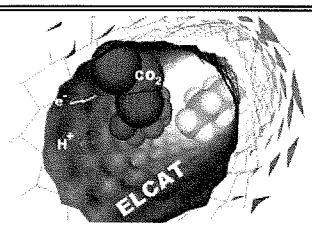

NEST Adventure

SIXTH FRAMEWORK PROGRAMME

CONTRACT N° : FP6-2003-NEST-A ; **PROJECT N° : 2400**
ACRONYM : ELCAT
TITLE : Electrocatalytic Gas-Phase Conversion of CO_2 in Confined Catalysts

Instrument : STREP ; **Thematic Priority** : NEST-ADVENTURE

PUBLISHABLE FINAL ACTIVITY REPORT

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Project Execution

The objective of the project was to investigate the feasibility of the electrocatalytic gas-phase conversion of CO_2 to liquid fuels (hydrocarbons and alcohols), and more specifically to investigate two alternative conceptual approaches to reach this objective. The first was based on the gas-phase conversion of CO_2 by reaction of protons (diffusing through a proton membrane) and electrons with CO_2 on metal nanoparticles located inside nanotubes in order to have a confinement of CO_2. The second approach was based on the same type of electrocatalyst, but using oxygen anion (O_2^-) conducting membranes to continuously subtract oxygen from the reaction environment and therefore reduce directly CO_2 with H_2.

The first approach was successful and it was proof-the-concept for the first time that using nanoconfined electrodes, based on metal particles confined in nanostructured carbon, and a Gas Diffusion Electrode similar to PEM fuel cells and operating in gas phase (differently from earlier studies working in liquid phase and flat-type electrodes, it is possible to convert CO_2 to liquid fuels (hydrocarbons and alcohols). More specifically, it is possible to form hydrocarbons and alcohols up to C8-C9 as carbon length, although the main products are C3 oxygenated (isopropanol or acetone, depending on catalyst). Increasing the reaction temperature from room temperature to 60°C there is an increase of one order of magnitude in the amount of products, being a critical factor the desorption from the electrode. Different type of electrocatalysts have been investigated, based on noble-metal and non-noble metals. The latter show a faster deactivation, which could be reduced operating with bimetallic electrocatalysts.

There is a very large interest in the conversion of CO_2 to fuels and the US DoE report "Catalysis for Energy" inserted this reaction as one of the three priorities and challenges for research. This project demonstrated that it is possible to convert CO_2 to isopropanol with the proposed novel concept, even if further activity is needed to develop on a commercial scale. It can be advanced, however, the possibility to develop "artificial trees" which can capture CO_2 and use solar energy (and water) to produce liquid fuels, still the best solution for intensive energy storage and transport. In fact, the developed electrocatalyst can be coupled in a novel photoelectrocatalytic (PEC) devices (also operating in gas phase instead that in solution as reported earlier in literature) to a TiO_2-based photoanode which produce electron and proton from water and solar energy. The electrons and protons are then used on the cathodic electrocatalyst (separated from the photoanode by a proton-conducting membrane) to reduce CO_2 to liquid fuels.

ELCAT project only demonstrated the feasibility of the electrocatalytic gas-phase conversion of CO_2 to liquid fuels and thus the performances of the full PEC device should be investigated in other projects, but the idea attracted a significant interest on the public side. Various divulgation articles, also in large diffusion newspapers, were dedicated to the project.

A side result of the project was also the development of improved electrocatalysts for fuel cells, based on a hierarchically design of the carbon materials, and the development of technologies for mass-production of carbon nanotubes at low cost. The second line of research, based on oxygen anion (O_2^-) conducting membranes, was not successful in terms of possibility of producing liquid fuels from CO_2, but produced interesting results to produce syn gas from CO_2 and for the design of innovative fuel cells based on the concept of Non-faradaic Electrochemical Promotion of Catalytic Activity (NEMCA).

The project was organized in three main workpackages: (i) synthesis of the materials, (ii) advanced characterization and reaction mechanism and (iii) reactivity studies. A fourth workpackage referred to the continuous action of coordination and project management. The consortium was coordinated from the University of Messina (Italy) (UM) and CNRS (CNRS – LMSPC, Université L. Pasteur, Strasbourg, France), Fritz-Haber-Institut der Max-Planck-Gesellschaft (Berlin Germany) (FHI-MPG) and University of Patras (Greece) (UP) were partners of it.

The objective of WP1 (Synthesis of Material) was the synthesis and base characterization of the samples to be tested in WP3 (reactivity). Advanced characterization of these materials, before and after reactivity tests, was made in WP2 (advanced characterization).

The initial activity in WP1 was centred on the synthesis of multi-walled carbon nanotubes (MWNTs) and in particular the preparation of opened nanotubes with a tailored diameter and their functionalization by (metal) deposition, the preparation of electro-catalysts constituted of copper, nickel and carbon nanofibers on yttrium stabilized zirconium (YSZ), and the preparation of electrocatalysts and assembly of the gas diffusion membrane electrode. After MidTerm research on this WP was centred on the optimization of the synthesis of MWNTs, in particular by incorporation of nitrogen atoms in the carbonaceous structure to improve the performances. A further objective was the analysis of the influence of different characteristics of the NTs on the metal deposition. Other activities regarded the optimization of the catalyst (metal) deposition inside the carbon nanotubes channel, and the preparation of electrocatalysts for both lines of catalytic tests.

A key concept developed within the project was that of confined electrocatalysts based on the use of metal nanoparticles in confined carbon nanostructures. These new electrode could be applied, as side spin-off activity, not only to the electrocatalytic reduction of CO_2 to liquid fuels, but also as new electrode for PEM or Solid Oxide fuel cells.

The objective of WP2 was the advanced characterization of materials prepared in WP1 and the analysis of the nanostructure/performance relationship. Several advanced characterization techniques, from high resolution microscopy to Raman and XPS wwre used. Based on the advanced characterization of the 1st generation of electrocatalysts, the 2nd generation materials was designed. In the latter period the activity was focused at a better identification of the reaction mechanism and of the structure-activity relationship. In particular, the effect of the CNT conductivity on the overall electrocatalytic performance, keeping constant all other parameters (CNT length and diameter) that would influence diffusion and mass transfer, was investigated.

The WP3 (Electrocatalytic and reactivity test) was the core of the project. The original workprogramme was structured to investigate the two alternative conceptual approaches to convert CO_2 described above. Accordingly, this WP has two main Tasks, in agreement with the two lines of investigation. A first Task is dedicated to the investigation of CO_2 reduction using H^+ conduction membranes. Initially, after construction and assembling of the reactor apparatus, the screening of the 1st generation samples (prepared in WP1), and the preliminary analysis of the effect of the reaction conditions was made. Later, research was focused on the analysis of the performance of 2nd generation samples, the detailed analysis of the effect of the reaction conditions, and the optimization of the reaction conditions.

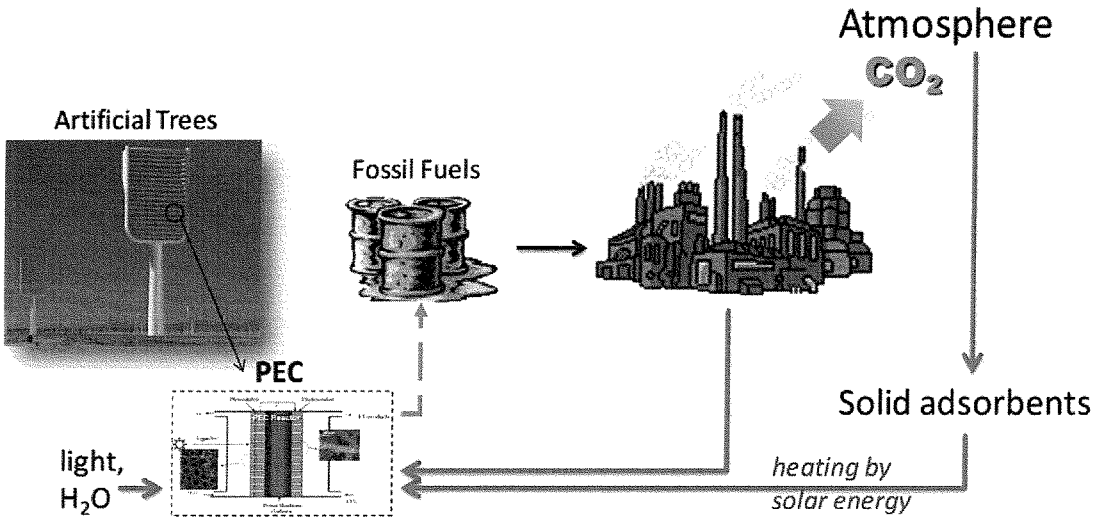
The second Task was dedicated to the investigation of CO_2 reduction using O^{2-} conduction membranes. Initial, the focus was on the construction and assembling of the reactor apparatus, the exploratory investigation of NEMCA effect in relation to CO_2 hydrogenation, and testing of different reactor configurations. Later the objective was the analysis of the performances of different kinds of electrocatalysts using different kind of reactor configurations .

WP4 was dedicated to management and coordination.

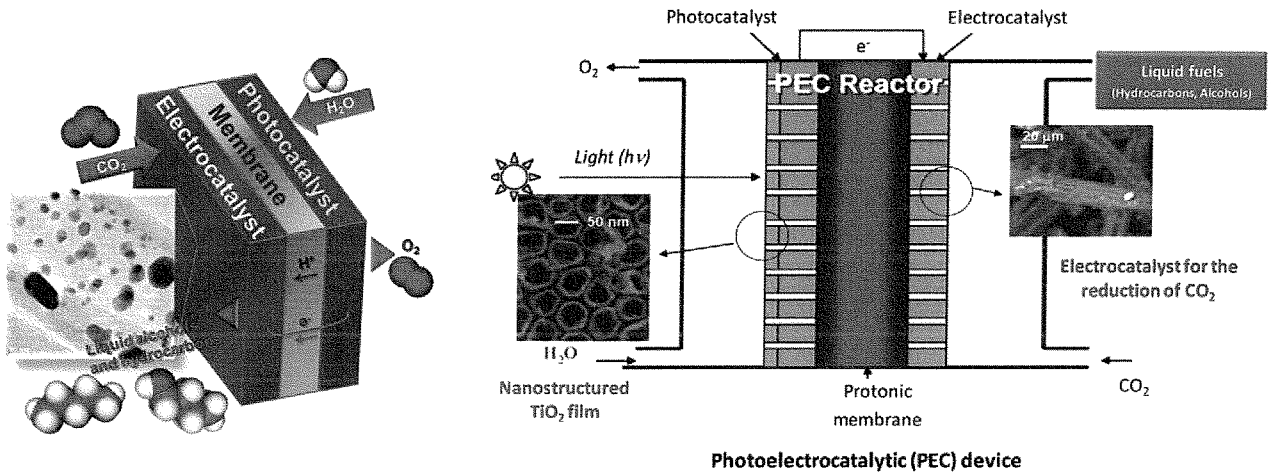
The main results of the project can be summarized as follows:

- it is possible working in gas phase and using nanoconfined electrocatalysts to form long C-chain hydrocarbons and alcohols at r.t. and atmospheric pressure
- it is not a FT-distribution, as originally hypothesized
- limit is the desorption of the products; increasing temp. improve of 1-2 order magnitude productivity, but mainly liquid C3 alcohols are produced
- use of carbon nanotubes based electrocatalysts instead of other nanostructured carbon-based electrocatalysts allow to maximize the formation of isopropanol from CO_2 electrocatalytic reduction

- working on bimetallic systems it is possible to improve stability which, however, still remains an issues
- it is still necessary to integrate electrocatalyst with photo catalyst in PEC (photoelectrocatalytic) reactor to make possible to realize an effective conversion of CO_2 to liquid fuel in "artificial tree" systems, as outlined in the scheme below, but the project make a first relevant step forward in this direction demonstrating that it is possible to convert CO_2 to liquid fuels using the proposed approach.



General scheme of converting CO_2 to liquid fuels in artificial trees



General schemes of PEC reactor for converting CO_2 to liquid fuels

Two are the main problems which should be overcome: (i) find a more efficient way to improve desorption of the products of reaction from the electrocatalyst, (ii) avoid transformation of the electrocatalyst during operations. Progresses have been made during the project, although further studies are necessary.

Dissemination and use

The project attracted a large public interest, for the need to find innovative solutions to the issue of CO_2. However, the project is of more general interest. In fact, in addition to the specific results listed above, the following aspects should be mentioned. In fact, the knowledge-based approach used in the project resulted in a series of advances also for other type of applications:

- New nanostructured electrodes for PEM fuel cells with improved performances (higher power density, improved stability with CO)
- New electrocatalysts using thin solid electrolytes
- Three electrode approach to improve PEM fuel cells
- Method for mass production of MWCT
- Method for producing nanoconfined C-based mater.
- Nanocarbon materials for energy storage

There is a large potential industrial interest on using CO_2 as raw material. In particular, with reference to the results opened by the project the following aspects must be cited:

- conversion of CO_2 to alcohols opens opportunities to use it as raw material
- in addition to PEC approach cited above, protons could be supplied from acid waste solutions (avoiding neutralization) and electrical energy from PV cells. This opens possibilities in shorter term (with respect to PEC approach) to convert CO_2 in SME's for which CO_2 storage solution cannot be used (small productions, distant from storage places).
- research opens new prospects for using the electrocatalytic approach also for other challenging reactions, for example the direct $CO_2 + CH_4 \rightarrow CH_3COOH$ reaction which is also an alternative way to store and transport methane.

However, due to the high challenging and long-term character of the project, the aim was to generate knowledge useful for above areas, and not directly generate results exploitable at the end of the project. In agreement, companies were not part of the Consortium. Exploitability requires further investigation and therefore defined exploitable results cannot be identified. There are not current activities related to commercialization, exploitation and demonstration of the results. Three exploitable knowledge of the project are summarized in the Table below.

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use	Patents or other IPR protection	Owner & Other Partner(s) involved
New electrocatalysts using thin solid electrolytes	Electrochemical elements: - Rh/YSZ/Pt - Rh/YSZ/Au - Pt/YSZ/Au - Cu/YSZ/Au	Chemistry Catalytic Reactors (MEPR)	2008	There is a first patent for the reactor, MEPR (US Patent, CT/GR2004/0 00006) which is capable to host these elements	UP
Method for mass production of MWCT	Procedure for synthesis and purification	Advanced materials Chemistry Electrode	2008	A previous patent (Fr. Demande (2003), FR 2832649) can be extended	CNRS-ULP
Electrocatalytic reduction of CO_2 to hydrocarbons in a PEM-type fuel cell	Device and electrode for CO_2 reduction	Energy and power plants Chemistry	2011	To be evaluated	UM CNRS-ULP

The targeted user groups are the following:

- SME's in the field of advanced functional materials (producing membranes and electrodes for fuel cells, carbon nanotubes for catalytic and microtechnology applications such as electronic and sensors)

- SME's or energy companies interested in developing novel solutions in the field of sustainable energy (including space applications)
- SME's or chemical companies interested in developing catalysts and membranes (electrochemically driven) to develop new process options having more efficient use of energy and/or resources

Exploitable Knowledge

1. *New electrocatalysts using thin solid electrolytes*
   This result refer to the preparation of electrochemical elements to be used in MEP Reactor, which is the first example of monolith-type reactor where the catalyst is electrochemical promoted (NEMCA effect). It may find application in environmental protection field (treatment of VOC, for example) as well as in process chemistry. The innovation related to the methodology of preparing the active components of this reactor. UP was the partner involved in the development of this result. The use of MEPReactor is still at an exploratory level, although the concept of the reactor was patented, and therefore it is still not possible to define the potential market neither obstacles to commercialization. Further R&D also at the fundamental level is needed before being possible to define these aspects, but this is in line with the exploratory character of NEST Adventure priority. The whole reactor with the electrocatalysts can be used by industry for several application concerning mainly air waste treatment. Until now there are no specific economic market considerations. This is under research in order to proceed with commercialization of the reactor. Of course further research and development work have to be done for the previous target.

2. *Method for mass production of MWCT*
   This result refers to the methodology of mass production of MWCT and specifically to the experimental conditions to prepare large amounts of MWCT by CVD method. MWCT find application in a large range of area from advanced materials to microelectronic, environmental protection and catalysis as well. The characteristic of this methodology is not only the mass production of MWCT, but also the applicability to the development of novel electrode for fuel cell type reactors. This aspect will be a key difference with respect to other methodologies, but it is necessary a further R&D experimentation before to exploit this aspect. CNRS-ULP was the partner involved in the development of this result, but with collaboration with FHI-MPG regarding the characterization and UM regarding the application as electrode. The need of further R&D at the fundamental level before being possible to define in a more detail the exploitability of this result is in line with the exploratory character of NEST Adventure priority.

3. *Electrocatalytic reduction of CO_2 to hydrocarbons in a PEM-type fuel cell*
   This result refers to the methodology of electrocatalytic reduction of CO_2 to hydrocarbons in a PEM-type fuel cell and specifically to the experimental conditions and type of electrocatalysts to form higher hydrocarbons (>C1, and up to C10 or over) in the electrocatalytic reduction of CO_2 using H^+-conductive membranes. The result refers also to the possibility of integration of this element into a photoelectrochemical reactor (PEC) to use solar energy and water to convert CO_2 to hydrocarbons. However, further intensive research is needed before to define the exploitability of this result which application ranges from the reduction of greenhouse gases in power plants, to more nice applications such as the production of hydrocarbons on Mars during the exploration of this planet. UM was the partner involved in the development of this result, but with collaboration with FHI-MPG regarding the characterization and ULP-CNRS regarding the preparation of the electrocatalysts..

The socio-economical potential impact of the knowledge generated in the project is great, because influences two of the major world problems: (i) sustainable energy production and (ii) reduction of greenhouse gas emissions. However, being a frontier research, the results are expected in a medium-long term and beyond the end of the project. As a consequence, there is the need to continue the research after the end of this project support.