



## SP5 Publishable Summary Report

*Based on the Del. 5.3.11.: Developments of the high temperature oxygen generation technology outside ENCAP in EU and USA*

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## **EXECUTIVE SUMMARY**

The aim of ENCAP's SP5 was to identify and develop promising, low cost advanced high temperature oxygen generation process options for use in the power plant processes of the previous SP's of the ENCAP project.

Interest in mixed ionic-electronic conducting (MIEC) materials for oxygen separation from air arose over the last decade when a number of new materials were developed and studied for their transport properties, chemical and thermal stabilities and potential applications. As MIEC membranes offer product separation and oxygen supply in one unit, their application to industrial processes such as air separation, oxidative coupling of methane and synthesis gas production in catalytic membrane reactors is an attractive option. Their inherent electronic conductivity removes the necessity of external circuitry to pump oxygen ions from one side to the other, simplifying reactor design and also removing contact resistances between electrodes and the membrane.

The focus of this study is laid on activities aiming at the transition of membrane reactors from laboratory to industrial scale applications in the United States and in Europe outside the ENCAP programme. The report is based on data collected in late 2007.

### ***Review of developments in Europe***

In order to achieve a high efficiency in the separation process, membranes of small thickness and high surface area per reactor volume are required. Catalytic modification of the membrane surface can increase the rate of surface processes and therefore the oxygen permeation performance when such mechanisms are limiting. In addition, practical considerations such as mechanical stability under process conditions and simplicity of preparation, sealing and manifolding must also be taken into account.

Current European activities aiming at the transition of membrane modules based on the mentioned concepts from laboratory to industrial scale applications outside the ENCAP programme are presented below.

### **Advanced Zero Emissions Power Plant Project**

The Advanced Zero Emissions Power Plant (AZEP) Project commenced in December 2001 and terminated in 2004. After a successful feasibility study previously performed by Alstom Power, Siemens and Norsk Hydro, a trans-European consortium including these companies plus Areva, Borsig, EniTecnologie, Paul Scherrer Institut (PSI), University of Ulster (UU), the Swedish Royal Institute of Technology (KTH) and Lund University (LTH) was established to develop the AZEP technology. The project addressed the development of a novel gas turbine based power generation process to reduce CO<sub>2</sub> emissions in a cost-effective way. The key element in AZEP was an integrated reactor in which: a) O<sub>2</sub> is separated from air by means of a mixed conducting membrane (MCM), b) combustion of natural gas occurs in a nitrogen-free environment and c) the heat of combustion is transferred to air by heat exchange. With regard to the oxygen production unit, extensive ceramic materials screening and qualification was carried out and components for modules were manufactured in cooperation with Areva T&D and Inmatec GmbH.

To demonstrate the integrity of the system, material improvements and scale-up of module manufacturing as well as extended module tests under process conditions were scheduled. It was further intended to launch a second project phase for another three years, focusing on MCM reactor integration into the gas turbine cycle and demonstration of the total concept in a pilot plant. It was estimated that the AZEP technology would be available for exploitation some five to seven years after completion of the first project phase, however, continuation of the project after the year 2004 was discarded and no information about current activities based on the AZEP project is available.

#### *OXYCOAL-AC Project at RWTH Aachen University*

Six research institutes at Rheinisch-Westfälische Technische Hochschule Aachen (RWTH Aachen University) and five industry partners have been working cooperatively since September 2004 to develop a CO<sub>2</sub> emission free oxycoal combustion process for electricity generation. The university institutions involved are the Institute of Heat and Mass Transfer (WSA), the Institute for Jet Propulsion and Turbo Machinery (IST), the Institute for Combustion Technology (ITV), the Institute for Chemical Engineering (IVT), the Institute of Automatic Control (IRT) and the Institute for Ceramic Components in Mechanical Engineering (IKKM). From industry side, contributions come from RWE Power AG, E.ON Energy AG, Siemens AG Power Generation, Linde AG and WS-Wärmeprozessechnik GmbH.

The OXYCOAL-AC technology is based on pulverised coal combustion in a CO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub> atmosphere and aims at high CO<sub>2</sub> concentrations in the flue gas for subsequent CO<sub>2</sub> capture and storage. A key component of this concept is a high temperature membrane system for oxygen production, where oxygen molecules are transferred from the pressurized air side across a mixed conducting membrane to the recirculated low pressure flue gas stream. After screening and testing available membrane materials for this application, especially perovskites, manufacturing processes for discs and tubes have been advanced and relevant material properties have been determined. In spring 2006, MEM-OXYCOAL was initiated as an additional research project, specifically dedicated to the development of membrane materials for the OXYCOAL-AC process. With the aid of numerical techniques and experimental investigations, varying thermal, mechanical and chemical conditions have been analysed and a module geometry has been designed.

Following basic and applied scientific research for the development of components and process simulation, a second project phase from December 2007 to the year 2010 is scheduled for the integration of components in a pilot plant. Testing of the pilot plant is claimed to result in specifications for a 40 MW<sub>th</sub> demonstration plant, which could be realised in a 2010 to 2013 timeframe. The overall target is to develop a commercial power plant based on OXYCOAL-AC technology with 400 MW electrical power.

*Ceramic membrane reactor R&D projects within the German Competence Network for Catalysis*

In May 2000, the German Federal Ministry for Education and Research (BMBF) has started an initiative for the encouragement of innovation-oriented research in the field of catalysis in Germany. The Competence Network for Catalysis (ConNeCat) was founded to close the gap between short term industrial R&D and basic research at universities and other research institutions. The BMBF supports ConNeCat by financing an organizational framework to improve dialogue and contact both between and within industry and non-industrial research facilities, and by co-funding outstanding research projects. In this context, three high priority "lighthouse" projects have been identified: a) Catalytic membrane reactor (CaMeRa) – Toolbox: Ceramic membranes for catalysis, b) Automotive emission control – Catalytic removal of NO<sub>x</sub> and soot particles from the exhaust gas of diesel engines, and c) Tuneable systems for organometallic multiphase catalysis (smart solvents/smart ligands).

The CaMeRa/Toolbox project has been carried out from October 2003 to September 2006. Project partners were Uhde GmbH, Bayer AG and Borsig GmbH from industry, Otto-von-Guericke-Universität Magdeburg, TU Berlin, RWTH Aachen and Leibniz Universität Hannover from academia and Fraunhofer Institute for Interfacial Engineering and Biotechnology (FhIGB), Karl-Winnacker- Institut (KWI), Hermsdorfer Institut für Technische Keramik (HITK e.V.) and the Institute for Applied Chemistry Berlin-Adlershof (ACA) as non-academic research institutions. New ceramic membrane components such as hollow fibres, dense and porous ceramic capillaries, bundles of capillaries as well as full ceramic and high temperature modules have been developed and catalytically functionalised. These components served as "toolbox" for the design of three different types of membrane reactors for technically relevant applications: a) partial oxidation of methane to syngas, b) hydrogenation of 1,3-cyclooctadien to cyclooctene and of  $\alpha$ -methyl styrene to cumene, and c) dimerization of propene to hexene. Additionally, software modules for catalytic membrane reactor development and optimum choice of operating parameters have been provided. The project has spawned seven patent applications and a multitude of publications in journals and books as well as national and international conference contributions

Due to the successful completion of the CaMeRa/Toolbox project and promising results obtained for BaCo<sub>x</sub>Fe<sub>y</sub>Zr<sub>z</sub>O<sub>3- $\delta$</sub>  perovskite hollow fibre geometries with regard to oxygen selectivity, oxygen flux and long-term stability, it has been decided to continue R&D on synthesis gas production by catalytic partial oxidation of methane in membrane reactors. For this purpose, Uhde GmbH, Borsig Membrane Technology GmbH, Borsig Process Heat Exchanger GmbH, FhIGB, the Leibniz Institute for Catalysis (LIKAT) in Berlin and the Institute of Physical Chemistry at Leibniz Universität Hannover have initiated the collaborative SynMem project in October 2006. The SynMem project aims at evaluating the transition from laboratory scale membrane components to rugged, industry scale systems with a multitude of fibres. This step requires new solutions for the nature and insertion of the catalyst and for the functionalisation of the gas separation module as well as for the gas-proof installation of fibres into the reactor. In addition to the perovskite materials studied this far, the development of CO<sub>2</sub> resistant ceramic hollow fibres for power plant applications is a further objective of the project.

### MEM-BRAIN Alliance

The MEM-BRAIN project pools the competencies of scientists and engineers from four Helmholtz Centres, namely the Research Centre Jülich (FZJ), Geesthacht Research Centre (GKSS), German Electron Synchrotron (DESY), and the Hahn-Meitner Institute.

The aim of the MEM-BRAIN Alliance is to develop ceramic membranes to lower pollutant and CO<sub>2</sub> emissions in coal-fired power plants. One type of membrane should break up the air into nitrogen and oxygen beforehand so that combustion can take place with pure oxygen. The emissions produced by this process are high in CO<sub>2</sub>, which can easily be extracted, while the production of harmful nitric oxides is avoided. Other kinds of membranes could then extract the CO<sub>2</sub>, enabling it to be disposed of.

The alliance will receive funding from the German Initiative and Networking Fund over the next three years. When the three years are up, plans are to make the alliance a research programme of the Helmholtz Association. Besides the institutions mentioned above, partners of the MEM-BRAIN Alliance are the Ernst Ruska Centre Jülich (ERC), Hermsdorfer Institut für Technische Keramik (HITK e.V.), Flemish Institute for Technological Research (Belgium), the Universities of Aachen, Bochum, Karlsruhe, Twente (Netherlands) and Valencia (Spain), and industry. The Helmholtz Association is a community of 15 scientific-technical and biological-medical research centres in Germany.

### Ceramic membrane reactor R&D for syngas and hydrogen production led by Linde Engineering

Since the beginning of November 2004, research on ceramic membrane modules and reactor development for syngas and hydrogen production have been carried out in a joint project between Linde AG Engineering Division, the Institute for Physical Chemistry and Electrochemistry at Dresden University of Technology (TU Dresden) and Hermsdorfer Institut für Technische Keramik (HITK e.V.). Financial support for project coordination, material characterisation and process development by Linde AG and TU Dresden and for material and module development by HITK has been provided by the German Federal Ministry of Education and Research (BMBF). The project was based on a previous three year collaboration financed by Linde AG.

With regard to quantity, dimensional accuracy and reproducibility, perovskite tubes were manufactured in a process suitable for industrial application. For the experimental investigations, the focus was laid on BaSr<sub>x</sub>Co<sub>y</sub>Fe<sub>z</sub>O<sub>3-δ</sub> materials, which showed excellent oxygen flux performance and were tested under process conditions. Problems occurred with regard to the chemical stability of the material under operating conditions as they usually occur in syngas reactors. After a longer period of operation, serious material decomposition set in on the syngas side of the membrane, leading to a destruction of the perovskite structure.

Beyond the exploration of material issues, a main objective of the project was the design of a pilot reactor and the conceptual development of a technical reactor. For this

purpose, long tubular membrane modules were chosen as principle design characteristic due to their relatively straightforward implementation and scalability.

In general, the project has shown that both material as well as process restrictions still represent major challenges for the technical implementation and application of a ceramic membrane reactor for syngas production. Due to the fact that currently no stable ceramic material under syngas conditions is available, research and development in perovskite materials and module manufacturing by HITK was scheduled to continue until the end of 2007.

### ***Review of developments in the USA***

In the mid 1980s British Petroleum, PLC (BP) (BP Amoco/Standard Oil) at their Naperville, IL Research Center developed the “Electropox” process that integrates oxygen separation with oxidation and steam reforming into a single process with a claimed economic advantage of 30-50% over conventional technologies. Initially voltage-driven ionic conducting ceramic membrane reactors were considered and then chemical potential-driven mixed conducting ceramic membrane reactors were developed. Oxygen separated with 100% selectivity from the air is contacted in situ on the fuel side of the membrane reactor with, e.g., methane in the presence of a catalyst to produce synthesis gas, liquid fuels or other chemical products. In 1995 BP Amoco and the Argonne National Laboratory were recipients of an R&D 100 Award for the development of strontium-iron-cobalt oxide (SCF) mixed-conducting perovskite membrane compositions for use in the Electropox process. Air Products and Chemicals, Inc. (APCI) and Praxair, Inc. have been leading separate large multi-company US DOE funded consortia since the late 1990s in attempts to develop these technologies through pilot-scale demonstration to pre-commercial scale, the latter building on the earlier BP work on the Electropox process. Other US companies and institutions involved in the early development of ceramic membranebased gas production technologies include: the Gases Technology Institute (GTI), Eltron Research, Inc. and ITN Energy, Inc.

### ***Air Products and Chemicals-led Programmes***

Air Products and Chemicals, Inc. (APCI) began its internal programme to develop Ion-Transport Membrane (ITM) technologies for gas production in about 1989 and soon thereafter contracted Ceramatec, Inc. to aid in the development of the critical ceramic modules. US government support was then obtained through the Advanced Technology Program (ATP) of the US National Institute for Standards and Technology (NIST) to continue this work from 1994 to 1997. Although the goal of demonstrating a functional Pilot Demonstration Unit (PDU) was not achieved during the ATP project, much progress was claimed on building fundamental knowledge as well as on materials and module design. Building on the ATP project, major US Department of Energy support was then secured for two separate but related APCI-led multi-years, multi-company, consortia to develop ITM based technology for large scale synthesis gas / hydrogen (ITM Syngas) and oxygen (ITM Oxygen) production, respectively. In the late 1990s / early 2000s APCI was also developing voltage-driven Solid Electrolyte Oxygen Separation (SEOS) ceramic membrane technology for small-scale oxygen applications. APCI’s recent emphasis in public presentations has moved from large scale syngas production to the development of pressure-driven

oxygen separation membranes for integration into large scale IGCC power plant applications.

### *Non-Cryogenic Oxygen Production using Ion-Transport Membranes*

Work on the ITM Oxygen programme commenced in 1998/1999 with the overall target of reducing the cost of oxygen by one-third compared to state-of-the-art cryogenic and pressure swing adsorption oxygen production technologies. As originally envisaged the programme was to be undertaken in three phases each of three years duration. Due to significant challenges faced in achieving some phase II Subscale Engineering Prototype (SEP) performance targets, the commercialization timeline has continued to slip. In recent publications the duration of the ITM Oxygen programme is reported as 11 years. Programme partners include: the US Department of Energy DOE through its National Energy Technology Laboratory (NETL); APCI; Ceramatec, Inc.; Concepts NREC; SOFCo Holdings EFS (originally McDermott Technology); GE Power (replacing Texaco Power and Gasification); the Pennsylvania State University; and the University of Pennsylvania. Eltron Research are no longer active in the ITM Oxygen programme, but Siemens (Westinghouse Power) joined the consortium in 2003 and Novel Edge Technologies joined in 2007 as the focus of the programme changed to large power plant integration options.

Phase I of the programme that was completed in 2001 at a total cost of c. \$25 million (\$12.5 million DOE funds, \$12.5 million APCI funds) focussed on materials and process R&D and the design, construction and operation of a c. 0.1 ton per day (TPD) Technology Development Unit. Phase II of the programme focussing on the design, construction and operation of the 1-5 TPD SEP is nearing completion. Phase III will focus on pre-commercial development at a scale greater than 25 TPD. Some phase III activities are reported as being underway.

APCI commissioned the SEP in April 2006 and have run a number of tests on this system that incorporates several of their 0.5 TPD planar architecture multi-layer ceramic membrane modules integrated into a pressure vessel. APCI claim that phase II of the ITM Oxygen programme has progressed successfully and that they have demonstrated the production of >99% oxygen from commercial scale modules and achieved an O<sub>2</sub> flux on a consistent basis that met or exceeded their target at commercial operating conditions. APCI claim now to be planning with the DOE for an expanded phase III program in which a 150 TPD O<sub>2</sub> plant (pre-commercial system) based on the ceramic oxygen separation membranes will be built and tested in 2008-2009. They are also in discussions with DOE for the development of a 2,000 TPD ceramic membrane based O<sub>2</sub> plant as part of the FutureGen program for implementation in 2012.

### *Synthesis Gas Production using Ion-Transport Membranes*

Work on the ITM Syngas programme commenced in 1997 with the overall target of developing technology for the low cost conversion of natural gas to hydrogen and syngas with 30% capital cost savings over conventional technologies. As originally envisaged the programme was to be undertaken in three phases over 8 years. Due to the challenges encountered in meeting some of the pilot scale targets, phase II of the programme was extended to late 2007 taking the expected programme completion

date to 2010. Programme partners include: the US Department of Energy through its Fossil Energy and Energy Efficiency Programs; APCI; Ceramatec, Inc.; Chevron Energy Technology Co.; Norsk Hydro; Eltron Research, Inc.; SOFCo-EFS Holdings LLC (originally McDermott Technology); The Pennsylvania State University; the University of Pennsylvania and the Pacific North West Laboratory.

In late 2007 APCI will make a series of presentations highlighting this technology, presenting the results from pilot testing (including oxygen flux data), the development of commercial scale modules, and recent flow sheet optimization and economic analyses. They claim that the potential economic benefits continue to look very promising.

### *Voltage-Driven Solid Electrolyte Oxygen Separation*

Because of resistive and other losses, voltages significantly higher than those calculated from the ideal separation energy are required to drive oxide ions through the dense membrane layer in voltage-driven ceramic membrane-based oxygen generation systems. This makes the energy requirements for these systems too high for large scale oxygen production. In the late 1990s and early 2000s Air Products was working on voltage-driven Solid Electrolyte Oxygen Separation (SEOS) ceramic membrane systems for smaller scale, for example, military, medical and analytical high-purity oxygen applications. Both Air Products (working with Ceramatec, Inc.) and Praxair (working with Litton Life Support now part of Northrop Grumman) made press announcements in 2000/2001 that electrically driven ceramic oxygen concentrators would be commercialized in 2004 in the home medical oxygen therapy market. Although both companies developed working prototypes, no commercial products have appeared.

### *Praxair-led Programmes*

In 1997 BP entered into an Oxygen Transport membrane (OTM) Alliance with Praxair, Inc., Amoco, Statoil and Sasol to advance the BP "Electropox" technology in an industrially sponsored development program. Philips Petroleum and Foster Wheeler subsequently joined the Alliance that is led by Praxair, Inc. It appears that the OTM Alliance was disbanded in 2004 at the end of phase II, but that Praxair has continued to progress various OTM technology options with partial funding support from the DOE for fundamental studies of basic problems in materials, catalysts, seals, membrane fabrication, model development, etc, involving the Universities of Alaska-Fairbanks, Houston, Illinois-Chicago and Missouri-Rolla in addition to Praxair, Inc. and BP Exploration Alaska Inc. Other significant multi-year DOE supported OTM projects include: advanced oxygen production for integration into IGCC power plants; the production and testing of synthesis-gas-derived ultra-clean fuels; advanced oxy-fuel boilers and process heaters for cost effective CO<sub>2</sub> capture and sequestration; and scale-up of hydrogen transport membranes for IGCC and FutureGen plants.

Praxair has selected tubular supported membrane architecture in direct contrast to the planar architecture selected by APCI. The competing designs are both said to make the membrane modules easier to seal and more readily manufactured. Although Praxair and its partners have evaluated both voltage-driven and pressure driven OTM systems for oxygen production and chemical potential driven OTM systems for syngas

and hydrogen production, their recent emphasis has been on ceramic membrane development related to their advanced boiler concept. Praxair are currently in phase I development and laboratory scale testing. The OTM fluxes achieved for a robust material currently is about 40% of target. Phase II involving a pilot scale design and demonstration is planned for 2009-2010.

The hydrogen membrane project is led by Eltron Research, Inc. with Noram Engineering, CoorsTek and Praxair as partners and commenced in 2005. The overall target of this project is develop a high throughput, low cost and impurity resistant process for hydrogen separation from coal derived synthesis gas utilizing an integrated moderate temperature hydrogen conducting (cermet or ceramic proton conducting) membrane and water gas shift catalyst system. They claim to have identified a potentially cheaper cermet membrane composition which matches the performance of Pd membranes and demonstrated its performance under full WGS conditions in 1.46 pounds hydrogen per day laboratory system. It appears only to be competitive with conventional technologies in integrated power plant cases. If phase I targets are met and appropriate commercialization partners can be attracted, then phase II involving a pilot plant demonstration is planned for 2008-2011.

### *Conclusions*

Initial R&D work into ionic conducting materials was mainly focused on the development of ceramic fuel cells (SOFCs) for power generation and on high temperature sensors such as the automotive oxygen sensor. Interest in mixed ionic-electronic conducting (MIEC) materials for oxygen separation from air arose in the '80s when a number of new materials such as  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{La}(\text{Co},\text{Fe})\text{O}_3$  were developed and studied for their transport properties, chemical and thermal stabilities and potential applications. Due to species transport in dissociated or ionized form rather than conventional molecular diffusion, MIEC membranes offer a unique separation mechanism and extremely high selectivity.

Intensified efforts in efficient energy utilization and greenhouse gas emissions reduction have stimulated research in MIEC membrane reactors. The most important application of high temperature ceramics in this context is high purity oxygen production as a replacement of conventional cryogenic air separation units for IGCC and oxyfuel power plant processes. Significant advances have been achieved through several initiatives since the late 1990s/early 2000s, especially through multi-company US projects led by Air Products and Chemicals, Inc and Praxair, Inc. In Europe, multi-channel architecture monolithic reactors have been built within the scope of the AZEP project and tubular composite structure modules are being developed within the OXYCOAL-AC project. Increasing both the ionic and electronic conductivity, improving the stability of the materials and efficient system integration are still the major challenges.

Besides R&D on high purity oxygen generators, considerable attention has been spent on the integration of the permeation process into chemical reactors. Membrane reactors, which combine reaction and separation or distribution and reaction in one unit, are the result of these efforts. Membrane reactors are used to enhance the reaction yield and conversion of thermodynamically limited reactions or to control the reaction

pathway by introducing a reactant such as oxygen into the reaction zone in a controlled manner.

Of all the potential applications for MIEC membranes, the partial oxidation of methane to syngas is claimed to be of particular commercial relevance with capital cost saving potentials up to 30 % over conventional technologies. To explore the use of membrane reactors for syngas production, a multi-company R&D programme was initiated in the US in 1997 under the leadership of Air Products and Chemicals, Inc. Due to challenges encountered during the pilot demonstration and prototyping phase, the originally envisaged completion date in 2005 was postponed to 2010. Programme updates covering results from pilot testing, the development of commercial scale modules, flow sheet optimization and economic analyses were scheduled for late 2007. In contrast to the planar module architecture employed by this US consortium, European activities predominantly concentrate on tubular geometries. Design of a pilot reactor and the conceptual development of a technical reactor were carried out under the leadership of Linde Engineering Division. Work within the German Competence Network for Catalysis is ongoing and aims at the transition from basic R&D to practical systems on the basis of ceramic hollow fibres. New ceramic components for partial oxidation, hydrogenation and dimerization reactions have been developed and catalytically functionalised, serving as "toolbox" for future innovation. Obstacles to be overcome are the insufficient stability of currently available ceramic materials in a reducing environment and unsolved process restrictions with regard to their technical and economical application.

Altogether, comparing membrane reactor development for oxygen and syngas production in the US to the European situation outside the ENCAP programme, American activities are more concerted in a sense that the main part of public funding is provided by a single institution, namely the US Department of Energy, and that multi-company consortia are spearheaded by technology leaders, in particular Air Products and Chemicals, Inc and Praxair, Inc. In Europe, both technical and scientific competence as well as funding initiatives are frequently scattered across countries and even across regions. Financial support in Europe is much lower than in the US, impeding the execution of long-term R&D programmes, contributing to slower progress and resulting in generally less optimistic forecasts with regard to a large scale application of MIEC membrane technology.