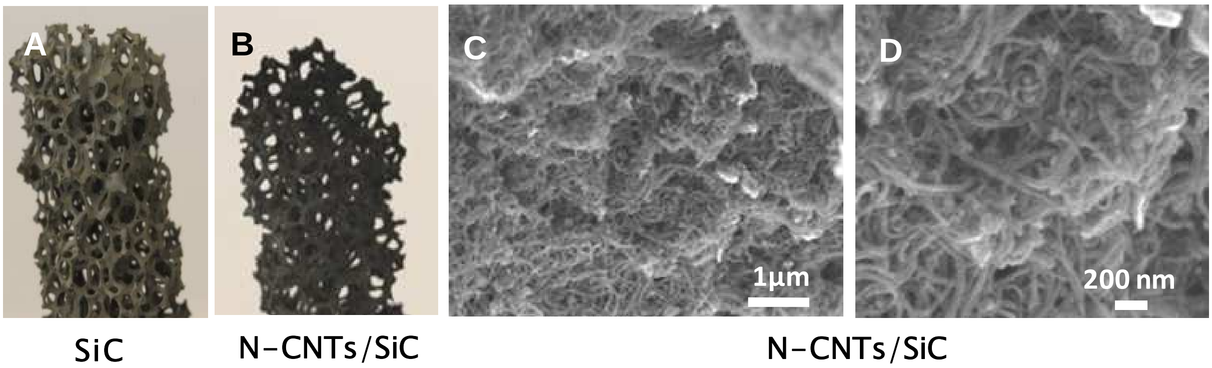


Figure 1-2. (**A, B**) Digital photos of the SiC and N-CNTs/SiC with 21 wt % loading showing the retention of the macroscopic structure. (**C, D**) SEM micrographs of the homogeneous N-CNTs layer on the SiC surface. The N-CNTs have an average diameter centered at 70±10 nm.

In addition, the main concern of the use of N-CNTs as metal-free catalyst, especially in the Oxygen Reduction Reaction (ORR), is linked with the residual iron-based catalyst which was remained inside the N-CNTs. Indeed, despite the repeated acid treatment some residual iron is still present inside the N-CNTs, either in the form of encapsulated iron nanoparticles or as atomic iron dispersed onto the nitrogen-carbon matrix. Such residual iron could plays a role in the ORR process according to the literature survey where iron-nitrogen sites have been advanced to be an active center for performing the ORR. In order to definitively phase-out the role of such iron species we have performed the ex-situ synthesis of nitrogen-doped carbon phase starting with an iron-free precursor named polymerized ionic liquids (PILs) or food stuff raw materials. The last method seems to be the most appropriate one for preparing nitrogen-doped carbon as metal-free catalyst. The metal-free composites obtained from these methods also display a much higher mechanical strength compared to those synthesized by a CVD method.

On this ground, a straightforward and environmentally friendly methodology for the preparation of highly N-doped CNMs starting from non-toxic, raw and abundant foodstuff starting materials has been developed. In particular, a shape-adaptable, highly N-doped mesoporous carbon phase has been properly grown as a metal-free "catalytic clothing" at the surface of macroscopically shaped supports. The synthesis has been carried out as follows: the support, being it nanoscopic or macroscopic, was impregnated with an aqueous solution containing food stuff raw materials, i.e. dextrose (sugar), citric acid (lemon juice), and ammonium carbonate (leavening agent), with a fixed concentration followed by appropriate thermal treatments at various temperatures to generate the N@MC layer on its surface (Fig. 1-3, top entry left). Such synthesis process can be applied for any kind of supports, i.e. SiC, alumina, according to the examples showed in Fig. 1-3 (top entry right). The mixing of the raw materials in water leads to the formation of an intermediate active phase containing both carbon and nitrogen which will be further converted into nitrogen-doped carbon phase upon impregnation onto the support followed by thermal treatments at appropriate temperature (Fig. 1-3 second entry, left). The STEM-EELS analysis (Fig. 1-3 second entry, right) evidences the formation of a N-rich carbon layer covering the surface of the macroscopic host structure, i.e. SiC. The thickness of the N@MC layer can be finely tuned by making successive impregnation/calcinations steps while the pore size can be modified by adding removable template such as polymer or ammonium carbonate.

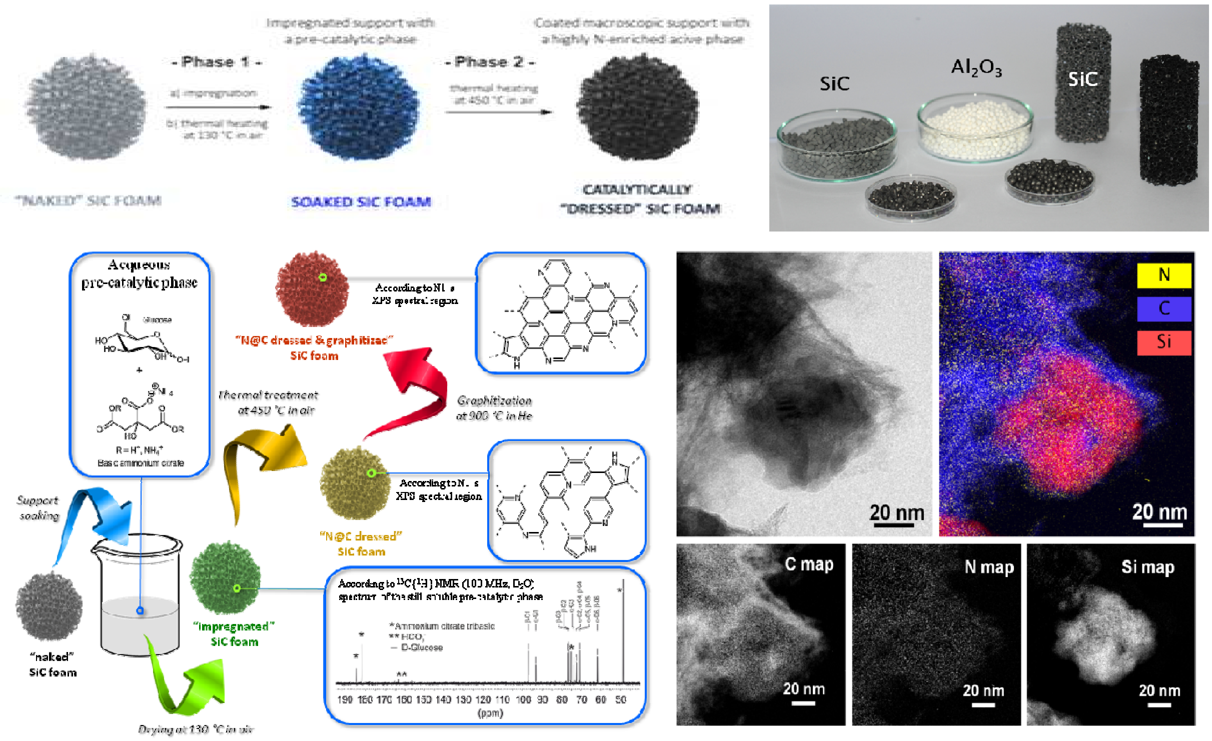


Figure 1-3. (**Top entry, left**) Schematic principle of the synthesis of the N@MC supported on SiC macroscopic host matrix. (**Top entry, right**) Digital photos of the N@MC deposited on different macroscopic supports. (**Second entry, left**) Schematic description of the synthesis process and the different thermal treatment steps. (**Second entry, right**) STEM-EELS analysis showing the N@MC layer coated on the SiC surface and the elemental mapping of the different elements inside the sample.

The developed methodology has been extended to the preparation of N-CNTs/SiC foams composites with higher mechanical strength; in particular, N-CNMs were used as a solid glue to anchor N-CNTs obtained by a ball-milling process developed by UPORTO. The materials have been thoroughly characterized and tested in catalysis (ORR and AOP) with outstanding catalytic results.

The proposed methodology offers a really sustainable and valuable approach to the generation of highly adaptable N-doped, carbon porous active phases (N@C) capable of "dressing" different macroscopically shaped host matrices starting from non-toxic and cheap raw materials. Major limitations like difficult scale-up procedures, high temperature material sensitivity, high production costs and environmentally unsafe protocols along with difficult materials handling (often caused by their prevalent powdery texture) have been conveniently overcome.

The influence of the synthesis parameters on the characteristics of the final composites will be also investigated and discussed. The mechanical strength of the N-CNFs deposited on the cordierite monolith is higher compared to that of the N-CNTs on the SiC surface. Such difference could be attributed to the deeper inclusion of the N-CNFs inside the cordierite matrix compared to that occurs on the SiC composite. However, the main drawback of the cordierite monolith is linked with the presence of straight channels with low mixing degree compared to that of the SiC foam where the random distribution of the struts leads to a high mixing degree of the gaseous and liquid reactants.

The catalyst prepared by NTNU (NCF20) was the catalyst performing best in ORR and PEMFC (single cell) tests. The catalyst N-CNF/Fe reported is the same catalyst as NCF20 in WP3.

The N-CNFs grown from Fe demonstrated a high ORR onset potential in acidic electrolyte (0.93V) in addition to good selectivity towards the four electron oxygen reduction and high durability. The N-CNF/Fe catalyst showed good stability after 1600 cycles. However, N-CNFs from Ni showed low ORR activity in acidic electrolyte and high selectivity towards the two-electron oxygen reduction. Physical characterization of the N-CNFs revealed differences in the microstructure, N-content and N-composition depending on the growth catalyst used during synthesis. It was also observed in HRTEM that encapsulated Fe particles were present. The transition metal could therefore affect the ORR indirectly by determining the incorporation of N and the microstructure of the N-CNFs, or directly by being part of the active sites for the ORR. The exact nature of the active site is thus still under debate. The roles of the nitrogen groups, oxygen groups and transition metal need further examination.

Highlights

The main highlights which were obtained in this WP are summarized below:

- Complete investigation of the influence of the synthesis parameters during the CVD process on the physical properties of N-CNTs and N-CNFs.

- The influence of the 1D doped-carbon loading on the final mechanical strength of the macroscopic composites which is a key parameter for subsequence development of such materials as metal-free catalysts.

- Development of organic functionalization as an alternative *ex-situ* exhoedral approach to the hetero-decoration of carbon nanomaterials that allows an easy and precise control of the doping groups using mild reaction conditions

- The new *ex-situ* doping strategy has allowed, for the first time, to establish an unambiguous relationship between structure and catalytic activity for ORR in complex carbon nanomaterials paving the way to the design of more active and efficient catalysts.

- Development of a radically new synthesis method starting from food stuffs raw materials for the production of N-doped carbon metal-free catalyst with controlled shape and size with outstanding catalytic performance.

- Mass production (kg) of the N-doped carbon (N@C), synthesized from the food stuffs raw materials, for the subsequence industrial development.

WP 2: Hydrodynamics modelling

The main aim of this WP2 was to develop multi-scale models linking kinetic modeling, CFD modeling and process simulation for the three main case studies: catalytic ozonation (as an example of advanced oxidation processes), oxidative dehydrogenation of light alkanes, and oxygen reduction reaction (for fuel cells application). The three case studies represent different scenarios, namely: (i) a gas-liquid-solid or liquid-solid reaction at close to ambient temperature, (ii) a gas-solid reaction with high demand on heat transfer through the foam material or reaction media, and (iii) gas-vapour flow with potential for condensation inside the foam. The requirements for optimal operation of the three different devices are very different. The common element is the need to connect the specific structure and materials of the foam with performance in mass and heat transfer. WP2 is split into several sub-tasks relating to specific aspects of model development. The bottom-up approach was used to develop multi-scale models, starting with establishing mechanisms for the three cases and kinetic modeling. The oxygen reduction reaction case study was excluded from WP2 since the main research challenge in this reaction is the catalyst activity and the main effort of the project with respect of this reaction was to develop a more active catalytic system.

The work has delivered several significant new results. Heat transfer, mass transfer and hydrodynamic measurements were performed. For this a new experimental system was developed at University of Warwick and provided new insights into mixing mechanisms within foams. Structure of foams was studied in detail using X-Ray tomography and new insight into heat conduction in these materials was elucidated through these observations. A new mechanistic kinetic model was developed for catalytic ozonation and a new mechanistic kinetic model was developed for oxidative dehydrogenation of propane. Based on experimental data obtained by project partners the models were completed with unique parameter sets and such predictive models are used to explore reactor design options. A pilot-scale reactor model was developed for the wet air oxidation process to aid process development by the FREECATS industrial partner (Adventech). This model linked molecular scale phenomena to reactor scale performance.

Based on the data on catalysts characterisation and kinetic measurements obtained in other WPs, as well as on the available literature data, possible reactions mechanisms were proposed for two cases with the studied catalysts. The detailed mechanistic kinetic models were coded with Matlab, gPROMS and Mathematica and tested with experimental data.

For the oxidative dehydrogenation of propene there are no detailed mechanistic kinetic models for catalytic reaction on metal-free catalysts. Within the project a comprehensive kinetic model was developed, exploring two main hypotheses of the mechanism of the reaction on the metal-free catalysts. This model was initially coded in Matlab, parametrised and a study of main factors influencing the reaction performance (selectivity and yield) was developed. The ODH model was then re-coded in gPROMS to allow parameter estimation on the basis of the experimental data obtained by project partners in WP3. Experimental data were received from CSIC for several doped nano-carbon catalysts. The gPROMS kinetic model was then trained on the experimental data and good model fit was obtained.

In the case of the wet air oxidation reaction, the reaction mechanism is relatively well studied and available in the literature. Using the mass transfer data obtained at UCAM, the experimental data obtained at UPORTO were used to train a kinetic model and then a process model was developed to simulate the behavior of the scaled-up reactor system. In this case the aim was to explore the range of residence times that provide complete conversion of a model pollutant (phenol) in a pilot-scale reactor with the FREECATS developed metal-free catalyst.

For the case of ozonation, a full kinetic model was developed in Matlab and trained on the data obtained at UPORTO. This is the first kinetic model with mechanistic description of catalytic ozonation.

Using conventional hot-disc technique, heat conduction coefficients were measured for a variety of silicon carbide samples produced by SICAT and functionalized or not with CNT (CNRS): samples with different cell sizes, with and without nano-fibrous carbon coating. The important finding of this work was the relatively low conduction of the bulk SiC material, which was unexpected. This finding stimulated more in-depth investigation of the structure of SiC material, beyond what was intended in DoW.

For this, two methods were explored: magnetic nuclear resonance imaging (MRI) and X-Ray tomography. The MRI technique was used at UCAM and X-Ray tomography at Warwick. The MRI technique was shown to be potentially suitable for investigation of flow through SiC, since the material itself gives no signal. However, spatial resolution of the image was insufficient. The X-Ray tomography provided exceptional images of the internal structure of the SiC material and the structure of the free space within the bulk foams. Based on X-Ray tomography images it became apparent the SiC bulk is highly porous, which explains the low heat conduction, in comparison with say, water. Further measurements of heat conduction in the foams with nano-fibrous carbon coating showed a very small improvement in the heat conduction coefficients.

The main finding from this work was the negligible contribution of the material itself in the process of heat transfer. The contribution of fluid in heat transfer is significantly larger and the main focus of the WP thus shifted to a detailed study of hydrodynamics and mixing in the SiC foam: the improved mixing due to the structure of the foams should lead to better mass transfer and good heat transfer via convective mechanisms.

Heat transfer and fluid flow through silicon carbide (SiC) foam material was simulated using commercial packages SIMULIA ABAQUS FEA/CAE 6.12 and ANSYS 14.0. Simulation work was performed with models based on the actual structure of the foam. The geometry models were obtained through x-ray microtomography and processed using SIMPLEWARE package (ScanIP for image processing and $^{+}$ScanFE for mesh generation). The finite element analysis of heat transfer with SiC foams provides data for further development of a SiC foam-based reactor for oxidative dehydrogenation. The CFD model is developed to improve our understanding the mixing of fluids through SiC foam.

Initial results on direct CFD simulation of single-phase flow and FE simulation of heat conduction using geometrical model of the foam structure and foam fluid domain obtained by micro-CT imaging. This model allows highly accurate representation of the actual solid body structure, including internal porosity, and of the fluid domain. Direct simulation of fluid flow and heat conduction using such models is a highly demanding computational problem and is frequently avoided by using periodic model structure, with fewer features. However, our initial modeling results show reasonable values of heat conduction, whereas CFD simulations reveal complex fluid mixing behaviour with apparent transition between fluid elements dispersion modes, which deserves further experimental and theoretical investigation.

Integrating different models into a multi-scale modeling and process simulation requires combining of the models. Within the FREECATS project the only case study that required this level of simulation is wet air oxidation. For this process a kinetic model was developed, mass transfer coefficients were measured, and process model combining kinetics and mass transfer was developed. The process model allowed simulation of water treatment at the pilot scale and these data could be used for process design. The limitation of this model is the absence of a first principles hydrodynamic model. The CFD model is currently a single-phase model, due to the limitations in the state of the art of multiphase CFD simulations. The complexity of the SiC foam structure makes it rather impossible to run full multiphase CFD simulations at present.

Highlights

Key achievements of WP2 include:

- Direct CFD simulation of mixing in complex SiC foam structure using real structure models
- Comprehensive mechanistic model of oxidative dehydrogenation on non-metallic catalysts
- Comprehensive mechanistic model of catalytic ozonation on non-metallic catalysts

WP 3: Catalytic testing - Optimization

The oxygen reduction reaction (ORR)

The ORR performance is significantly influenced by the N-CNT properties such as nitrogen content according to the results. This later is directly influenced by the synthesis temperature as shown in Figure 3-1. Increasing the synthesis temperature leads to a decrease of the nitrogen content, i.e. 4% to 1.9% N for the samples synthesized at 700 and 800°C, respectively, in the N-CNTs samples which directly reflected by a loss of the E_{ON} performance.

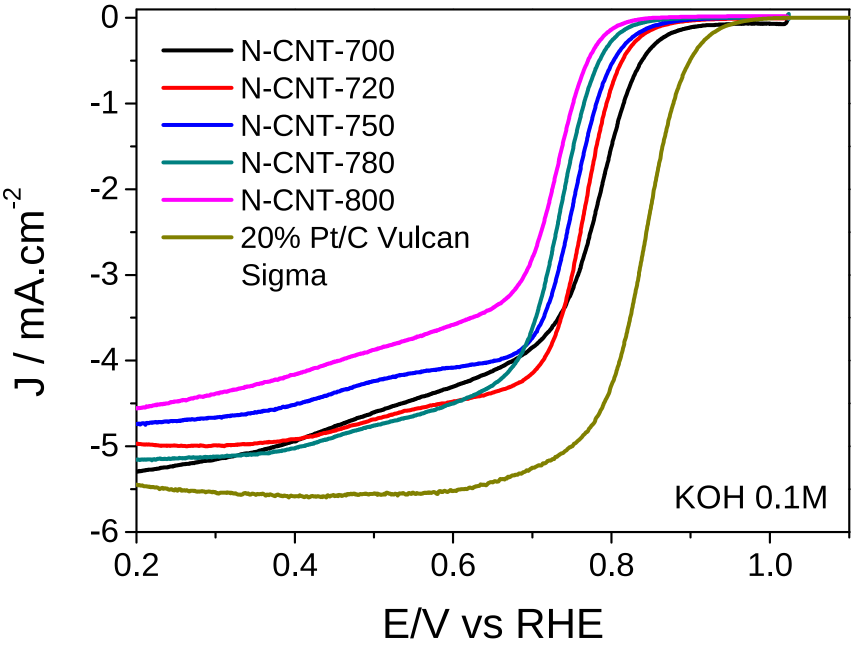


Figure 3-1. Voltammograms recorded on the RDE setup of the Pt/C and the different N-CNTs samples synthesized at different temperature for the ORR experiments.

The results obtained indicate that the N-CNT-700BW (without any chemical treatment after synthesis) displays the highest ORR performance compared to that of the Pt/C catalyst (Figure 3-2). The ORR mechanism on the N-CNT-700BW is close to the four electrons one while for the same catalyst, after chemical treatment to remove the growth catalyst, the lower electrons transfer was observed along with a significant shift of the E_{ON} towards lower value with respect to the Pt/C catalyst. The H_2O_2 intermediate product observed in the Rotating Ring Disk Electrode (RRDE) between the two catalysts also confirms the lower electrons transfer on the acid washed sample.

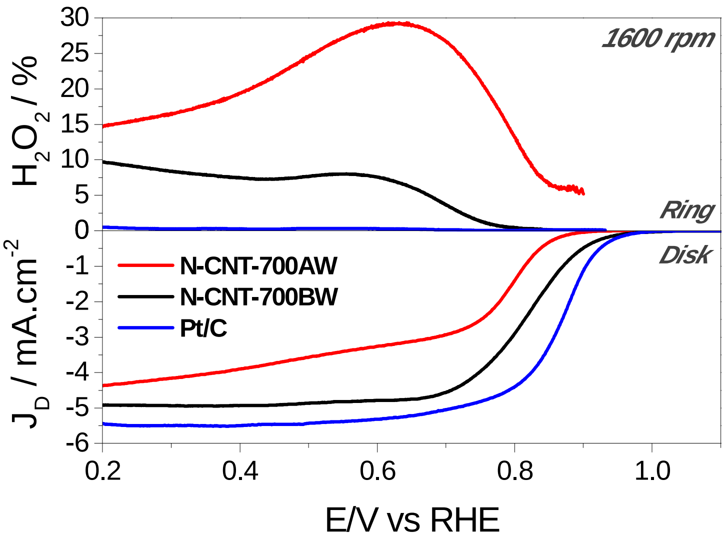


Figure 3-2. Voltammograms recorded on the RRDE setup of the Pt/C, N-CNT-700BW and N-CNT-700AW catalysts for the ORR experiments.

The iron-free N@MC catalyst with 6% N, prepared from a mixture of dextrose/citric acid/ammonium carbonate displays a similar ORR performance to the N-CNT-700BW which confirms the intrinsic ORR activity of the nitrogen-doped carbon active phase for this catalytic process (Figure 3-3A). The high ORR performance of the N@C/SiC (∅ 40 µm) could be attributed directly to the higher nitrogen content in the sample as discussed above for the CVD N-CNTs samples. The iron-free PIL-800/SiC shows the lowest ORR performance which could be attributed to the low dispersion of the nitrogen-doped carbon phase on the SiC support.

The long-term cycling tests indicate that the N@C/SiC displays a higher resistance towards deactivation than the Pt/C catalyst (Figure 3B). However, for the Pt/C catalyst the final ORR activity remained high despite the severe deactivation compared to the N-C-based catalysts.

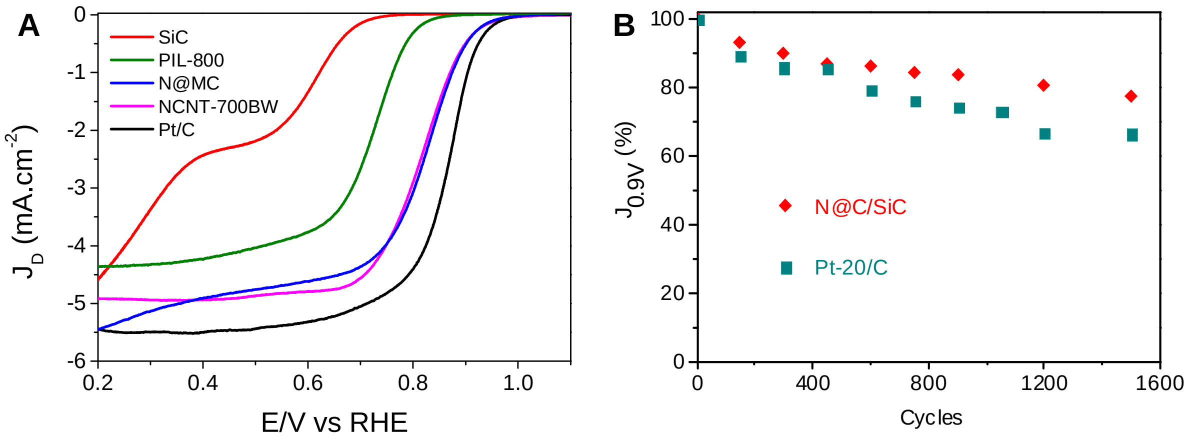


Figure 3-3. (A) ORR performance recorded on the different nitrogen-doped catalysts: PIL-800: iron-free nitrogen-doped carbon phase prepared from the thermal decomposition of a polymerized ionic liquids (PILs) on SiC, N@MC: iron-free nitrogen-doped carbon phase prepared from the thermal decomposition of a mixture of dextrose, citric acid and ammonium carbonate on SiC, N-CNT-700BW: nitrogen-opded carbon nanotubes synthesized by a CVD method and is used as such without acidic treatment to remove the residual iron growth catalyst. The ORR performance is compared with that of the commercial Pt/C catalyst. (B) Cycling tests on the N@C/SiC and the Pt/C catalysts.

Half-cell tests in liquid alkaline electrolyte and fuel cell tests utilizing alkaline PEM membrane technology was performed at CNRS, whereas Prototech performed tests in real acidic fuel cell based on Nafion membrane technology.

For the fuel cell single cell experiments the N-CNT-700BW was selected for bench marking with the Pt/C catalyst (Figure 3-4). It is worth to note that for the single cell test a higher Pt loading catalyst, i.e. 40 wt % instead of 20 wt %, was evaluated.

The results obtained in alkaline solution have demonstrated that the N-CNT-based catalyst exhibits a significantly lower ORR performance per unit weight compared to the Pt-based catalyst with similar catalyst loading. The ORR activity, expressed as power density, of the N-CNT catalyst is about 10 times lower at 25°C and 25 times lower at 75°C. Increasing the N-CNT loading results in a poorer ORR activity due to the problem of diffusion and/or accessibility of the reactant through the membrane layer.

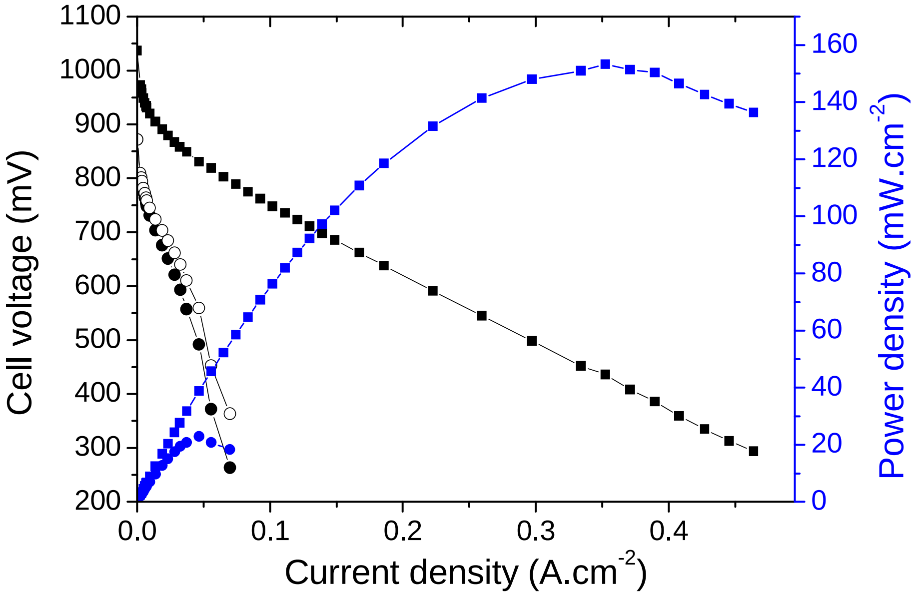


Figure 3-4. ORR single-cell performance between Pt/C and N-CNT-700 catalyst confirming the low ORR performance of this later due to the problem of sheet resistance and layer diffusion.

Prototech tested MEAs prepared with four new metal-free catalysts for ORR in a single cell (acidic) fuel cell test bench utilizing Nafion-based fuel cell technology. The following tests were performed:

- compared the activity of the catalysts in real fuel cell conditions;

- performed screening for the optimal ionomer (Nafion) content in the cathode catalytic layer (using roll-printing layer preparation technology);
- assessed the possibility to improve performance by increasing the ORR catalyst loading;
- assessed the short-term stability of the prepared MEAs;
- ORR electrodes with NTNU NCF20 07/11/13 catalyst were prepared using an alternative method of spray-coating (spraying onto the GDL) in an attempt to improve the oxygen catalytic layer performance
- Finally the performance of MEA was further improved by introducing pore-formers into the cathode catalytic layer. The most promising pore-forming agent was chosen.

Conclusions from from this work are

- The NTNU NCF20 catalyst had the absolute best performance in our tests, demonstrating 2-3 times higher current densities at the same cell voltage. The absolute values of cell power density, however, were much lower than that of standard Pt-based catalysts (initially 9 mW/cm^2 at 0,47 V vs. 500 mW/cm^2 at 0,48 V).
- Attempts to improve the fuel cell performance by increasing the ORR catalyst loading from 2 to 3 and 10 mg/cm^2 resulted in poorer performance instead, indicating problems with the oxygen catalytic layers, most likely mass transport limitations.
- Short-term stability test on the MEAs featuring 2 mg/cm^2 NTNU NCF20 07/11/13 catalyst showed no signs of degradation in 8-9 hours of galvanostatic operation.
- The initial performance of the MEAs featuring NTNU NCF20 catalyst has been significantly improved by changing the technology of layer formation (spraying instead of roll-printing) and introducing pore-forming agents. Both measures improved the mass-transport by increasing the layer porosity. The resulting MEA power density was increased to 25 mW/cm^2 at 0,48 V.
- The NTNU NCF20 catalyst was the most promising, and was selected for fuel cell stack testing and durability tests.

Oxidative dehydrogenation (ODH) of short chain alkanes

The work contains activity and selectivity data and kinetic model for the 3 generations of hetero-doped carbon catalysts. Since none of the consortium member companies are end users of ODH of light alkanes, the midterm review meeting decided not to carry on with upscaling and benchmarking of this process. However, fundamental work on kinetic modelling including verification with experimental data has been performed by the partners as long as resources could permit.

Despite the high selectivity obtained at ODH conditions, the maximum productivities are around 0.3-0.4 Kg h^{-1} Kg cat.$^{-1}$ due to the low conversions attained at temperatures around 673 K. According to our literature survey, the best CNF-based catalyst from our work has propene yields and mass productivities comparable to the best reported results for other carbonaceous catalysts. These values do not reach the industrial target, which is a propene yield around 50% and productivity around 1 Kg h^{-1} Kg cat.$^{-1}$. The main results of the catalytic testing in ODH of propane are that CNF and reduced graphene oxide outperformed CNT in terms of selectivity and conversion. The doping with nitrogen performed in this project led to high activity but very low selectivity, presumably because of the lack of control over the type of nitrogen environment. When the preparation allowed for control over the type of nitrogen, it was not resistant to the harsh conditions of this reaction. The dopant leading to the highest selectivity among all tested was phosphorous using triphenyl phosphine as precursor. The future research should hence focus on these materials, trying to increase the conversion and maintaining the same selectivity.

Advanced oxidation processes (AOP)

The work is centered on testing the performance of the materials prepared in WP1 in the catalytic ozonation (COZ) and catalytic wet air oxidation (CWAO) of organic pollutants. For this purpose the following steps were followed:

i) Screening tests to select a set of promising catalytic materials for specific target pollutants using the samples prepared and characterized in WP1.
ii) Experimental data obtained to support kinetic modelling performed in WP2.
iii) Comparison between batch (catalyst in suspension) and continuous (using structured catalysts) operation, including process aspects, such as catalyst lifetime, operation parameters (temperature, pressure, contact area, flow rates) and operation mode (downflow, steady state vs periodic operation to support the work in WP4).
iv) Experimental data obtained to support reactor modelling performed in WP2.
v) From a process point of view, demonstration of long term activity and stability of carbon materials when employed as direct catalysts in laboratory batch and flow reactors
vi)

Target pollutants

Oxalic acid was selected as model compound to study the catalytic activity of the carbon materials because it is a common final oxidation product resulting from several organic pollutants and it is usually refractory to single ozonation. Since the phenolic compounds are the focus of the project, phenol was also selected to perform the catalytic studies. Some endocrine disruptor compounds (EDCs) were also tested using monoliths, such as, nonylphenol, metholachlor and atrazine. Four surfactants, supplied by Adventech, were also submitted to ozonation in the presence and absence of commercial MWCNT under semi-batch operation.

Several carbon materials in powder form were initially tested: N-doped MWCNTs prepared by CNR using an ex-situ functionalization approach; carbon nanofibers prepared by CSIC; commercial MWCNTs modified by UPORTO in order to introduced O-/S-/N- containing surface groups; commercial MWCNTs submitted to ball-milling treatments by UPORTO (with and without N-precursors); graphene based samples prepared and modified by UPORTO in order to introduce N-containing surface groups; carbonized polyacrylonitrile fibers prepared by UP; and N-doped GO based carbon nanomaterials prepared by CNR. According to the catalytic performance of the carbon samples tested, carbon materials immobilized in structured supports were also tested in the oxidation processes: CNF and N-CNF covered honeycomb monoliths prepared by CSIC; foams prepared by SICAT/CNRS/UP doped with the most promising catalyst tested in the powder form.

The main conclusions obtained from the COZ tests performed with powder materials are presented below:

1. Regarding materials received from CNR, the pristine MWCNT is more effective in ozonation of oxalic acid than the functionalized MWCNT, which may suggest that the catalytic activity of the carbon nanotubes containing nitrogen depends on the type of the nitrogen on the surface of the catalyst.
2. The carbon nanofibres prepared by CSIC showed good catalytic performances in catalytic ozonation using oxalic acid and phenol as model compounds. The original and N-doped CNFs lead to a faster removal of the compounds.
3. The ozonation of oxalic acid and phenol performed using CNTs functionalized by UP with different heteroatoms (mainly oxygen, sulphur and nitrogen containing groups) allowed to conclude that the presence of nitrogen groups leads to a faster removal of the compounds,

whereas the introduction of acidic oxygen containing groups on CNT surface, as well as sulfonic groups, leads to a remarkably decrease of the catalytic activity of the CNTs.

4. The modifications performed by UPORTO on undoped carbon nanotubes by ball-milling have a significant influence on their textural and morphological properties, but the chemical surface is not changed. The surface area increases, whereas the particle size of agglomerates decreases with the ball-milling treatment time until 240 min for 15 vibrations/s. Ball-milling showed to be an effective method to increase the performance of MWCNT as catalysts in ozonation process.
5. N-doped carbon nanotubes prepared by ball milling by UP showed high catalytic activity in COZ. The dry treatment produces samples rich in nitrogen and revealed good catalytic performances in the catalytic ozonation of oxalic acid.
6. Concerning the graphene prepared and modified by UP, it was concluded that graphene treated with melamine significantly improves the mineralization of oxalic acid and phenol.
7. The influence of the surface chemistry was evidenced by comparison of carbonized fibers prepared by UP, for which the surface area is negligible. The presence of nitrogenated groups on the surface, particularly pyridinic (N6) groups, favours the oxidation of oxalic acid. The important role of nitrogenated and basic oxygenated surface groups on the reaction mechanism was evidenced.

Concerning the catalytic tests performed with catalysts in structured form under continuous operation, the main conclusions are:

CNF covered honeycomb monoliths prepared by CSIC

1. The best results are obtained when using a N-doped CNF active phase, and a high channel density honeycomb as supporting structure. Combining both is thus expected to lead to an optimized catalyst for scale-up of this process.
2. It should also be noted that whereas phenolic treatment via catalytic ozonation is generating even more toxic intermediate species (an opposite behaviour is expected for higher conversions), it clearly improves the biodegrability of the initial solution.

Foams produced by SICAT and functionalized by CNRS

1. The functionalization of the foams with CNTs improved their performance in catalytic ozonation of oxalic acid, obtaining a conversion similar to those obtained with the monoliths supplied by CSIC.
2. However, there is fiber loss from the foam structure during the oxidative process, even after exposing the foam to ultrasonication. Thus, it should be ensured that carbon fibers will not be released during ozonation. The use of nitrogen-doped carbon composite N@C, synthesized by a new method developed conjointly by the CNRS and CNR, as a solid glue to anchor the N-CNT on the SiC foam surface allows us to resolve the problem linked with matter loss during operation.

In agreement with the results obtained in the lab-scale systems, a set of recommended optimal operating conditions for the continuous catalytic ozonation tests were proposed using the catalyst N-doped CNF coated monoliths/ N-doped CNF coated SiC foams (with no release of CNF)

For continuous CWAO, N-doped CNTs, obtained by ball milling of CNT with melamine, showed the best results among the powder catalysts tested on phenolic compounds. A deactivation phenomenon was observed. SiC foams were covered with the best catalyst tested in the powder form by CNRS and were also tested as catalysts for the continuous CWAO process. Comparing the results of the foams with those obtained with the powder catalyst at the same operating conditions, it is noticeable that the phenol removal was higher with the foam. After the CWAO process, a slight decrease of the biodegradability of the effluent was achieved using the SiC foam recovered with N-CNTs. Two CNF coated monoliths received from CSIC were also tested as catalysts for the continuous CWAO process. Comparing the performance of the foams and monolithic catalysts tested, better results were observed for the foams.

Catalytic experiments under batch and continuous operation were performed to support kinetic modelling of the processes and reactor modelling. In COZ, hydraulic characterization of the reaction system using the CNF covered honeycomb/monoliths prepared by CSIC and foams produced by SICAT/CNRS were study. It was evaluated two-phase and three-phase systems, gas feed bubble size, CNF loading, channel densities, foams porosity, nitrogen groups on the CNF, contact area. In CWAO, concerning the good catalytic results obtained with the sample CNT-BM-M (in powder form and supported on SiC foam), kinetic studies on CWAO process were performed in batch and continuous operation, using phenol as model pollutant. Influence of the stirring rate, temperature, dissolved oxygen concentration and initial phenol concentration was evaluated. The kinetic studies carried out show that there are several parameters influencing the CWAO reaction, but their influence is different for the batch or continuous operating reactors, and consequently, the results of one of the reactors may not be used to extrapolate the results of the other.

In agreement with the results obtained in the lab-scale systems, a set of optimal operating conditions were recommended for the continuous CWAO tests using the catalyst containing N-doped CNF coated monoliths/ N-doped CNF coated SiC foams (with no release of CNF).

Highlights

- The initial performance of the MEAs featuring NTNU NCF20 catalyst has been significantly improved by changing the technology of layer formation (spraying instead of roll-printing) and introducing pore-forming agents. Both measures improved the mass-transport by increasing the layer porosity. The resulting MEA power density was increased to 25 mW/cm^2 at 0,48 V.
- Regarding ODH of propane, carbon nanofibers and reduced graphene oxide showed better performance than carbon nanotubes. The doping with nitrogen performed in this project led to high activity but very low selectivity. The dopant leading to the highest selectivity among all tested was phosphorous using triphenyl phosphine as precursor. Although the results are not very far from industrial targets in terms of yield, they do not meet industrial requirements in terms of durability of the catalyst.
- Regarding AOPs, the screening tests with N-doped carbon materials, in powder form or supported in a macrostructure, using different target compounds revealed the positive effects of N-surface groups directly linked to the carbon nanotubes surface; SiC foams as structured catalysts presented a better catalytic performance than monoliths, being selected for the two AOP processes.
- The synthesis methods used for preparing the N-CNTs/SiC composite require the use of relatively low cost and non-toxic raw materials along with lower energy consumption for use in AOP processes.

WP 4: Validation of materials and process in integrated micropilot plant

The objectives for WP4 were to scale up catalyst synthesis, validate performance and to generate technical data for benchmarking against conventional PGM catalysts.

The optimal operating conditions have been identified using results from testing and/or data extracted from literature. For fuel cells, operating conditions carried out on single cells in both acidic (Prototec) and alkaline (CNRS) media have been used. For AOP, operating conditions for continuous catalytic wet air oxidation (CWAO) and for continuous catalytic ozonation (COZ) have been identified. UPORTO has produced several grams of the sample CNT_BM_M, which was found in WP3 to provide the best catalytic performances in the AOPs tested. After a work to strongly anchor this active phase onto SiC foams, the resulting material has presented better performances than the previous tested catalysts. Regarding the COZ process, the catalytic SiC foams have not showed significant deactivation (tested for 34h). The regeneration of the CWAO catalyst revealed that a thermal treatment at 600ºC under nitrogen flow allows regeneration of the catalysts although a significant deactivation of the catalysts during the first 20 h of operation is observed. After a scale-up study and a production of the NTNU_NCF20 catalyst, which was found to provide the best performances in ORR, Prototech produced a 10 cell fuel cell stack. Stability tests of ORR catalysts have been performed in a FC stack for 400 hours and for CWAO in continuous flow for 100 hours.

The aim was to identify the critical properties of both catalyst and reactor design to get relevant results from testing at the pilot scale. Target of catalyst design was needed as guideline for WP1 (Material preparation and characterization), for selecting the best candidates for scale-up and for producing the structured catalysts to be used in pilot tests. For fuel cells, the reactor design was fixed by the existing set-up available at the end user (Prototech). For other applications considered in the project (AOP and ODH), a review of (i) lab scale operating conditions used in WP3 and (ii) industrial constrains of each application has been presented. Target specifications for catalyst and reactor design for pilot scale have been proposed after discussing limitations coming from kinetics and hydrodynamics (WP2) and the final industrial constrains. Due to this work, the decision was taken at M24 that work on scaling-up of the ODH process will be given less priority.

The best catalyst candidates for fuel cells and AOP were identified and selected for scale-up:
Fuel cells: For fuel cells, results obtained on single cells have been presented in acidic or alkaline media. The tested catalysts (N-CNT-720, NTNU_NCF20, N-CNF-Fe750, N-CNF-Fe/EG650 or N-CNT-700) have been compared to commercial Pt-based catalysts. According to the results and conclusions, all N-doped CNT catalyst tested in ORR single cells show significantly lower performances than Pt-based catalysts at similar loading. Utilization of usual catalyst deposition techniques led to mass-transport limitations when increasing the CNT catalyst loading, and couldn't be considered promising for the scale-up at that time.

AOPs: For AOP, the preliminary catalytic tests performed for continuous catalytic wet air oxidation (CWAO) or continuous catalytic ozonation (COZ) have been presented for selected samples based on the results of WP3 (CNT-powder, CNF-monoliths or CNF-Foams). For the COZ process, the N-doped CNF supported on high channel density honeycomb showed the best results whereas the N-doped CNT supported on foams showed promising performances although showing a high level of CNT leaching after the first sonication step. For the CWAO process, the performances using N-doped CNT obtained after ball milling of commercial CNT with melamine (CNT-BM-M) showed very good results but also a rapid deactivation.

Concerning the ORR reaction, Prototech developed a new strategy to prepare MEAs with the use of pore formers that improved the porosity and thereby the mass transport, resulting in improved performances. At M30, the decision was taken to go to the scale-up with the catalyst giving the best results i.e. the NTNU_NCF20.

Concerning the AOPs, the work was pursued by CNRS and UP trying to solve the CNT leaching. Thanks to the method developed by CNRS and CNR, foams decorated with CNT-BM-M *via* a carbon glue coating could be obtained and showed improved performance.

The work concerning the catalyst scale-up has been divided into 4 main steps carried out by different partners:

1) SICAT used its existing demo-plant for the production of SiC or C based macroscopic structures to be used as host structures as designed in task 4.1.SICAT has produced SiC foams as host for catalysts decorated with N-CNT from CNRS. The catalysts have been tested at UPorto in AOPs. The method used to produce the foams and the issues encountered for specific shapes and cell sizes have been described in details (D5.2).

2) The preparation of N-CNTs decorated SiC foams as macroscopic metal-free catalyst and the detailed characterization of the different samples are described in WP1. In summary, the best N-CNTs/SiC (pellets, ring and foam) composites are obtained with a growth catalyst containing 3 or 5 wt% of iron and for a reaction temperature of 720°C. The N-CNTs total loading cannot be exceeded 20 wt% as at higher N-CNTs loading the macroscopic shape of the composite becomes fragile leading to the breakdown during the transport and handling. In a parallel study, CNRS and CNR have actively contributed to the production of N@C/SiC catalysts (starting from the SiC scaffolds made available from SICAT) as described in Task 1.3. The synthesis method is based on the use of an aqueous precatalytic solution (prepared from dextrose, citric acid and ammonium carbonate) to be deposited as a homogeneous N-rich layer on the SiC macroscopic host structure. This methodoly has been developed to overcome the problem of mechanical resistance of the final composite and also to avoid the use of iron in any synthesis step. The synthesis method developed allows the partners to produce N@C/SiC in a large amount as a proof-of-concept of the viability of the method for mass production. The N@C/SiC pellets (1 x 2 mm) have been prepared in a large scale, i.e. 0.5 kg, in order to assess the feasibility of the synthesis method. The as-synthesized catalyst has been characterized by different techniques and the results obtained confirm the complete reproducibility of the method for producing large amount of catalyst. The macroscopically shaped SiC-based catalysts have been successfully employed for performing ORR and AOP at CNRS and UP, respectively.

3) UPORTO has produced several grams of the sample CNT_BM_M, which was found in WP3 to provide the best catalytic performances in the AOPs tested, and they were used by CNRS to prepare several sets of N_CNT/SiC foam composites using an optimized method based on the methodology described in the previous point. These macro-structured catalysts were used in COZ and CWAO under continuous operation.

4) NTNU has produced 7.1 grams of catalysts (NTNU_NCF20) for the MEAs produced by Prototech. Whereas a first reactor could produce up to 2g of catalyst, work has been performed at NTNU in order to scale-up the production. Promising results have been obtained to produce 20g of catalyst per batch (scale-up by a factor of 10) and still give a homogeneous product with the same performance. This catalyst has been tested in a 10 cell FC stack of 75 cm^2.

Concerning deactivation/durability test in COZ, the foams and monoliths studied practically does not show deactivation after 34 h and 100 h, respectively, under continuous operation. The long duration CWAO experiments revealed a significant deactivation of the evaluated catalysts during the first 20 h; after that their catalytic performance remains practically constant.

In the case of COZ, regeneration experiments were not performed since it was verified that the tested catalyst practically does not deactivate during the evaluated period (34 h for foams and 100 h for monoliths). The regeneration of the most promising materials was evaluated in CWAO. Regeneration tests were carried out on two catalysts: one under powder form (CNT-BM-M) and another under the structured form i.e. the CNT-BM-M prepared by UP and supported on the 30 and 20 ppi SiC foams (SICAT) by CNRS by different impregnation methods.

The regeneration approaches applied revealed that the thermal treatment at 600°C under nitrogen flow allows the best regeneration of the catalysts; nevertheless a significant deactivation of the catalysts during the first 20 h of operation is also observed.

The scale-up of the ORR catalyst led to the production of 11 large 75 cm² MEAs using the NTNU_NCF20 catalyst. Prototech has successfully utilized the novel metal-free N-CNF catalyst for ORR at the cathode of a 10-cell Nafion-based fuel cell stack. The performance of this stack has directly been compared to the performance of N-CNF-based cell with a Pt-based cell in the same stack. The difference in power density was at least 8,5 times (100 mW/cm^2 to 11,7 mW/cm^2).

The long-term durability testing of the stack was performed for 400 hours, and the integral voltage degradation rate of the stack at constant current of 0,02 A/cm^2 amounted to 162 µVh^{-1}. It is likely that insufficient humidity of the cells far from the middle of the stack was a major factor leading to degradation. The curves at “400 hours” graphs also show very low open-circuit voltage of cells 3, 7 and 10, suggesting thinning of membranes and/or pinhole formation (see Figure 5.5, D4.7). The post-mortem analysis of the stack should shed more light on the degradation processes inside the stack; *this work is beyond the scope of the Project and will be done separately*.

To conclude, the N-CNF catalytic material is still a promising ORR FC catalyst, and its development should be continued to identify the active sites and the mechanisms of its activity, address the mass-transport limitations at the FC electrode and alleviate the FC degradation.

The decision to go for the 10-cell stack was made at the 4th Consortium meeting. The arguments were that considerable resources have been used by Prototech to perform the single-cell fuel cell tests. Besides, the 30+ cell stack available at Prototech was used for another type of membranes (high-temperature PEM, based on phosphoric acid–doped polybenzimidazole). At the time of the Project planning it was unclear, but became obvious later that this type of fuel cell is unsuitable for the N-CNF catalyst due to high operating temperature (160 – 180 °C), therefore, a new stack was needed. To finish, the active area of the “old stack” with 30 cells was 45 cm^2 per cell, while the new 10-cell stack was 75 cm^2/cell, making a total of 750 cm^2 for the stack, more than 50% of the originally planned active area (1350 cm^2). The performance/durability test of the ORR catalyst does not really benefit from increasing the cell number in the stack above 10 at such an early development stage. As a consequence, the results obtained have the same relevance.

Highlights

- Catalysts have been selected for further testing for ORR, COZ and CWAO
- A method has been developed to decorate foams with CNT-BM-M *via* a carbon glue coating method which showed improved stability.
- The optimal operating conditions have been identified for ORR and AOP
- Stability tests of ORR catalysts have been performed in a FC stack for 400 hours, and for CWAO in continuous flow for 100 hours.

WP 5: Technical, Economic and Ecologic assessment for scale-up

The objectives of WP5 are to evaluate sustainability metrics for the developed new catalytic processes and benchmark against conventional (PGM) catalytic technologies. The introduction of noble metals on the surface of both CNTs (CNT-O and CNT-BM-M) led to a decrease of their performance as catalysts in ozonation of oxalic acid. In the case of CWAO the CNTs impregnated with platinum exhibit similar phenol removals as correspondent supports, but produce higher amounts of toxic intermediates. The rare earth metal based catalysts are shown to be clearly inferior in both studied AOP processes.

An economic and market application assessment of the new metal-free N-doped nanostructured carbon catalyst for ORR reaction in a PEM fuel cell has been performed using a case of 1 kW backup power unit. Capital and operating expenses combined for the projected lifetime of the system were compared and the assessment clearly shows that the performance and durability of the new catalyst must be improved to become competitive on the market. The key focus of FREECATS is on reduction in use of resources and replacement of noble metals. The results of the life cycle study indicate a significant reduction in environmental impacts due to removal of noble metals.

This benchmarking of the metal-free catalyst in view conventional ones is very helpful for selecting the future best candidates and/or processes for scale-up. Technical data are extracted from literature and/or from previous studies in order to compare and further optimize the novel catalysts. For fuel cells, a benchmark of Polymer Electrolyte Membrane Fuel Cell (PEMFC) performance is presented based on data collected on commercially available Membrane Electrode Assembly (MEA) products. For Advanced Oxidation Processes (AOP’s), a comparison between the different processes and catalysts used by Adventech is realized. The efficiency of the processes on lab-simulated industrial wastewater is compared to results obtained on real water (from olive mill process, winery and landfill leachate).

Fuel cells: The data show that the performance of commercially available PEM MEAs depends greatly on the gas pressure and humidity. At 0.7 V the current density is ranging from 0.49 to 1.2 A/cm^2 at beginning of life, with a most common value of 0.6 A/cm^2. It is worth mentioning, that this current density decreases substantially with MEA ageing (see Figure 6). For example, for Primea 57, the beginning of life value of 0.68 A/cm^2 at 0.7 V turns into 0.4 A/cm^2 at approximately 1000 hours of accelerated degradation testing. During steady-state PEM FC operation the performance degradation usually is within 10 μVh^{-1}, with an average of 5.3 μVh^{-1}.

AOP: Several scientific studies were performed to test the performance of different catalysts applied in Advanced Oxidation Processes (AOP’s) to treat the industrial wastewaters. In most of the cases, the studies were performed with a lab-simulated industrial wastewater which has a different behavior than the real one. In fact, the lab scale experiments achieve good performances in short/medium term tests, but the long term operation with real wastewater at industrial scale shows that no catalyst have a good performance, mainly in what concerns the lixiviation of the active part in the processes under NTP (Normal Temperature and Pressure) conditions. With various technologies tested, it is concluded that there are three primary factors to their application: removal efficiency of organic matter, increased biodegradability and ease of implementation technology.

Additionally, catalytic performance comparison of the metal-free samples, prepared during the FREECATS project, with the performance of the traditional metal supported samples in the AOPs (CWAO and COZ) was studied. For that purpose, the N-doped sample which presents the best catalytic results (CNT-BM-M), as well as the original carbon material used to its preparation (CNT-O), were impregnated with a noble metal (platinum) by incipient wetness impregnation method producing two samples (1%Pt/CNT-O and 1%Pt/CNT-BM-M, wt%). As an example of rare earth metal based catalyst, cerium oxide was prepared by precipitation method (CeO_2 sample). After that, the prepared samples were assessed as catalysts in CWAO of phenol and in COZ of oxalic acid. Concerning the last AOP, CNT impregnated with other noble metals, such as palladium and ruthenium (1%Pd/CNT-O and 1%Ru/CNT-O, wt%, respectively), were also tested. The rare earth metal based catalyst (CeO_2) clearly presents the worst catalytic performance in both studied AOP processes (CWAO and COZ). Concerning samples impregnated with noble metals, their introduction on the surface of both CNTs (CNT-O and CNT-BM-M) led to a decrease of their performance as catalysts in ozonation of oxalic acid. In the case of CWAO, the CNTs impregnated with platinum exhibit similar phenol removals as the correspondent supports, but produce higher amounts of toxic intermediates. Thus, it can be concluded that CNT-BM-M catalyst may be able to replace the metal catalysts in both AOPs studied.

For fuel cells, the way to proceed for a scale-up is described and the steps and issues encountered during this set-up are presented. For AOP, an industrial plant for the continuous catalytic wet air oxidation (CWAO) is documented in the project. The design of the reactor is described in detail taking into consideration the catalytic results and the severe operating conditions of the process. Some possible improvements are also mentioned. Regarding the catalytic support scale-up, the SICAT process is described in detail. A foam design is proposed to fulfil the CWAO reactor after feasibility work to obtain fully open cells foams with controlled dimensions.

Scale-up of the MEA production was done during the period January-February 2015. The 7,1 g batch of the NTNU_NCF20 catalyst from NTNU was received and processed into catalytic ink. The detailed procedure and materials list is described in section 5.3 of the Deliverable 4.7. In order to scale up from the small single cells, technology of applying the catalytic ink to much larger electrodes had to be validated. The problem which usually appears during this step is a highly non-uniform coating, because for small single cells the ink is usually applied by hand-spraying using spray gun. A solution to this is utilizing automated coating machines. A screen-printer machine was recently obtained by Prototech, and they have undertaken a study to validate the applicability of screen-printing technology for the large MEAs production using the established ink formulations. For the ORR electrode the screen-printer produced less porous layer (even visually) than spraying and, as expected, sprayed electrodes performed much better. There was no room in this Project to re-develop the ink formulation to suit for the screen-printing, and therefore all the large electrodes for the fuel cell stack were produced by a combination of screen-printing (HOR) and manual spraying (ORR).

The case study chosen to assess the performance of these new catalysts was the treatment of a synthetic wastewater containing phenols, which aims to simulate an olive mill wastewater. The performance of the new catalysts were measured through the fulfilment of EU directive 91/271/EEC concerning BOD5 and COD, biochemical oxygen demand and chemical oxygen demand, respectively, specifications that should be lower than 25 mg/L and higher than 125 mg/L, respectively, or by the increasing of biodegradability represented by a ratio of BOD5/COD higher than 0,3. Both catalytic ozonation (CO) and catalytic wet air oxidation (CWAO) are processes that can be used for olive mill wastewater treatment. CWAO is the selected technology for scale-up due to the possibility that this process could offer to instantaneously increase Adventech's market.

The performance of catalysts was evaluated addressing the maximum phenol removal and the results showed that CNT_MB_M foam 30ppi catalyst presented a good performance under operating conditions of 160ºC and 8 bar of oxygen partial pressure. The design of an up-scaled plant was then performed, considering a volumetric flow of 0.5 m3/h, reactor temperature of 160ºC and oxygen partial pressure of 8 bar, using the CNT_MB_M foam 30ppi catalyst. After some time of usage, the catalyst has to be regenerated.

From an industrial point of view, the most viable and challenging industrial process was the CWAO. As a consequence, the reactor design has been described for a CWAO industrial process using beta SiC foams as a support. All the equipment needed to set up this plant and the P&ID have been described. Based on the data obtained in WP4, a full industrial project of the CWAO technology was done. The project was performed in a 3D CAD software including piping, electrical and pneumatic project. Improvements to optimize the entire process have also been proposed.

The first stage of the process is the cutting of the polyurethane (PU) foam in the desirable dimensions. This cutting can be performed with a hot wire. The cutting machine is computer-controlled. Thus, through cutting software, the program required to create the desired PU foam is generated by the engineer and the data are transmitted to the hot wire via a controller. This technology is widely used to cut the PU foam and is available at SICAT facilities. Regarding the reactor dimensions (Ø 159mm), this cutting step of the PU template can be envisaged at SICAT as the apparatus has capability up to 600mm in diameter. The second step of the process is the infiltration of the PU foam with a slurry containing the SiC precursors, i.e. basically a silicon-containing resin. Once the PU template is infiltrated, the foam passes through a series of rolls to get a homogeneous distribution of the slurry through the entire volume and to remove any excess of slurry. Then, the pieces are blown using compressed air to obtain fully open cell foams to minimize pressure drop in the final catalyst. The maximum foam dimensions to be impregnated are linked to the size of rolls and homogeneity of the slurry distribution along the roll length. With the envisaged reactor size and from technical point of view, the production of foams with 159mm diameter has been demonstrated at SICAT facilities. Finally, the two last steps are the drying and the thermal treatment performed near 1400°C to convert the precursor formulation into SiC. Regarding the thermal treatment, SICAT has developed a large expertise in producing SiC. As a consequence, a larger development up to industrial scale wouldn't be an issue.

Economic and market application assessment for WAO

Catalytic wet-air oxidation (CWAO) is an advanced oxidation process (AOP) for wastewater treatment containing complex, hazardous and toxic compounds from different industries, such as pharmaceutical, chemical, textile, etc. The interest in AOP is increasing over years due to the ineffectiveness of biological treatment in decomposing such difficult compounds. However, a good performance of this process is related to high cost catalysts, usually precious metal based, which inhibits a more frequent use of CWAO. Additionally to the catalyst cost factor, the destruction of this type of contaminants requires severe operating conditions, such as high temperature and pressure, which reinforces the importance of safety management. During the project of any industrial process, it is common practice the development of process flow diagrams (PFD) as well as piping and instrumentation diagrams (P&ID). While PFD only show the main equipment of a process and the most important variables, like temperature and pressure of a stream, a P&ID goes further in the description of the overall process including all instrumentation needed, control loop and software functions. An economic analysis is another important factor when setting up a new facility. Even at an early stage of the project it is recommended to determine the estimated CAPEX and OPEX cost in order to have an idea of the amount of money needed to invest in equipment, as well as the expected operation expenses..

CAPEX also includes any service needed such as project and engineering services, as well as wages paid to employees engaged to put the asset in use. Operational costs, or OPEX, concerns to the costs of on-going, day-to-day basis expenditures to keep the business, system or equipment running. Business OPEX can be divided in two categories: Marketing expenses and Administrative expenses.

The first category is directly related to the selling of a product or service, while the second one is not directly related but is crucial for the business. OPEX costs include also wages, licensing fees, office expenses, small repairs, raw materials and utilities, among others. In this particular case, OPEX costs are calculated for a set of equipment, therefore no marketing or administrative expenses are included. Raw materials were also not considered in these costs because only air is needed and it comes from atmosphere.

For CWAO the 1%Pt/CNT-O and CNT-BM-M catalysts exhibit similar phenol removal. Concerning the TOC removal, 1%Pt/CNT-O presents a better performance. The production of the toxic intermediates analysed (benzoquinone and hydroquinone) was lower with the CNT-BM-M catalyst which means that this catalyst may be able to replace the metal catalysts, especially if the CWAO treatment is to be used as a pre-treatment before a biological treatment.

COZ: Among all catalysts studied the rare earth metal oxide based catalyst (CeO_2) clearly presents the worst performance. Concerning samples impregnated with noble metals, it seems that the introduction of noble metals on the surface of CNT (1%Pt/CNT-O, 1%Ru/CNT-O, 1%Pd/CNT-O samples) led to a slight decrease of their catalytic performance. The same trend is observed when the nitrogen groups are present in the surface of the carbon support (1%Pt/CNT-BM-M, in which CNT-BM-M is used as support). The CNT-BM-M catalyst exhibit the best catalytic performance.

Economic and market application assessment for fuel cell stack

Economic and market application assessment for the fuel cell system utilizing the new doped nanostructured carbon catalyst is based on calculating the integral cost of ownership. An integral cost of ownership is the sum of all capital and operational expenses that one has to have when using a fuel cell system during its lifetime. These costs are calculated based on the current fuel cell market data, performance and degradation data obtained in this Project (described in Deliverables 3.2, 4.2 and 4.7) and literature and commercial data available for the state-of-the-art fuel cell systems (Deliverable 5.1). The final assessment of the potential of this technology, its viability and user acceptability for fuel cells takes into account the obtained cost values and general knowledge of fuel cell market and technology.

A fuel cell system consists of one or several fuel cell stacks and auxiliary components, usually referred to as balance-of-plant (BOP): pump(s), filters, tubing, humidifiers, control, sensors, electrical interface etc. Since no system was intended to be built around the fuel cell stack tested in this project, the cost of the BOP components is estimated as a percentage of the FC stack cost (based on experience from SotA systems). The model fuel cell system is a 1 kW auxiliary power unit designed to provide backup power.

The analysis shows that the Nafion membrane accounts for half of the total MEA cost, and the ORR catalyst makes up a total of only 9%. When the MEAs are mass-produced, the total cost of goods contained in the MEA tends to the raw materials cost, and here the Pt cost really shows itself, making the ORR catalyst a total of 30% of the MEA cost. Hence, it is evident that the N-CNF catalyst really has potential for cost reduction, as it’s cost is only a fraction of the Pt cost. It accounts for about 3 % of the MEA cost in the as-built scenario and about 0,003 % in the mass-produced scenario. The total MEA cost is therefore reduced as well, so MEAs featuring N-CNF ORR catalyst can be almost 30% cheaper than the SotA ones. However, with the current performance obtained from the fuel cell testing in FREECATS, each MEA provides less power than a SotA MEA, so one has to use more MEAs to get the same power output from the FC stack.

The amount of cells needed for the N-CNF stack depends on the catalyst (MEA) performance. For the calculation an increase of about 6,5 times in comparison to the test results obtained in the project was assumed (from 3,6 W/cell to 23,8 W/cell). It shows the important point that the performance of the novel MEAs featuring the new catalyst needs to be reasonably close to the performance of the SotA MEAs, otherwise the capital expenses for stack components outweigh the gain in the price of a single MEA.

The assessment of total ownership costs shows that both capital costs and operation costs of the system featuring the novel N-CNF catalyst (which performs lower than the SotA Pt catalyst and degrades faster) are higher than that of the SotA system. The capital costs are higher due to the lower cell performance, which requires one to have more cells, multiplying the amount of stack structural elements. The operation expenses are higher because of the lower efficiency and higher degradation rate. This result leads to an important conclusion: Any fuel cell catalyst aimed as a platinum or Pt-group metal replacement has to yield a similar fuel cell performance (even with much higher loading) to be competitive on the market (at least while platinum is still available). Specific threshold numbers, however, depend on the application and will vary greatly with the power rating required (from few watts to tens and hundreds of kilowatts) and expected lifetime. It is possible that a system of a few watts (portable battery charger) might benefit from the new catalyst earlier due to larger possible price margins and lower capital cost per unit.

Environmental, Risk and Safety Assessment

A of key aspects in development of novel technologies is their sustainability, which includes minimal environmental impact and risk to humans, economic potential and positive societal impact. This task describes the proposed environmental and cost benchmarking methodology for the FREECATS developed catalysts and processes. The purpose of the environmental and cost assessment is to obtain numerical benchmarked data to support the decision making process for post-project further development and ultimate adoption of the developed technology. Since environmental and cost assessments of novel products and processes are mature methods, it is proposed to utilise the accepted methods of multi-indicator assessment within gate-to-gate system boundaries, followed by LCA and eco-efficiency assessment. Sustainability metrics data related to nitrogen-doped carbon nanofibres was performed by University of Cambridge using the data on the synthesis of carbon nanofibres provided by NTNU. In the FREECATS project the main objective was to eliminate noble metals from catalysts and develop new materials containing non-metal dopants, while retaining catalytic activity and selectivity. For environmental assessment of the impact of transition from noble metal to non-noble metal-based catalyst the most important consideration is the removal of all the impacts associated with mining and refining of noble metals and manufacture of noble metal-based catalysts. For this reason within FREECATS a new life cycle assessment case study was developed and compared directly with the previous case study. Here we compare manufacture of Pd-CNF/SMF (Pd deposited on carbon nanofibres, deposited onto sintered metal fibres) with the manufacture of N-CNF (nitrogen-doped carbon nanofibre) catalysts, produced by similar CVD methods.

LCA is best used as a comparative method, since absolute values of impacts are too inaccurate due to multiple assumptions used in developing life cycle inventories. The comparative life cycle assessment performed here is a cradle-to-gate evaluation that was designed to reveal the contribution of raw materials on the environmental impacts from the process. In this case the new LCA case study for the nitrogen doped carbon nanofibres shows the significant reduction in the impacts compared to the metal-based catalyst. This illustrates the significance of eliminating noble metals in catalysts not only from the point of view of cost and availability, but also from the point of view of environmental impact of technology.

Highlights

- A 10-cell fuel cell stack was produced for demonstrating feasibility for ORR scale-up.
- An industrial CWAO plant was designed and on the basis of catalytic performances obtained during the project.
- 400 pieces of 159*30 mm foams could be produced with success by SICAT.
- The CNT-BM-M catalyst outperforms PGM catalysts and may be able to replace the noble metal catalysts in both studied AOPs.
- An economic and market application assessment of the new metal-free N-doped nanostructured carbon catalyst for ORR reaction in a PEM fuel cell has been performed.
- The performance and durability of the new ORR catalyst must be improved to become competitive on the market.
- The life cycle study shows significant reduction in environmental impact due to replacement of noble metals.

WP 6: Dissemination, training and exploitation

FREECATS results are disseminated through publications, conference contributions, and our website (www.freecats.eu). In turn these activities will facilitate exchange of information between the FREECATS consortium and potential end-users of the materials and processes – other than those already involved in the project and with the wider community. A large dissemination event was organised in Trondheim in June 2014: *The 6th International Symposium on Carbon for Catalysis, CARBOCAT-VI.* An impressive number of publications and presentations have emerged from the project work. Plans have been drawn up to commercially exploit the catalyst technology developed within the project and possible markets, prices and distributors. 6 PhD candidates are being educated within the project framework at UPORTO, NTNU and CSIC. In addition, 21 post-doctoral fellows have been working in the project at CSIC, CNR, CNRS, UCAM, UP, Warwick and NTNU. They will be ambassadors and dissemination vectors of the knowledge built in FREECATS. It is also important to observe that the gender balance among the PhD/postoc candidates is relatively good; 11 female, 16 male. Several master projects (5) have also been carried out in collaboration with FREECATS.

A business plan for the AOP using the new developed metal-free catalyst has been produced. The business plan includes the assessment of costs of goods sold and materials consumed, the prevision of sales and services provision. These plans allowed the determination of the income statement and the forward estimates, as well as the cash-flow evolution during the five years from 2016. From these business and financial plan it was possible to conclude that the project is profitable, with positive cash-flow after two years of activity.

The new metal-free catalyst developed under the FREECATS project may be used in both Catalytic Ozonation (COZ) and Catalytic Wet Air Oxidation (CWAO). The main advantages of the use of the FREECATS catalyst are the absence of expensive metals, lower cost and equivalent efficiency. As outlined in WP5, the metal-free structure of the new catalysts avoid the fluctuation on price caused by the frequent variation in price of rare earth metals and PGM commonly used in these kind of conventional catalysts. The lower cost of the new catalyst associated to equivalent efficiency improves the competitive edge of both AOP's technologies.

In addition, the requirements needed for the new N-CNT catalyst to be competitively commercialised for the FC stack is highlighted. The market application assessment performed led to the following conclusions:

- The assessment clearly shows that the performance and durability of the new catalyst must be improved for it to become competitive on the market
- A more general conclusion was made: any fuel cell catalyst aimed as a platinum or Pt-group metal replacement has to yield a similar fuel cell performance (even with much higher loading) to be competitive on the market, at least in the situation where platinum is still available
- The N-CNF catalytic material is still a promising ORR FC catalyst, and its development should be continued especially because of the limited Pt resources and their inevitable depletion with the growth of the fuel cell industry. It may also be that a combining N-CNF and PGM in the catalysts can lead to significant reduction of PGM content in fuel cell catalysts.

Highlights

- A large dissemination event was organised in Trondheim in June 2014: *The 6th International Symposium on Carbon for Catalysis, CARBOCAT-VI.*
- A large number of publications in prestigious journals are produced during the course of the project, several with contributions from more than one FREECATS partner.
- The business plan for the AOP shows that the new metal-free catalyst developed in the FREECATS project may be applied in both Catalytic Ozonation (COZ) and Catalytic Wet Air Oxidation (CWAO) with positive cash-flow after two years of activity.
- Fuel cell catalyst regarded as PGM replacement has to yield a similar fuel cell performance to be competitive in the market. The N-CNF catalytic material is still a promising ORR FC catalyst, and its development should be continued.