

## Helmholtz Alliance „ MEM-BRAIN “

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### Final Summary 2007 - 2011 of the Alliance

*“Publishable”*

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## 1. Introduction

Of all the current strategies for fighting climate change, reducing carbon dioxide emissions is the number one priority. And while renewable energies are increasingly being used, coal plants and natural-gas plants will continue to be one of the main ways of meeting the world's growing energy needs. At present, they contribute 40 percent of global CO<sub>2</sub> emissions, a percentage that must drop significantly and sustainably. Therefore, the reduction or elimination of CO<sub>2</sub> emissions from power plants fuelled by coal or gas is a major target in the current socio-economic, environmental and political discussion.

To reduce CO<sub>2</sub>-emissions by 50 to 60% till 2050, as proposed by EU and other industrial countries, a significantly contribution of carbon capture and storage (CCS) is required.

Existing concepts for CO<sub>2</sub> capture require a great amount of energy. This has a negative impact on the efficiency of power plants, puts a heavier burden on the environment and ultimately leads to higher costs for generating electricity. A promising alternative is the use of innovative membranes that can separate carbon dioxide, hydrogen, nitrogen and oxygen with a far smaller reduction in efficiency compared to conventional separation technologies.

The key scientific and technological challenges associated with membrane systems are ensuring high permeability, specific selectivity and long-term stability up to 100,000 hours. Membranes that are already used for gas separation in other fields (e.g. the chemical industry) are still far from suitable for large-scale industrial applications, as necessary in power production. Strategies for novel membranes bring materials science and technology into the main focus of research and technology development. Examples include functional layers and porous structures in the nanometre range, as well as the development of mixed-conducting oxides by means of theoretical materials design approaches and the design of components under operating conditions based on their physico-chemical and mechanical properties. The optimized integration of membrane systems into power plants, as well as the analysis of the entire system, encourages these efforts.

To develop this innovative technology and make it ready for use, experts from Helmholtz Centres recently joined forces with leading German and international partners from research centres, universities and industry to create the Helmholtz Alliance MEMBRAIN.

For the first project phase which lasts from October 2007 to June 2011 the integrated "MEM-BRAIN" project was funded with €11 million from the Helmholtz Association's Impulse and Networking Fund. The cooperating organisations are contributing with the same amount from its own resources so that the total budget is €22 million.

The principle advantage of the project is the parallel, networked (iterative) development of membrane materials by (i) design of components and equipment, (ii) integration into power plants and the related process engineering, and (iii) energy systems analysis.

The Helmholtz Alliance "MEM-BRAIN" consists of 12 research organizations: Forschungszentrum Jülich (FZJ, D), Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research (HZG, D), DESY/HASYLAB (D), Helmholtz Zentrum Berlin (HZB, D) and Ernst Ruska-Centre (ER-C, D), Fraunhofer Institute for Ceramic Technologies and Systems, Hermsdorf (IKTS, D), Flemish Institute for Technological Research (VITO, B), Consejo Superior de Investigaciones Científicas (CSIC, E), and the universities of Aachen (RWTH, D), Bochum (RUB, D), Karlsruhe (KIT, D), and Twente (UT, NL). Five industrial partners ensure that the results are applied in an industrial context: EnBW (D), GMT (D), Plansee SE (A), Shell (NL), and Siemens (D). The project is meeting a long-term scientific and technological challenge with a time horizon for significant commercialization after 2020.

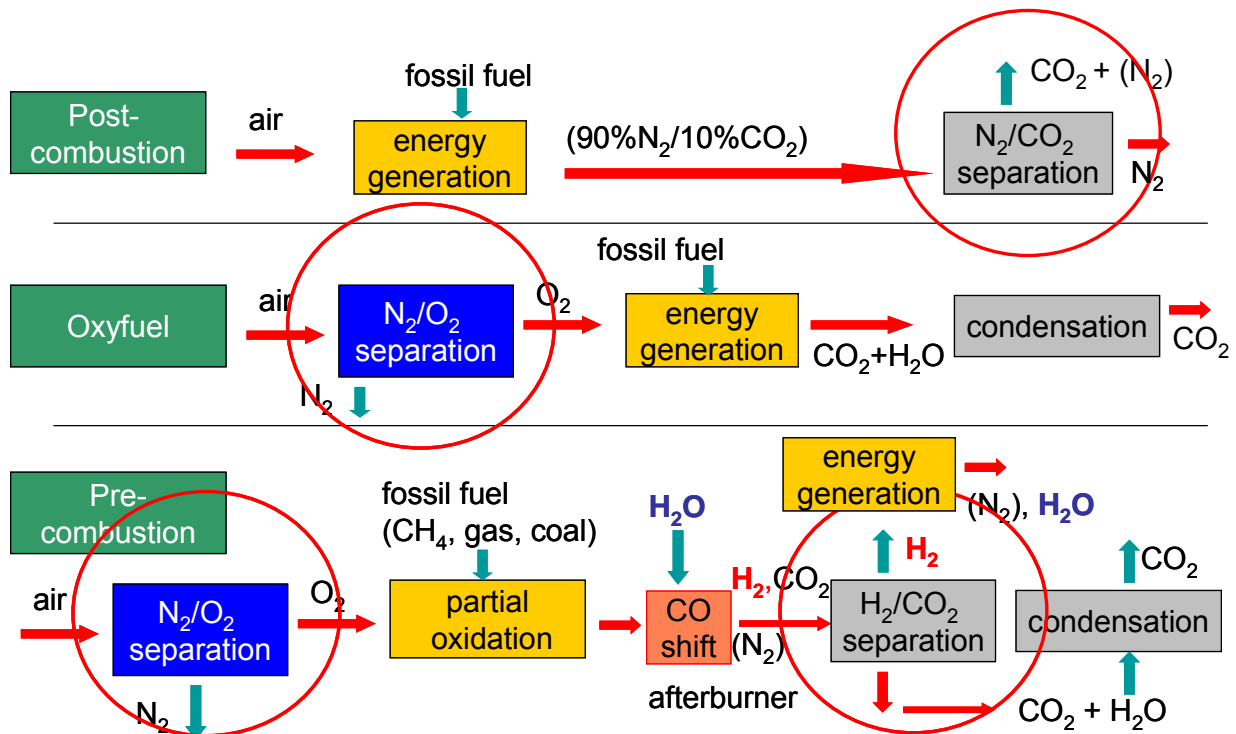
The MEM-BRAIN Alliance also focuses on promoting new talent with its PhD programmes and summer schools, so that young scientists and engineers can learn about the latest developments in membrane technology at an early stage.

## 2. The four Research Topics of MEM-BRAIN

A breakdown of the membrane research targets by MEM-BRAIN programme is displayed in Figure 1. It can be seen that membranes must be engineered with corresponding gas separation tasks, as listed below:

- post-combustion ( $\text{CO}_2/\text{N}_2$  separation)
- pre-combustion ( $\text{H}_2/\text{CO}_2$  separation) and
- oxyfuel combustion ( $\text{O}_2/\text{N}_2$  separation) (**Figure 1**).

### Power Plant Concepts for $\text{CO}_2$ -separation in fossil power plants



**Figure 1:** The three  $\text{CO}_2$  capture concepts

To address the needs of the target research processes in **Figure 1**, it is important to focus on membranes that can be designed for each specific application. Bearing this in mind, full consideration has been given to the following membranes:

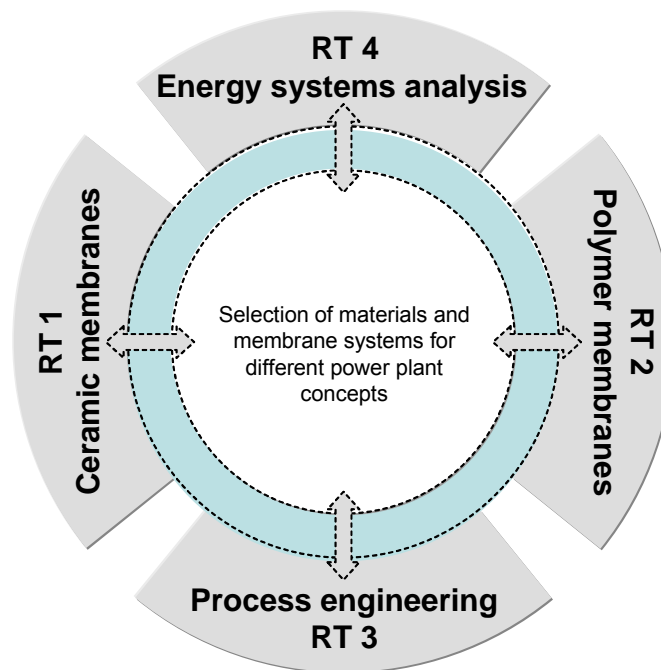
- Polymeric membranes working at temperatures of up to  $200^\circ\text{C}$  are candidates for pre-combustion and in particular post-combustion processes.
- Microporous ceramic membranes operating at temperatures of up to  $400^\circ\text{C}$  can be used for pre-combustion and possibly for post-combustion capture.
- Dense ceramic membranes are necessary for oxyfuel processes working at temperatures between  $800\text{-}1000^\circ\text{C}$  (mixed ionic-electronic conductors, MIEC) and are possible candidates for pre-combustion operation at temperatures above  $600^\circ\text{C}$  (mixed proton-electronic conductors).

To address the described challenges, the work of the Alliance has been structured into four research topics. The technical basis is provided by two of the topics in the field of materials science, one developing ceramic membranes, and the other developing polymeric membranes. The main scientific challenge is the development and manufacture of novel

membrane systems with high permeability, specific selectivity and long-term stability under operating conditions. These systems must be incorporated into power plants and an energy system defining additional boundary conditions.

The wide-ranging competencies in the Helmholtz Alliance and the strong relationships among its partners make it possible to pursue two other tasks in addition to membrane development – analysing the use of membranes in individual plant processes and evaluating the economic and ecological elements of plants as a whole in all their different forms. Process analysis and system evaluation both rely on the results of materials scientists – see **Figure 2**.

### Structure of the MEM-BRAIN Alliance



**Figure 2:** Co-operation between the Research Topics of MEM-BRAIN

In turn, however, they provide these scientists with valuable information for designing the new materials. This kind of cross-pollination and regular interaction between project partners helps ensure that work remains focused on practical application from the start, while quickly providing the results needed to tackle the urgent problem of climate change.

In the following chapters you will find a summary of the results of the 4 Research topics in particular.

### 3. Summary of the status in the four Research Topics

#### 3.1 Research Topic 1: “High and intermediate temperature ceramic membranes”

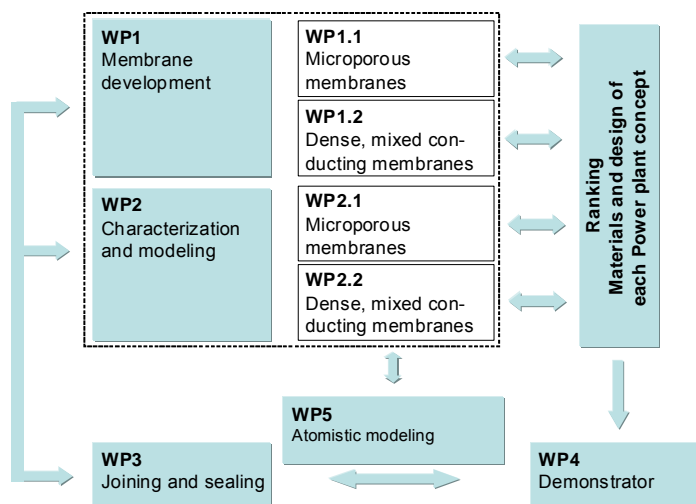
##### 3.1.1 Introduction RT1: Ceramic membranes

The overall goal of Research Topic 1 (RT1) was to identify and develop promising, low cost, advanced ceramic membranes which can be integrated in different power plant process scenarios (post-combustion, pre-combustion, and oxyfuel combustion) aimed at CO<sub>2</sub> capture. In post-combustion, the membrane should separate the CO<sub>2</sub> from the flue gas (primarily nitrogen); in pre-combustion processes the membrane should separate H<sub>2</sub> from CO<sub>2</sub>; in the oxyfuel combustion process the membrane should separate O<sub>2</sub> from air, keeping nitrogen out of the flue gas, so that it is easier to concentrate the flue gas to an almost pure stream of CO<sub>2</sub>. Molecular sieving membranes (zeolite membranes and sol-gel derived membranes, ≤400 °C) provided very good options for use in H<sub>2</sub>/CO<sub>2</sub> separation schemes in addition to dense proton-conducting ceramic membranes operating at elevated temperatures (400-700 °C). For the oxyfuel combustion process oxygen mixed ionic-electronic conducting (MIEC) membranes operating above 800 °C offered high potential for reducing the cost of oxygen generation. A vivid exchange of information and samples between the partners Forschungszentrum Jülich, Helmholtz-Zentrum Geesthacht, Helmholtz-Zentrum Berlin, Karlsruhe Institute of Technology KIT, RWTH Aachen University, University of Twente (NL), Ernst-Ruska Centre, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Flemish Institute for Technological Research VITO (B), Consejo Superior de Investigaciones Científicas CSIC (E), and the companies EnBW, Siemens and Plansee was established.

As a directive for the planned research the following targeted fluxes and selectivities of the different types of membranes were agreed:

Membrane	Flux	Selectivity	Operating conditions
Zeolite membrane	H <sub>2</sub> : ~5 m <sup>3</sup> /(m <sup>2</sup> ·h·bar)	H <sub>2</sub> /CO <sub>2</sub> ≥ 30	= 400\ C
Sol-gel derived membrane	H <sub>2</sub> : ~5 m <sup>3</sup> /(m <sup>2</sup> ·h·bar)	H <sub>2</sub> /CO <sub>2</sub> ≥ 30	= 400\ C
Oxygen mixed ionic-electronic conducting membrane	O <sub>2</sub> : ~10 ml/(cm <sup>2</sup> ·min)	infinite (N <sub>2</sub> leakage = 1%)	= 800\ C
Proton-conducting membranes	H <sub>2</sub> : ~1 ml/(cm <sup>2</sup> ·min)	infinite (CO <sub>2</sub> leakage is circumstantial)	= 600\ C in presence of CO <sub>2</sub>

It was emphasized that the data must be handled with care as the membrane performance will be dictated by the actual process conditions. More generally speaking, the aim of the work in RT 1 was to find a proper balance between flux, selectivity and reliability of long-term operation to achieve a viable option for integration in a power plant cycle. The following five work packages (WP) were included in RT1. The main results of these work packages will be summarized in this report whereas results of membrane characterization will be included in work package 1.

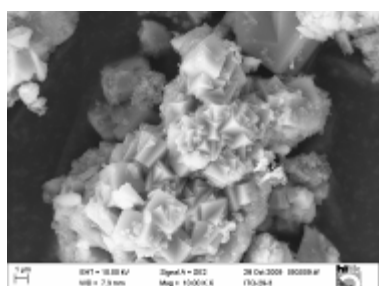


### 3.1.2 Materials synthesis and processing of ceramic membranes

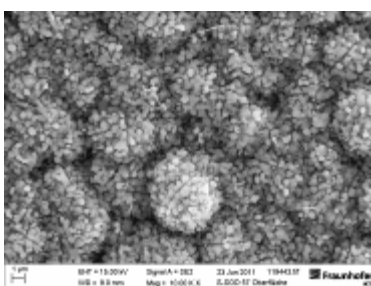
#### Zeolite membranes

The zeolites NaA and hydroxy sodalite (H-SOD) are interesting candidates for H<sub>2</sub>-separation because of small pores of 0.4 nm and 0.3 nm build by 8- and 6-ring structures respectively. A high alumina content of 50 % of the framework atoms limits the chemical, thermal and hydrothermal stability. Therefore the alumina free, pure silica zeolite A ITQ-29 was investigated (**Figure 3**). In parallel, a method of stabilizing the SOD-structure by anion substitution process was developed (S-SOD, **Figure 4**). Both zeolites ITQ-29 and S-SOD showed excellent thermal and hydrothermal stability in air and in industrial gas compositions of coal gasification.

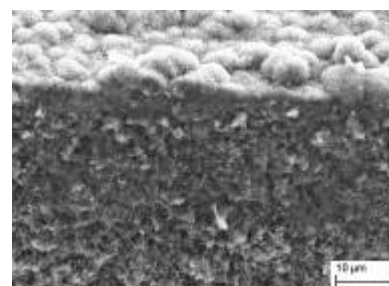
Because of the high viscosity of the synthesis gel only cracked layers were obtained during ITQ-29 membrane synthesis. In contrast, properly intergrown S-SOD layers with a thickness in the range of a few micrometers and without impurities were prepared inside of 250 mm long porous ceramic tubes by seeding (nano seeds and slurry technology) and hydrothermal treatment (**Figure 5**).



**Figure 3:** ITQ-21 powder sample (SEM).

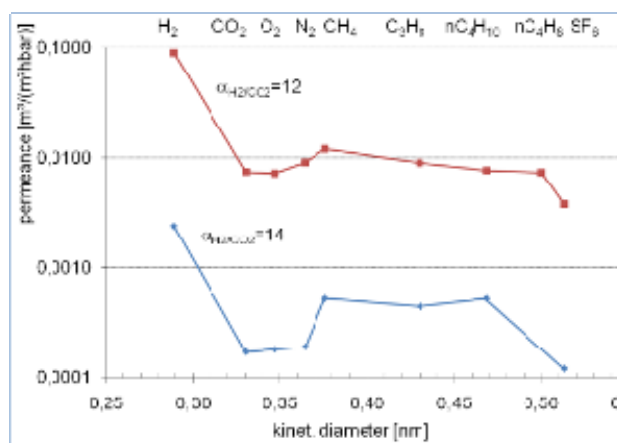


**Figure 4:** S-SOD powder sample (SEM).



**Figure 5:** Cross-section of a S-SOD-membrane inside of 250 mm long Al<sub>2</sub>O<sub>3</sub> support tube (TEM).

By single gas permeation a 14 times higher permeation of hydrogen in comparison to CO<sub>2</sub> was measured (**Figure 6**). So within MEM-BRAIN a thermal and hydrothermal stable membrane for a size selective separation (mol sieving effect) of a H<sub>2</sub>/CO<sub>2</sub> mixture was prepared for the first time. The reduction of the still existing membrane defects (permeation of big molecules) and the enhancement of the H<sub>2</sub>-permeance are in the focus of the ongoing research and are requirements for an industrial application of the new zeolite membranes.



**Figure 6:** Single gas permeation measurements of different S-SOD-membranes prepared inside of 250 mm long ceramic support tubes

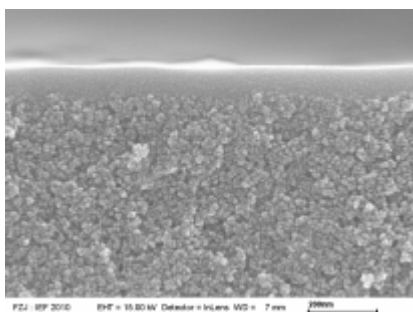
## Sol-gel membranes

Sol-gel membranes were prepared on porous planar and tubular  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or 8Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> supports by dip-coating methods, where sols with different particle sizes were used as coating liquids. In a first step, mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or graded TiO<sub>2</sub> or ZrO<sub>2</sub> sublayers with an average pore size of 5 nm to 3 nm were deposited, starting from sols with a particle size in the range 60 nm to 30 nm. The active toplayer of the membrane was a SiO<sub>2</sub>, ZrO<sub>2</sub>, 8Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> or 50TiO<sub>2</sub>-50ZrO<sub>2</sub> thin film with a thickness in the range 50-200 nm. Nanoparticles of these materials were prepared by a precipitate-free hydrolysis-condensation synthesis method, starting from metal-organic precursors which is called “sol-gel” synthesis.

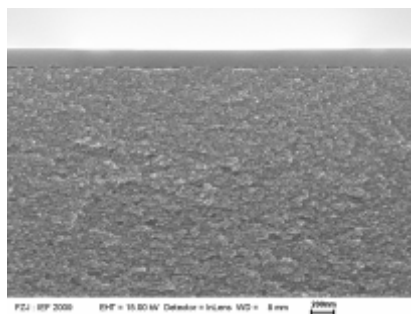
Gas permeation tests showed a decrease of permeation in the order He > H<sub>2</sub> > CO<sub>2</sub> > N<sub>2</sub>, suggesting a “molecular sieving” process for the membranes with SiO<sub>2</sub> based toplayers. The best results were obtained for samples with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous membranes as carrier layers (**Figure 7**). SiO<sub>2</sub> membranes prepared from conventional “TEOS” alkoxide precursors showed an average H<sub>2</sub>/CO<sub>2</sub> selectivity of 30 and a typical H<sub>2</sub> permeation of 150-350 l/(h·m<sup>2</sup>·bar) at 200 °C. Based on these results a novel type of multilayer membrane composed of much more stable mesoporous 8YSZ carrier layers and an amorphous SiO<sub>2</sub> toplayer has been developed (**Figure 8**). Permeation tests demonstrated also a “molecular sieving” behaviour. H<sub>2</sub>/CO<sub>2</sub> selectivities ranged from 5 to 12, with an average value of 7–8. The H<sub>2</sub> permeation of such membranes was significantly increased to an average of 2000–3000 l/(h·m<sup>2</sup>·bar) at 200°C.

Another novel development included the application of so-called “BTESE” precursors for the formation of hybrid thin film gas selective toplayers, with Si-C bonds incorporated (**Figure 9**) stabilizing the 3-dimensional Si–O network. Results from gas permeation tests demonstrated again a “molecular sieving” behaviour. Preliminary tests showed a H<sub>2</sub>/CO<sub>2</sub> selectivity of 50 in combination with a H<sub>2</sub> permeation >1500 l/(h·m<sup>2</sup>·bar) at 200°C, outperforming all similar hybrid carbon-SiO<sub>2</sub> layers today developed and reported in the literature.

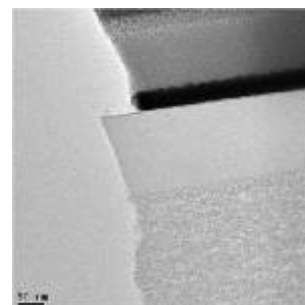
The formation of crack-free non-silica toplayers was also extensively investigated during the project, resulting in a variety of novel membrane types with thin films consisting of materials like ZrO<sub>2</sub> (tetragonal polymorph), 8Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (cubic) and 50TiO<sub>2</sub>-ZrO<sub>2</sub> (amorphous). Gas permeation showed either no selectivity or a complete dense membrane without any permeance of H<sub>2</sub> as well as CO<sub>2</sub>. Although no practically useful material was achieved with these approaches, valuable experimental data have been acquired to understand the gas transport mechanism through a sol-gel membrane. Summarized, our results support the theory that an amorphous SiO<sub>2</sub> toplayer is formed of 5-, 6-, 7-, 8- and also larger Si–O bonded rings which enable H<sub>2</sub> permeation. On the contrary, the non-silica toplayers are apparently characterized by a more dense atomic packing hindering H<sub>2</sub>-permeation, irrespective of the crystalline properties of the material.



**Figure 7:** Cross-section of a SiO<sub>2</sub>-membrane from TEOS-precursor on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sublayer (SEM).



**Figure 8:** Cross-section of a SiO<sub>2</sub>-membrane from TEOS-precursor on 8YSZ sublayer (SEM).



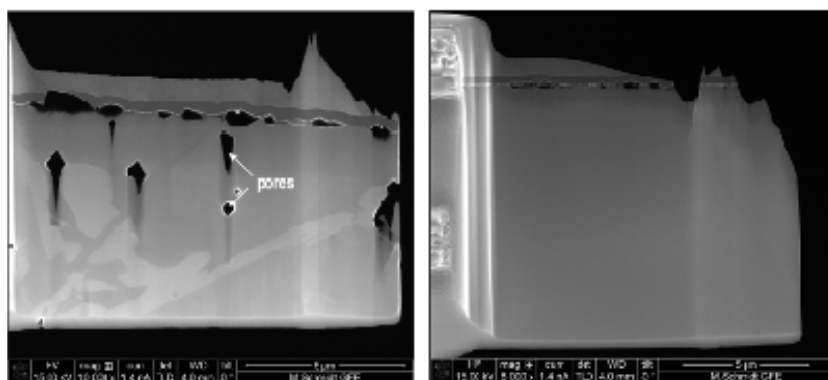
**Figure 9:** Cross-section of a SiO<sub>2</sub>-membrane from BTSE-precursor on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sublayer (TEM).

## Oxygen mixed ionic-electronic conducting membranes

Activities in the field of Oxygen Transport Membranes (OTM) were concentrated towards basic research of the mixed oxide ionic-electronic conducting perovskite-type oxide  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF), and compositions derived therefrom, and development of different methods for the design and fabrication of membranes.

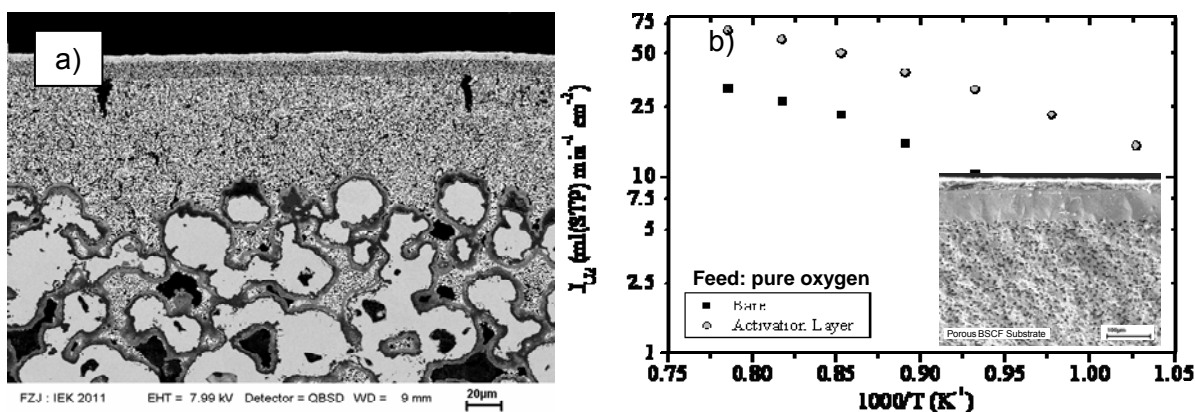
BSCF has emerged as an exceptional mixed conducting oxide with a great promise for use as a membrane in oxygen separation, provided that its structural and chemical stability can be improved. The material exhibits extremely fast oxygen transport and associated surface exchange kinetics at elevated temperatures as measured using a variety of techniques (e.g. electrical conductivity relaxation,  $^{18}\text{O}$ - $^{16}\text{O}$  isotopic exchange and oxygen permeation). The electronic structure has been determined using *in-situ* X-ray absorption spectroscopy, showing that the Co and Fe 3d bands partially overlap with the O-2p band. An important corollary of this observation is that valence change of the oxide ions, in addition to that of the transition metal cations and/or formation of oxygen vacancies, constitutes one of the charge compensation mechanisms in the material.

The stability of BSCF in reducing atmospheres, at 700-900°C, extends to oxygen partial pressures as low as  $10^{-14}$ – $10^{-12}$  atm, as measured using combined coulometric titration and high-temperature X-ray diffraction (XRD). Intensive studies using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and XRD, however, indicate that the material suffers from a sluggish phase transformation at moderate temperatures. TEM images and SAED patterns suggest that below approximately 825°C an immiscibility gap is apparent in the phase diagram of BSCF. The hexagonal polymorph, which is formed and preferably nucleates at the grain boundaries, is found to be closely related to the parent cubic perovskite. The decomposition kinetics can be adequately described by the Johnson-Mehl-Avrami equation. Anomalies in the creep behaviour of BSCF can be associated with the cubic-to-hexagonal phase transition, while anomalies observed in the stiffness, fracture stress, and toughness behaviour observed at 200-400°C can be associated to a transition in the spin state. A recent and very promising development concerns the suppression of the cubic-to-hexagonal phase transformation by partial substitution of (Co,Fe) with selected dopants. **Figure 10** demonstrates that corresponding substitution with 3 mol% Zr prevents formation of the hexagonal polymorph at 800°C. Finally, it should be mentioned that BSCF is found prone to poisoning by impurities of  $\text{CO}_2$  in the gas phase. Purging BSCF membranes with high concentrations of  $\text{CO}_2$  leads to an immediate cessation of the oxygen flux, due to the formation of surface carbonates. The flux is found to decline over time upon exposure of the membrane to atmospheric concentrations of  $\text{CO}_2$  (~ 400 ppm).



**Figure 10:** HR-TEM micrographs of pure BSCF (left) and 3 mol% Zr-substituted BSCF (right). Images were recorded after annealing of the specimens at 800°C for ~280 h in air. While partial transformation of the cubic phase to 15R and 2H hexagonal polymorphs occurs in pure BSCF, phase transformations do not occur in Zr-substituted BSCF.

Three different membrane geometries have been pursued in the project, including tubular, hollow fibres, and planar. Extruded tubular BSCF membranes have been incorporated in a demonstration unit as described in more detail below. Hollow fibre membranes, with inner and outer diameter 2.7 and 3.5 mm, respectively, have been prepared by spinning using a phase-inversion process. A noticeable improvement in performance is found when these are prepared using sulphur-free precursor polymers and/or coated with a surface activation layer to enhance the surface exchange kinetics. It is further found that optimization of the spinning process, thereby eliminating the presence of macro-voids, greatly improves the mechanical strength of the ceramic fibres. Finally, planar asymmetric supported membrane structures have been developed, using either metallic or ceramic supports. The challenging task to combine a metallic support with a perovskitic membrane layer comprised different steps. At first, a selection of suitable materials was done considering thermal expansion behaviour as well as inevitable reactions at high temperatures required. It turned out that an alumina scale forming Ni-base alloy (NiCoCrAlY) showed suitable compatibility to the membrane material  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF). Two porous interlayers were developed in order to bridge the coarse porosity of the support and the thin dense layer. The top layer was applied using magnetron sputtering, **Figure 11a**. Although the gas-tightness is not yet sufficient to enable performance testing, such novel membrane architecture is succeeded the first time. Ceramic supported membrane structures were achieved using tape casting, having a thickness in the range 20-70  $\mu\text{m}$  and support porosity of up to 41%. Moreover, an additional porous activation layer was applied to promote the surface exchange kinetics. Each layer consists of BSCF which circumvents undesired chemical reactions of the different parts. These membranes show unprecedented high oxygen fluxes as demonstrated in **Figure 11b**.



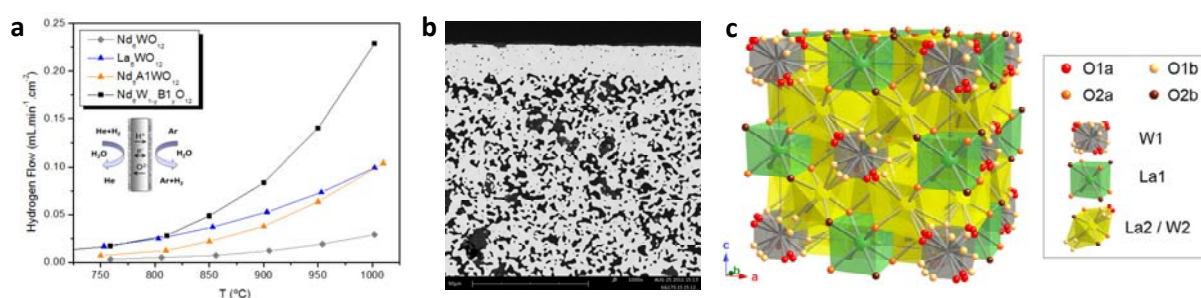
**Figure 11:** a) metal supported LSCF membrane, 11 b) Temperature dependence of the oxygen flux through a ceramic supported BSCF membrane either with or without an activation layer. Inset: SEM micrograph of the activated membrane

The oxygen permeation through BSCF membranes either tubular (hollow fibre) or planar (disc) was successfully described considering both materials science and fluid dynamics. This revealed the presence of polarization resistances and surface exchange limitations already using relatively thick membranes. These effects will increase when reducing membrane thickness. Therefore, an activity has started to fully understand the overall oxygen permeation process in order to create a consolidated model which allows process engineers to design advanced membrane modules.

## Ceramic proton conducting membranes

Proton conducting membranes are based on mixed protonic-electronic conductors, which under certain chemical gradient enable the separation of hydrogen from gas mixtures with theoretically an infinite selectivity. Two main drawbacks have prevented the application of this kind of membranes in real systems, i.e. low stability in CO<sub>2</sub> and H<sub>2</sub>S and limited mixed (ambipolar) conductivity.

At the beginning of the project, a novel class of ceramic materials based on the compound La<sub>6</sub>WO<sub>12</sub> was selected among the different known proton conductors. La<sub>6</sub>WO<sub>12</sub>-based materials were reported to show unique mixed protonic-electronic conductivity. The first activity conducted in MEM-BRAIN aimed to understand the crystalline structure and the transport mechanisms. A great effort has been carried out to resolve the structure of La<sub>6</sub>WO<sub>12</sub>, which required the combination of neutron powder diffraction (NPD) and high resolution synchrotron X-ray diffraction studies. The structure is a fluorite *Fm3m* with several intrinsic oxygen vacancies (**Figure 12c**). The presence of vacancies allows the oxide ion transport at given environmental conditions while enables the oxide hydration and consequent proton transport through the lattice at temperatures in the range from 400-1000 °C. The hydrogen permeability through La<sub>6</sub>WO<sub>12</sub>-based oxides, which is directly related to its ambipolar conductivity, has been improved stepwise during the project by following careful doping strategies. As basis for doping, the compounds La<sub>6</sub>WO<sub>12</sub> and Nd<sub>6</sub>WO<sub>12</sub> were taken while material preparation was accomplished via sol-gel, freeze-drying and solid state reaction routes. The doping entailed the partial substitution of Ln-atoms, W-atoms or both simultaneously. The final optimized materials show a hydrogen permeation rate one order of magnitude higher than the undoped compounds (**Figure 12a**). The resulting IP regarding the doped materials has been protected through the filing of a patent (DE 102010027645.6 – assignees FZJ-IEK and CSIC). The materials remain stable after treatment in CO<sub>2</sub>-rich reducing and also in H<sub>2</sub>S-containing (100 ppm) environments at 30 bars. Furthermore, membrane showed a stable hydrogen permeation at 850 °C over one week operation using CO<sub>2</sub> (15% in Ar) as sweep gas. A parallel development achieved the reproducible preparation of large batches (100 g) of single phase La<sub>6</sub>WO<sub>12</sub> by solid state reaction. Additionally, other synthesis methods based on sol-gel complexation and freeze-drying were developed to obtain single-phase Ln<sub>6</sub>WO<sub>12</sub> nanopowders. Finally, asymmetric membranes supported on porous La<sub>6</sub>WO<sub>12</sub> substrates have been developed (**Figure 12b**).

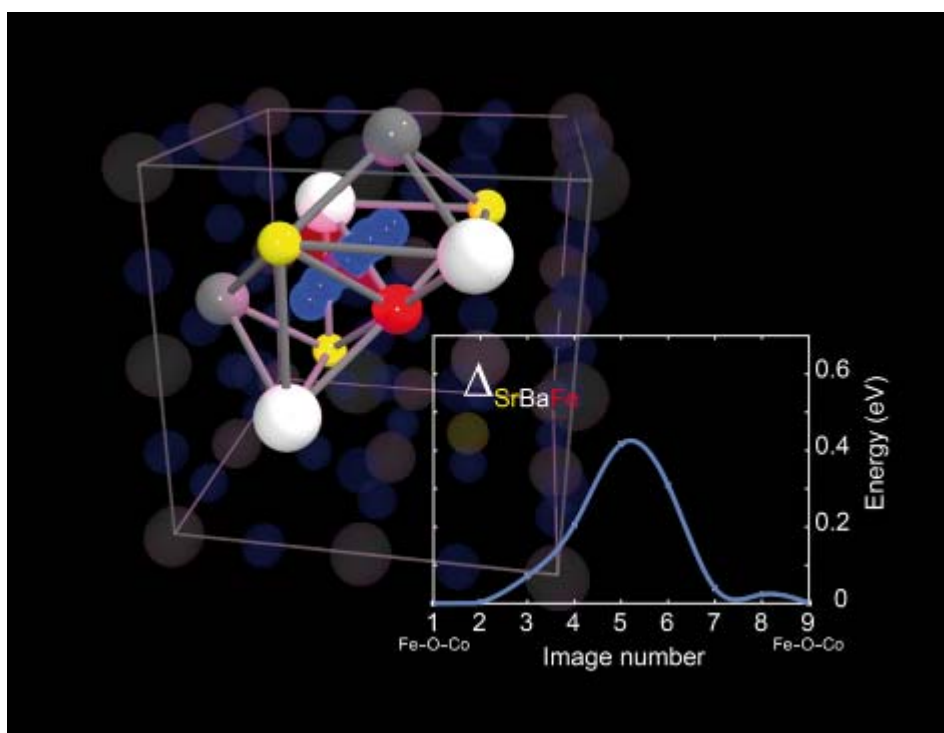


**Figure 12:** a) Permeation flux of different doped materials; **12 b)** SEM image of a supported membrane; and **12 c)** scheme of the resolved structure of La<sub>6</sub>WO<sub>12</sub>

Optimization of the manufacturing process through inverse tape casting is in progress aiming to improve the scalability and minimize membrane bending.

### 3.1.3 Atomistic Modelling

*Ab initio* calculations can be used to gain detailed mechanistic insights on an atomistic level. Within the MEM-BRAIN alliance such *ab initio* calculations were used to investigate the thermodynamic stability of BSCF and to explain the stability differences between the cubic perovskite phase and the hexagonal phase. The stability is directly coupled to the  $\text{Ba}^{2+}/\text{Sr}^{2+}$  content and the vacancy concentration of the material. It could be shown that an increasing number of oxygen defects (vacancies) and a larger  $\text{Sr}^{2+}$  content stabilize the cubic perovskite structure. Since these calculations are, by definition, valid at 0 K only, they served as a basis for subsequent, more sophisticated lattice-dynamical calculations. Hereby, the influence of doping on the stability of BSCF was investigated at elevated temperatures by theoretical means. Theory suggests that substitution of cobalt by nickel destabilizes the structure whereas Mn-doped BSCF is favoured over the unsubstituted compound within a wide temperature range between 0 and 1600 K. The origin of the stabilization was found in the COHP chemical-bonding analysis; by depopulating antibonding interactions in the Co–O bond at the Fermi level, the structure eventually gets stabilized.



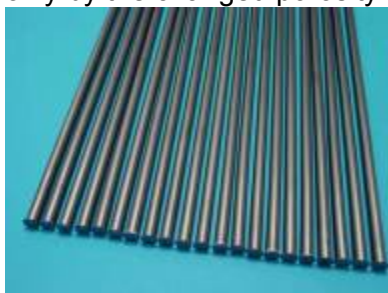
**Figure 13:** Example for a jump and its corresponding energy profile of an oxygen atom moving into a vacancy inside  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ . The saddle-point configuration is designated as  $\Delta_{\text{SrBaFe}}$ . For reasons of clarity, the other atoms in the unit cell have been faded.

The transport properties of BSCF were investigated by calculating the energy barrier for an oxygen-hopping process. The oxygen atom jumps from its original position into a neighbouring vacancy. In the computational model used, only one oxygen atom jumps into a nearby vacancy at a given time. The calculated energy profile, corresponding to the oxygen atom moving through the saddle-point configuration, is shown in **Figure 13**. The calculated energy barrier of about 0.4 eV is in good agreement with experimental results.

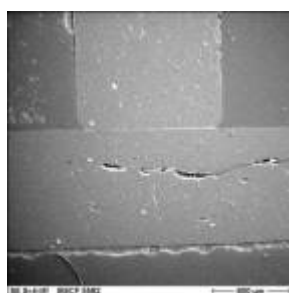
#### WP 4: Joining and sealing of ceramic gas separation membranes

Conventional joining and sealing techniques can be used for temperatures up to 400 °C under oxidizing conditions and up to 800 °C in inert atmospheres, but commercial sealing is not available for higher temperatures under oxidizing conditions. Corresponding to the challenging and harsh operation conditions, the activities in the project were focused on mixed conducting membranes used for oxygen separation. Main targets were the closing of tubular membranes at one end, the building up of advanced membrane components and the joining of ceramic membranes to steel.

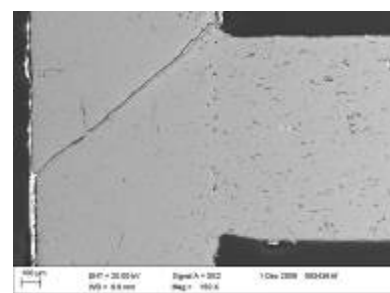
Two methods for joining of ceramic parts to each other were developed based on reactive air brazing (RAB) and on doping-supported diffusive reaction sintering (DDR) realizing a pure ceramic joining. After testing the thermal stability up to application temperature both techniques were used for closing of membrane tubes (**Figure 14**) used in the demonstration unit. RAB joining often resulted in an only partially filled joining gap (**Figure 15**) caused by sublimated silver. But wetting agents of the braze supported a self-tightening by enhanced sintering. The joining area for DDR joined tube end shown in **Figure 16** could be detected only by the changed porosity.



**Figure 14:** membrane tubes closed at one end.



**Figure 15:** RAB joint after testing for 1500 h.



**Figure 16:** DDR joint after testing for 1000 h.

RAB and ceramic joining techniques were also used for the preparation of hollow fibre modules to enhance the package density and the oxygen flux. Hollow fibres and capillaries were combined with machined BSCF discs to modules (**Figure 17**, **Figure 18**). Oxygen permeation agrees very well with the results obtained for individual capillaries.



**Figure 17:** Hollow fibre bundle with a length of 50 mm, joined by DDR method.



**Figure 18:** Hollow fibre bundle with a length of 250 mm joined by RAB method.

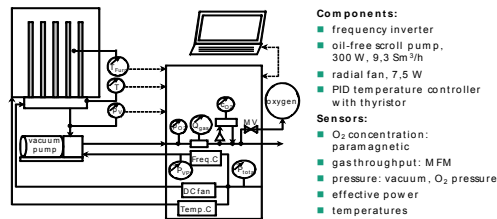
Joining of BSCF with steel was carried out using steel 1.4841. Tensile stress was always generated inside the ceramic part independent from the joining geometry. For that reason, a simple flat geometry was used characterized by a stump joining of ground tube ends without any guidance. Different coatings on steel were tested to improve the adhesion and gas-tightness of the joining. Gas-tight joining were obtained using a RAB braze containing 5 w-% copper oxide. A cast braze tape was combined with a braze paste of the same composition. Some gas-tight BSCF-steel tubes were obtained and tested in the demonstration unit for 250 h and 3 cycles.

### 3.1.4 Construction of demonstration unit and testing

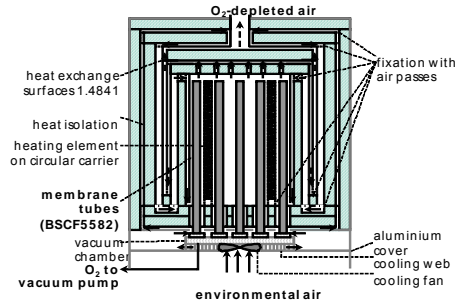
A demonstration unit has been constructed and built by Fraunhofer IKTS using O<sup>2</sup>/e<sup>-</sup>-mixed conducting membranes (**Figure 19**). Due to safety requirements the demonstration unit was designed for the separation of O<sub>2</sub> from environmental air by a vacuum pump (**Figure 20**). 19 BSCF membrane tubes with a total membrane area of 0.2 m<sup>2</sup> were mounted in a furnace similar constructed as a heat exchanger (**Figure 21**).



**Figure 19:** Demonstration unit at Exhibition of the Hannover Fair.



**Figure 20:** Wiring scheme of the demonstration unit.



**Figure 21:** Drawing of the furnace of the demonstration unit.

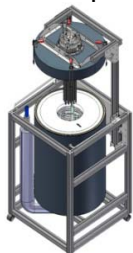
A stable O<sub>2</sub> production of 2.7 L\_STP/min at 850 °C was achieved at a vacuum level around 17-20 mbar O<sub>2</sub> with ambient air at feed side. Experimental O<sub>2</sub> fluxes agree well with simulated ones. The variation of the O<sub>2</sub> flux with vacuum pressure and driving force can be described according Wagner's equation. Presently, the total operation time amounts 2060 h, 35 thermal cycles with 5 K/min are finished.

Long term tests were performed at 800 °C and 850 °C with fast changes of the pump frequency to vary the vacuum pressure and the entailed driving force for O<sub>2</sub> permeation resulting in chemically induced stress and finally axial cracks of several tubes (**Figure 22**). This could be prevented by limiting the maximal changing speed of the vacuum pump frequency to 15 Hz/min.

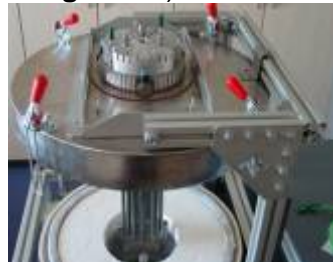


**Figure 22:** Bubble test of a defective membrane tube after long term test and a detail view on an axial crack.

A second stage of a demonstration unit was designed and built for higher oxygen throughputs up to 20 L\_STP/min allowing the testing of advanced membrane components developed (**Figure 23 - Figure 26**)



**Figure 23:** CAD design of the second stage demonstration unit.



**Figure 24:** Top view with the membrane tubes mounted in the top cover plate.



**Figure 25:** Schematic drawing of the built-in cross-flow heat exchanger.



**Figure 26:** Second stage demonstration unit after completion.

### 3.1.5 Summary RT 1: Ceramic membranes

Research topic 1 of the Helmholtz Allianz MEM-BRAIN was a unique network of 14 European research institutes accompanied by 3 companies with the goal to identify and develop inorganic membranes for zero emission power plants. On this way a critical mass competitive to other groups and networks in the world has been established first time.

**Materials development** has been carried out starting broad and focusing more and more during the project. In the field of zeolite membranes a sulphur stabilized sodalite was identified as the only zeolite stable under pre-combustion condition. Among the sol-gel materials hybrid thin films with Si-C bonds incorporated were favoured. Lanthanum tungstate's showed the highest mixed protonic-electronic conductivity whereas the conductivity was optimized by partial substitution of La. In the field of oxygen mixed ionic-electronic conducting membranes the project stayed with  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ . A stable window of application adapted to the oxyfuel process was identified.

**Membrane preparation** was successfully performed with all materials. The growth mechanism of sodalite membranes is not yet well understood resulting in a small percentage of interparticle pores limiting the selectivity. Defect free sol-gel membranes could be prepared on flat substrates with a thickness in the range of only 50 nm. A hydrothermal stable mesoporous intermediate layer was developed from yttria stabilized zirconia to replace the unstable  $\gamma$ -alumina layer. Ceramic proton conducting membranes were prepared as monolithic discs. First time thin oxygen mixed ionic-electronic conducting membranes were prepared on porous substrates confirming the expected rise of oxygen flux.

A huge progress in fundamental understanding of all materials and membranes was achieved by incorporating high sophisticated methods of **characterization**. Especially the phase transitions and phase stabilities of ceramic proton conducting membranes as well as oxygen mixed ionic-electronic conducting membranes were clarified.

The movement of different ions was calculated by **atomistic modelling** helping to understand the macroscopic transport of hydrogen and oxygen.

Strategies of **joining and sealing** were successfully developed and tested for oxygen mixed ionic-electronic conducting membranes. Membrane tubes were closed on one end, capillaries and hollow fibres were bundled.

A **demonstration unit** for oxygen mixed ionic-electronic conducting membranes containing 0.2 m<sup>2</sup> membrane area was built already in an early stage of the project. It was successfully operated over a long period and was shown on different fairs, exhibitions and meetings. The long term tests confirmed the oxygen flux from lab tests. A second stage of a demonstration unit was built considering the experiences from the first one.

The **Final targets** in terms of flux and selectivity were achieved for oxygen mixed ionic-electronic conducting membranes and sol-gel membranes. Ceramic proton conducting membranes require thin supported membranes and higher operating temperatures to meet the desired targets. Zeolite membranes still suffer from limiting intergrowing.

The challenge of membrane development within research topic 1 of Helmholtz Allianz MEM-BRAIN based on the big number of partners, the different types of membranes and the limiting time was very well mastered. The chance of using inorganic membranes in power plant application in the future was further increased. Additional projects will be required to continue the membrane development and membrane up-scaling. Hopefully it will be possible to keep the spirit of this network.

### 3.2 Research Topic 2: “Polymeric and hybrid membranes for temperatures up to 200°C”

Material synthesis, membrane manufacture and characterization, and module development on a pilot scale for separation in temperature ranges of up to 200°C is a second research topic. Polymeric membranes are the furthest developed option.

Polymeric and organic/inorganic hybrid membranes are being developed for CO<sub>2</sub>/N<sub>2</sub> separation (post-combustion process) as well as for CO<sub>2</sub>/H<sub>2</sub> separation (pre-combustion process). In contrast to the ceramic membranes described above, these membranes are more permeable for CO<sub>2</sub> than for H<sub>2</sub>. In addition to pure polymeric membranes, new hybrid organic/inorganic membranes with inorganic molecular sieves are being prepared.

Technically useful polymeric gas separation membranes are either of integral asymmetric type or thin film composite membranes composed of a porous support and a polymer layer of a second polymer material. The active separation layer of both membrane types consists of a very thin film of dense polymer material. Depending on the material properties of the envisaged polymer either integral asymmetric or thin film composites are preferred. For technical applications the final membrane should be designed to provide both, high flux at a considerable high selectivity. The materials selection focused on commercial polymers with polyethyleneglycole (PEG) units as a guarantor for high CO<sub>2</sub>-solubility and, therefore, high selectivity. The polymers Pebax® 1657 and Polyactive™ with reported selectivities of CO<sub>2</sub>/N<sub>2</sub> = 45 – 60 and permeabilities of ~70 (Pebax®) and ~150 Barrer (Polyactive™) were chosen.

A supporting membrane from polyacrylonitrile (PAN) with the required porosity and a gas flow >100 m<sup>3</sup>/m<sup>2</sup>hbar was prepared and furnished with a thin polydimethylsiloxane film to serve as a gutter layer for the selective separation layer. With Pebax® a CO<sub>2</sub> flux below 1 m<sup>3</sup>/m<sup>2</sup>hbar at a CO<sub>2</sub>/N<sub>2</sub> selectivity of 50 was approached. By the addition of 50 wt-% low molecular weight PEG a marked increase in permeability by a factor 2 at similar selectivity for CO<sub>2</sub>/N<sub>2</sub> was measured. The end-capping of the PEG's hydroxy groups by methyl groups resulted in a further 4 times increase in permeability of CO<sub>2</sub> to 600 Barrer. The CO<sub>2</sub>/N<sub>2</sub> selectivity stayed about constant, however, the CO<sub>2</sub>/H<sub>2</sub> selectivity increased by more than 50% to 15. This unexpected behaviour was examined in detail and published. The most interesting result is the decrease in crystallinity of the Pebax®/PEG blends accompanied by an increase of both, CO<sub>2</sub> solubility and diffusivity. The end capping of the low molecular weight PEG with methyl groups to methyl ethers further depressed the crystallinity as explained by stopping the hydrogen bonding capacity of free OH-groups of the PEG.

The 2<sup>nd</sup> selected polymer, Polyactive™, is a polyester-copolymer composed of PEG, butanediol and terephthalic acid. It showed already without additives a CO<sub>2</sub> permeability of about double of Pebax®. Fine tuning of the PEG/alkanediol unit further increased the CO<sub>2</sub> permeability to 180 Barrer. However, working with the commercial available Polyactive™ and blending with 40 wt-% of: PEG, PEG-BE (PEG monobutyl ether) and PEG-DBE (PEG dibutyl ether) increased the CO<sub>2</sub> permeability from 150 (without additive) to 200 (PEG), 400 (PEG-BE) and 700 Barrer (PEG-DBE). This was accompanied by a decrease in CO<sub>2</sub>/N<sub>2</sub> selectivity to 40. On the other hand, the CO<sub>2</sub>/H<sub>2</sub> selectivity increased from 10 to 12.4. The morphological characterization revealed a reduced crystallinity of the blends compared to the pristine Polyactive™. Thin film composite membranes on PAN support with gutter layer produced a CO<sub>2</sub> flux of up to 5 m<sup>3</sup>/m<sup>2</sup>hbar with CO<sub>2</sub>/N<sub>2</sub> of ~60. This corresponds to a thickness of the polyactive separation layer of about 50 nm as measured by SEM. The Polyactive-type polymer with the higher molecular weight of 120 kDa and PEG units of 4 kDa produced higher fluxes with better selectivity than a polyactive with only 41 kDa and PEG units of 1 kDa at the same wt-% of PEG units in the polymer. On technical scale CO<sub>2</sub> fluxes of 2-3.6 m<sup>3</sup>/m<sup>2</sup>hbar at CO<sub>2</sub>/N<sub>2</sub> = 52-69 using the 1.5 kDa type were reached. With the other type 4 kDa the highest fluxes of 5-6 m<sup>3</sup>/m<sup>2</sup>hbar CO<sub>2</sub> at a lower CO<sub>2</sub>/N<sub>2</sub> selectivity of 33 could be obtained. Mixed gas measurements of the composite membranes revealed even at high feed gas pressures up to 20 bar no or only a very little reduction in flux or selectivity.

For operation with humid feed gases facilitated transport membranes can be applied. Under the influence of water  $\text{CO}_2$  forms with primary or secondary amino groups carbamates that decompose at the permeate side of the membranes. On balance the  $\text{CO}_2$  flux can be favoured over the flux of the other gases to be separated. Polyvinylamine based membranes were obtained by cross-linking with diepoxides. Additionally, ammonium groups were introduced by epoxy functionalized quaternary amines. At 100% relative humidity a permeability of >850 Barrer at a  $\text{CO}_2/\text{N}_2$  selectivity of >50 was obtained at 30°C. Higher temperatures increased the permeability further, however, on cost of selectivity.

For blending with PEG-containing polymers poly(4-acetyl morpholine) (PAM) was synthesized. Blends up to 30 wt-% were obtained. In the dry state the addition of PAM to both, Polyactive™ and Pebax® decreased the permeability, mainly by a stronger decrease in diffusivity than the detected high increase in solubility could compensate for. In humid atmosphere, however, the Polyactive™ blend with 30 wt-% PAM showed an about similar permeability compared to pristine Polyactive but the  $\text{CO}_2/\text{N}_2$  selectivity reached 63 compared to only 40 for pure Polyactive.

Mixed matrix membranes, both, from Pebax® or Polyactive™, revealed generally a lower permeability at similar or slightly lower selectivity. To make thin film composite membranes out of these materials is not promising and was not attempted.

### 3.3 Research Topic 3: „Process engineering and system integration“

RT3 deals with the system integration of membranes for  $\text{CO}_2$  capture into coal fired power plants (PP). It links the detailed material investigation and the application of the new technique under the given boundary conditions of a power plant. Thus the topic develops new process concepts for an efficient integration of the investigated membranes. It provides simulation models of the process as well as of the membranes and the modules. The approach enables a fast evaluation of the proposed concepts and defines the requirements for the separation process and material properties of the membranes (RT1 and RT2). The topic analyses three technical lines: post-combustion (WP2, FZJ-IEK3), pre-combustion (WP3, RUB-LEAT) and oxyfuel combustion (WP4, RWTH-AVT). For these applications different separation challenges for the membranes have to be met:  $\text{CO}_2/\text{N}_2$  in WP2,  $\text{CO}_2/\text{H}_2$  or  $\text{H}_2/\text{CO}_2$  in WP3 as well as  $\text{O}_2/\text{N}_2$  in WP4 and optional in WP3. The overall  $\text{CO}_2$  purity and separation ratio for sequestration was defined with 95mol-% and 90%, respectively.

The evaluation within RT3 involves the comparison of the energy penalty, including compression of  $\text{CO}_2$  to 100bar, in contrast to conventional power plants without  $\text{CO}_2$  capture (WP1) and to conventional  $\text{CO}_2$  separation methods. The latter is done by reference data taken from the literature: chemical absorption ( $\Delta\eta_{\text{net}}=9\text{-}12\%$ -points, WP2); physical absorption ( $\Delta\eta_{\text{net}}=9\text{-}14\%$ -points, WP3) and cryogenic air separation ( $\Delta\eta_{\text{net}}=8\text{-}10\%$ -points, WP4). Further the costs of electricity (CE, base is 2010) for the new processes were calculated according to procedures and reference costs found in the literature. For polymeric and ceramic membranes the prices were assumed to be 50 and 1000€/m<sup>2</sup>, respectively, and the life time was set to three years. Selected results for an operation capacity of 8000h/a and a  $\text{CO}_2$  certificate price of 30€/t<sub>CO<sub>2</sub></sub> are presented in the attached table.

In order to calculate the necessary membrane areas, 1D membrane models were developed based on the mass transport equations received from RT1 and RT2 for the respective separation problem and applied material. The models are able to determine the permeation rate ( $j$ ) with respect to the change of partial pressures and temperature along the membrane surface.

In WP1 (RUB-LEAT, RWTH-AVT) simulation models of a conventional pulverized coal fired PP (Referenz Kraftwerk NRW, hard coal,  $\eta_{\text{net}}=45.9\%$ , 44€/MWh, Germany) and a gasification PP (hard coal,  $\eta_{\text{net}}=47.1\%$ , 46€/MWh, Puertollano, Spain) were set up to provide boundary conditions for the steam/water cycle for pre-combustion capture and oxyfuel as well as the flue gas composition and mass flow rate for post-combustion capture.

In WP2 polymeric membranes are integrated after the desulphurization unit to separate the CO<sub>2</sub> from the flue gas (~14 mol-%). Single staged or cascaded 3-end membrane systems with feed and permeate pressure varying between  $p_{feed}=1-4\text{bar}$  and  $p_{permeate}=0.1-1\text{bar}$ , respectively, were investigated. A polyactive membrane with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 50 and a permeability of  $Q=3\text{Nm}^3/(\text{m}^2\cdot\text{h}\cdot\text{bar})$  was chosen. Further the effect of water vapour in the flue gas was studied. It has a higher permeability than CO<sub>2</sub> (approx. factor 10) resulting in two effects: (1) It increases the energy demand of the vacuum pump but (2) it also increases  $j_{CO_2}$  since the permeated H<sub>2</sub>O decreases  $p_{CO_2}$ . A removal of 2/3 of the flue gas water fraction by upstream pervaporation is necessary. Due to the limited selectivity the simple single-stage membrane process is problematic. The given CO<sub>2</sub>-separation ratio cannot be achieved without lower purities. At a CO<sub>2</sub>-separation ratio of 50% ( $p_{feed}=1\text{bar}$ ,  $p_{permeate}=0.1\text{bar}$ ) a purity of 73mol-% can be achieved at a  $\Delta\eta_{net}$  of 4.0%-points. To increase the CO<sub>2</sub> purity to 95%, cascaded systems must be applied. The  $p_{feed}$  of the 1<sup>st</sup>/2<sup>nd</sup> stage are 1/4bar, the  $p_{permeate}$  is 0.1/1bar. By restricting the CO<sub>2</sub> separation ratio from 90 to 70% a  $\Delta\eta_{net}$  of 7.1 instead of 12%-points can be achieved. The calculated specific membrane area ( $a_{mem}$ ) is  $4.7\text{m}^2/\text{kW}_{net}$  with 2% accounting for the 2<sup>nd</sup> stage. The CE for the cascaded system are 72€/MWh. By increasing the permeability by a factor of 3 and the membrane life time to 5a the CE of 66€/MWh are competitive with the CE of the reference PP.

In WP3 the conventional IGCC process has been adapted to pre-combustion capture by introducing a sour water-gas-shift (WGS). Different membrane materials and process concepts were investigated. All concepts have in common that the H<sub>2</sub> and the CO in the CO<sub>2</sub> rich stream has to be post-combusted by pure O<sub>2</sub> in addition. Additionally, the pre-combustion capture benefits from the high pressure level in the raw gas or feed stream (approx. 23bar). Polymeric CO<sub>2</sub> selective membranes could be installed after the H<sub>2</sub>S removal unit but the today's available selectivity of 10 is too low. A cascaded system as applied in WP2 would disproportionately increase the energy penalty. For ideal polymeric membranes with a CO<sub>2</sub>/H<sub>2</sub> selectivity of 150,  $\Delta\eta_{net}$  has a value of 8.7%-points ( $a_{mem}=0.32\text{m}^2/\text{kW}_{net}$  for  $Q=0.4\text{Nm}^3/(\text{m}^2\cdot\text{h}\cdot\text{bar})$ ). Ceramic H<sub>2</sub> selective membranes can be installed (1) after H<sub>2</sub>S removal or (2) as an in situ H<sub>2</sub> recovery during the WGS (WGS membrane reactor). RT1 reported a permeability of  $Q=1.53\text{Nm}^3/(\text{m}^2\cdot\text{h}\cdot\text{bar})$  and the assumed H<sub>2</sub>/CO<sub>2</sub> selectivity for these types of membranes was 500. The concepts benefit from the possibility to apply a sweep stream on the permeate side. Therefore excess N<sub>2</sub> of the air separation unit can be used. This increases the driving force and lowers the membrane area. In the case of using a WGS membrane reactor the equilibrium during the WGS reaction is shifted to H<sub>2</sub>. The efficiency losses for case (1) and (2) are 9.1 and 6.8%-points, respectively. The calculated specific membrane area is for both in the range of  $0.25\text{m}^2/\text{kW}_{net}$ . The CE for the ideal polymeric case is 59€/MWh and lower than that of the reference IGCC. By applying more expensive ceramic membranes the CE rises to about 71€/MWh. By increasing the membrane life time to five years also the concepts with ceramic membranes have CE below the reference IGCC (66€/MWh). Variations of the operating hours of an IGCC were performed since they are typically lower than conventional PPs.

In WP4 the reference power plant was adapted to oxyfuel conditions with a flue gas recirculation. 3- or 4-end membrane operation concepts can be applied to separate O<sub>2</sub> from air by means of oxygen transport membranes (OTM). Since no flue gas stable material exists today, only 3-end operation without membrane contact to the flue gas is feasible. The combination of preheated pressurized air feed ( $p_{feed}=5-20\text{bar}$ ) and vacuum on the permeate side is considered to be favorable to establish the needed oxygen partial pressure ratio ( $\Pi$ ). The air is preheated (825°C) in the boiler to reach the operation temperature of the membrane. In the membrane unit the O<sub>2</sub> is separated to a certain percentage which is fixed by the O<sub>2</sub> separation ratio ( $\xi$ ). A permeation rate of  $1\text{Nm}^3/(\text{min}\cdot\text{cm}^2)$  at  $\Pi=5$  was reported by RT1 for tubular OTMs. The  $\Delta\eta_{net}$  depends mainly on the energy demand of the vacuum pump, since it is the second largest energy consumer after the CO<sub>2</sub> compression unit. This results in a direct dependency of  $\Delta\eta_{net}$  on  $\Pi$  and  $\xi$ . It is considered that the optimal O<sub>2</sub> separation ratio  $\xi$  is 50% while  $p_{feed}$  is specified by the applied  $\Pi$ . For a thermodynamic

optimum, values of  $\Pi=3$ ,  $\xi=50\%$  and  $p_{feed}=7\text{bar}$  with a  $\Delta\eta_{net}=5.9\%$ -points have been calculated. In order to lower the membrane area, higher  $\Pi$  values need to be applied. For  $\Pi=10$ , the optimal membrane process design parameters are  $\xi=50\%$  and  $p_{feed}=15\text{bar}$  but an increased  $\Delta\eta_{net}$  of 7.2%-points results. The corresponding  $a_{mem}$  are 1.5 and  $0.45\text{m}^2/\text{kW}_{net}$ , respectively. The CE are calculated to:  $\Pi=3$ : 128€/MWh and  $\Pi=10$ : 69€/MWh. The CE are mainly dominated by membrane specific costs. By additionally increasing  $j$  by a factor of 3 the CE decrease to 73 and accordingly 51€/MWh. The results show that by increasing both  $\Pi$  and  $j$  the CE reaches the range of the reference PP and even is lower.

Oxyfuel and pre-combustion capture by means of membranes can compete with conventional capture systems regarding  $\Delta\eta_{net}$  and CE under given boundary conditions. Post-combustion capture is only competitive if the separation ratio of  $\text{CO}_2$  is decreased to 70%. A minimum price of  $\text{CO}_2$  certificates of 30 €/t<sub>CO2</sub> must be given to make these technologies economical viable. A further development of membrane materials towards higher permeability and life time is needed. Especially, in the case of ceramic membranes a cheap production strategy is required since the CE are mainly dominated by the price of membrane. All  $\text{CO}_2$  capture processes by membranes lack of pilot scale experience under real conditions. Only a further investigation of the materials and suitable membrane modules under real conditions can prove the practical and industrial application as well as the assumptions and results of the thermodynamic simulations.

**Table 1:** CE,  $\eta_{net}$ , and specific membrane area for all capture routs. (Costs are calculated according to the report 2010/2011, CO<sub>2</sub> separation for the capture routes is 90% and 95% purity if not marked. All calculations are for hard coal. Only changed results with respect to the base case are shown in the variation section)

Base cases:			Post combustion	Oxyfuel	Pre combustion			
	Units	Ref. PP	CO <sub>2</sub> selective polymeric cascaded system <sup>c)</sup>	OTM Oxy <sup>a)</sup>	Ref. IGCC	CO <sub>2</sub> selective polymeric <sup>b)</sup>	H <sub>2</sub> selective ceramic	membrane Reactor
net power	[MW]	555	469	484	365.90	322.7	329.2	341.24
net efficiency $\eta_{net}$	[%]	45.9	38.8	40.0	47.1	38.4	38.0	40.3
specific membrane area $a_{mem}$	[m <sup>2</sup> /kW <sub>net</sub> ]	-	4.7	1.5	-	0.32	0.25	0.26
cost of electricity	[€/MWh]	43.55	64.25	125.10	46.27	55.21	70.31	70.28
<i>fixed costs</i>	[€/MWh]	19.15	35.46	93.84	23.60	29.35	44.30	45.70
<i>capital cost</i>	[€/MWh]	14.09	21.90	28.16	16.70	20.06	25.17	25.21
<i>plant maintenance</i>	[€/MWh]	2.85	3.36	5.07	3.37	4.20	4.13	4.99
<i>membrane plant maintenance</i>	[€/MWh]		7.59	57.57		0.78	11.38	13.00
<i>wages</i>	[€/MWh]	1.41	1.66	1.45	2.58	2.56	2.51	2.43
<i>insurance, overheads</i>	[€/MWh]	0.79	0.93	1.59	0.95	1.12	1.10	1.06
<i>variable costs (coal, operating materials etc.)</i>	[€/MWh]	24.40	28.79	27.42	22.66	25.86	26.01	24.58
additional costs for CO <sub>2</sub> (30€/t <sub>CO2</sub> )	[€/MWh]	22.59	8.00	2.59	21.35	3.95	0.76	0.85
cost of electricity with CO <sub>2</sub> certificates	[€/MWh]	66.14	72.25	127.69	67.62	59.16	71.08	71.14
<b>Variations:</b>								
Variation 1			Q <sub>CO2</sub> =9 Nm <sup>3</sup> /m <sup>2</sup> /h/bar	j=3Nm <sup>3</sup> /min/cm <sup>2</sup>	Operating hours 4600h/a /7000h/a			
membrane area	[m <sup>2</sup> /kW <sub>net</sub> ]	-	1.6	0.47	-	-	-	-
cost of electricity with CO <sub>2</sub> certificates	[€/MWh]	66.14	67.19	73.17	85.10 / 71.00	80.85 / 63.55	103.82 / 77.41	104.92 / 77.67
Variation 2			Variation 1+life time 5a	Variation 1 + $\Pi=10$ , $p_{feed}=15$ bar				
net efficiency	[%]	-	-	38.7	-	-	-	-
membrane area	[m <sup>2</sup> /kW <sub>net</sub> ]	-	1.6	0.45	-	-	-	-
cost of electricity with CO <sub>2</sub> certificates	[€/MWh]	66.14	66.18	51.02	-	-	-	-
Variation 3			Increased membrane life time 5a					
cost of electricity with CO <sub>2</sub> certificates	[€/MWh]	66.14	69.21	101.23	67.62	58.89	66.91	66.37
a) $p_{feed}=7$ bar, $\Pi=3$ , $\xi=50\%$ , $j \approx 1$ Nml/min/cm <sup>2</sup> at $\Pi=5$ b) ideal CO <sub>2</sub> /H <sub>2</sub> selectivity =150 c) Cascade after 67% H <sub>2</sub> O removal from flue gas, CO <sub>2</sub> separation =70%, permeability of 3Nm <sup>3</sup> /(m <sup>2</sup> *h*bar), CO <sub>2</sub> /N <sub>2</sub> selectivity of 50								

### 3.4 Research Topic 4: „Energy systems analysis“

Main object of the work in Research Topic 4 (RT 4) was the assessment of specific technical, environmental and economic aspects of CO<sub>2</sub> capture as a component of the whole CCS process chain. In particular, the three aims were:

- WP 1: Characterization of techno-economic requirements for the capture technology from subsequent processes, e.g. transport and storage;
- WP 2: Assessment and quantification of the impacts on the environment associated with the introduction of membrane-based CCS technology;
- WP 3: Developments of scenarios for the potential of membrane-based CO<sub>2</sub> capture in the energy system as part of a climate protection strategy.

#### **WP 1: Characterization of specific technical and economic aspects concerning CO<sub>2</sub> transport and storage**

In a detailed assessment two different compression processes for typical Oxyfuel and IGCC flue gases were calculated, comparing different compression and purification systems (distillation column versus flash drum). The results show the relation between increasing energy requirement to reach a higher CO<sub>2</sub> purity and higher storage capacity depending on the impurities of the flue gas. There are generally no strong technical barriers to provide high purity of CO<sub>2</sub>, however increasing purity requirements are likely to induce additional costs and energy requirements resulting in higher losses of plant efficiency.

Additionally, in a literature survey important requirements resulting from transport and storage processes were identified. In December 2008 an EU directive for “Geological storage of carbon dioxide” was launched and implemented into German law in 2011. However, the definition of the CO<sub>2</sub> stream quality in those directives is quite unspecific. A CO<sub>2</sub> stream shall consist “overwhelmingly” of carbon dioxide, without further specification.

In an economic evaluation of transport of CO<sub>2</sub> costs from already operating CO<sub>2</sub> pipeline projects were used to estimate costs for new transportation pipelines. Costs for onshore and offshore use were considered, including expenditures for recompression and maintenance. The estimated costs for onshore transport are 0.1 – 7 €/100tkm, while for offshore transport they are 0.2 – 11 €/100tkm. These costs are mainly influenced by the utilized capacity, leading to a high flow rate next to the capacity limit. Cost reduction potentials exist in material selection and the introduction of new laying technology, especially for offshore use. Optimal pipeline routes, e.g. along existing infrastructure, decreases costs as well. Information about the costs for storage varies widely. Main reason is the strong dependence of investment cost on geological conditions. The drilling costs are mainly influenced by the storage depth and the conditions of cap rocks. Generally, onshore storage is less expensive than offshore storage. For onshore storage in aquifers a range of 1 – 6 €/tCO<sub>2</sub> can be expected, offshore storage costs are 1.5 – 11 €/tCO<sub>2</sub>. Additional costs for monitoring are assumed to be 0.03 – 0.05 €/tCO<sub>2</sub>.

#### **WP 2 Screening LCA for membranes and power plants and resource balances**

For a comprehensive evaluation of environmental impacts an analysis that focuses exclusively on CO<sub>2</sub> emissions is not enough. Other emissions or substances used in CCS technologies induce other environmental impacts which have to be recognized as well. A life cycle approach, including into the analysis upstream processes like additional fuel and material supply as well as downstream processes such as waste treatment, provides an adequate method for a comprehensive evaluation of all environmental effects. At this membrane-based CCS technologies compete with other concepts.

For each CCS process route (post-combustion, oxyfuel, pre-combustion) a basis power plant without capture, one plant with a competing capture technology and one membrane-based capture system was modelled. **Table 2** names the specific technologies considered for the different process routes.

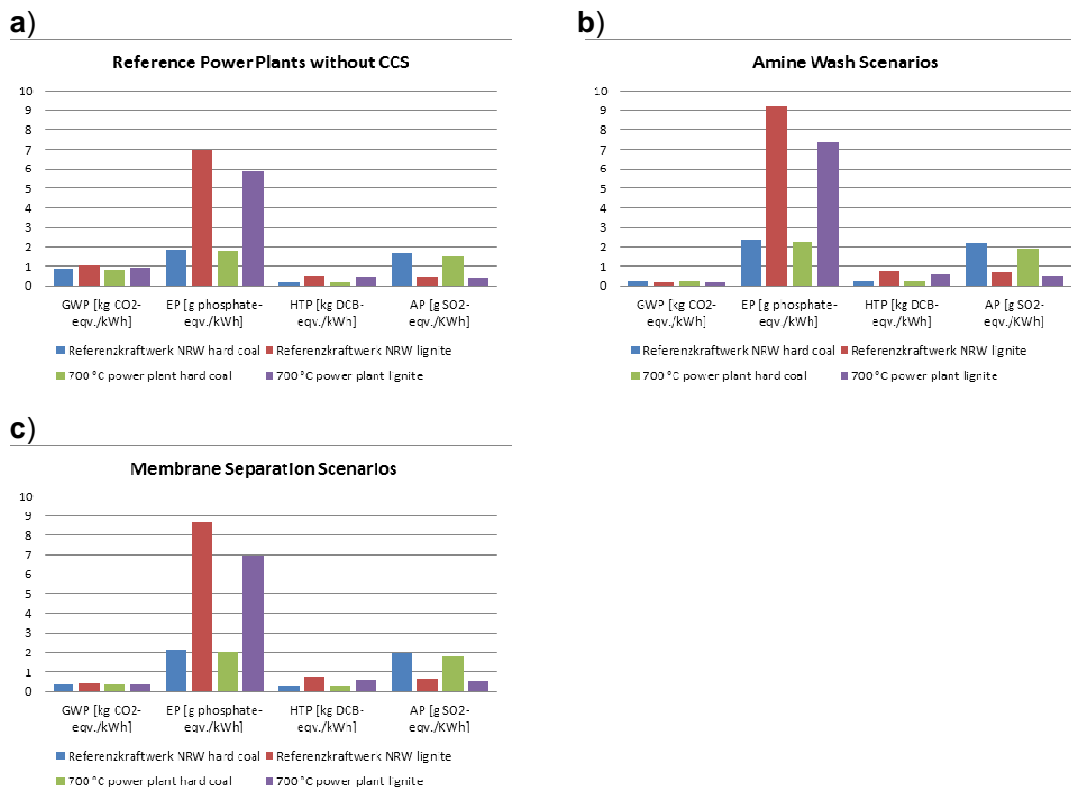
**Table 2:** Power plant technologies for comparison

	Reference power plant	Competing capture technology	Membrane-based capture technology
Post-combustion	RP NRW	Amine Wash	Polyactive
Oxyfuel	RP NRW	Cryogenic air separation	BSCF, three-end modus
Pre-combustion	IGCC	Rectisol Wash	microporous membrane

To account for different technology development states a modern supercritical (600°C) and a future ultra-supercritical (700°C) coal fired power plant was the bases for the modelling. In a first step the process simulation/optimisation data of RT 3 were transformed into a life cycle approach. The comparison of the different power plant types is performed on a basis of 1 kWh of electricity produced (functional unit in LCA). In the life cycle inventory (LCI) a full inventory is set up for each power plant type by describing all relevant inputs and outputs for each process step. The described power plant systems are then extended by upstream processes and downstream processes. Also construction and dismantling of components of the power plants and air separation facilities are included in the analysis. In the Life Cycle Impact Assessment (LCIA) the gathered and aggregated inputs and outputs of the system are categorized and allocated to impact categories. Depending on the investigated systems the following impact categories were considered: Global warming potential (GWP), cumulated energy demand (CED), acidification potential (AP), eutrophication potential (EP), human toxicity potential (HTP) and photochemical ozone creation potential (POCP).

### Post-combustion

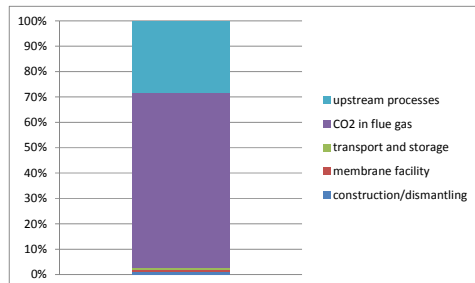
For the post-combustion system six hard coal and six lignite power plants were considered. The necessary information for the polymeric Polyactive membrane was provided by RT 2 and the thermodynamic power plant modelling by RT 3 (separation degree 70%). **Figure 28** shows the equivalents of some impacts for the different system without CCS (a), with Amine wash (b) and with membrane based capture (c).



**Figure 28:** Environmental equivalent impacts of power plants per kWh<sub>electricity produced</sub> without CCS (a), with Amine wash (b) and with capture by Polyactive membrane (c)

The Global Warming Potential (GWP) emissions are between 800 and 1.100 g CO<sub>2</sub>-eqv./kWh for the scenarios without CCS. When looking at the scenarios using a CCS technology, reductions down to 150 – 430 g CO<sub>2</sub>-eqv./kWh are possible. All other impacts increase when using CCS post-combustion technology.

**Figure 29** displays exemplarily the fractions that the different phases of the process chain have on the total GWP for a power plant using membrane CCS technology.

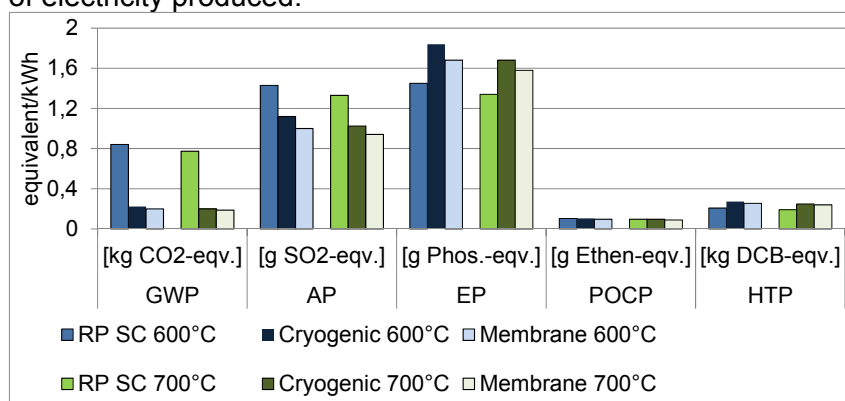


**Figure 29:** Fraction of process chain phases on the total GWP for a CCS plant using membranes

The biggest impact arises from the emissions in the flue gas. Also the upstream processes are not negligible. Other inputs from other phases like construction/dismantling, membrane facility or transport and storage only have insignificant impacts.

## Oxyfuel

For the oxyfuel system six hard coal power plants were compared. The necessary information for the BSCF membrane module was set up in cooperation with RT 1 and RT 3. **Figure 30** shows exemplarily the environmental effects of the six systems. The different impact categories are expressed in the specific equivalent of the particular category per kWh of electricity produced.



**Figure 30:** Selected environmental impacts of power plants per kWh<sub>electricity produced</sub>

The results show, that for both oxyfuel power plants the GWP and AP decrease compared to conventional power plants, while POCP is hardly affected and EP and HTP increase. The membrane technology shows a better performance in all impact categories, mainly due to lesser efficiency losses. The upstream coal process chain (mining and ocean coal transport) as well as downstream waste processes for ashes account mainly for the overall environmental effects. For HTP the production of the BSCF membrane module, especially the housing of the module becomes relevant as well. The results for the membrane-based air separation rely strongly on the assumed life time of the module and the membranes themselves. For the results shown in **Figure 30** an optimistic membrane life time of 40 years was assumed. Sensitivity analyses with lesser life times (one, five years) have shown the impacts on the results.

## Pre-combustion

For pre-combustion a similar comparison is anticipated between a modern IGCC plants, with and without a Rectisol process and a membrane based CO<sub>2</sub> capture. However, long time

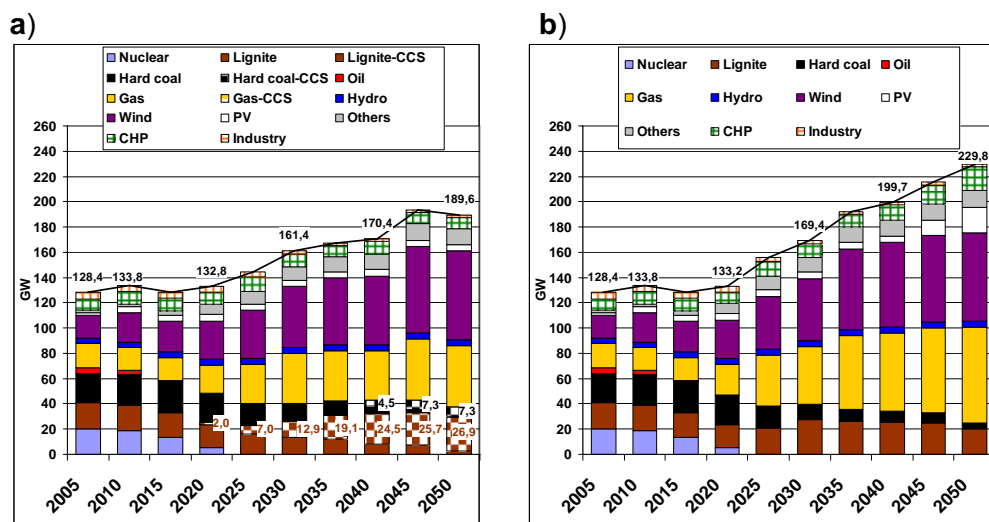
stability tests for the H<sub>2</sub>/CO<sub>2</sub> membrane are essential to define membrane performance parameters which have to be integrated into the modelling.

### Resource analysis

A resource analysis for the BSCF membrane material was performed. The EU commission defined Cobalt as one of 14 critical raw materials for the EU, mainly because of the increasing importance of the consumption (e.g. batteries, super alloys), a high regional supply risk (only supplier DR Congo) as well as high competition in demand (especially from China).

### WP3: Energy systems model analysis

CCS represents one measure amongst many other mitigation options. By means of the IKARUS optimization model, scenarios have been generated that permit CCS to be classified within the framework of a national mitigation strategy for Germany. Different reduction targets are considered. It is assumed, that CCS technology is available after 2020 as new power plants as well as for retrofitting older plants already in operation. CCS technology fired by coal (especially lignite) is an interesting option within a national CO<sub>2</sub>-mitigation strategy. For a 69% reduction target about 27 GW lignite fired power plants have to be installed (including 7 GW retrofitted power plants) in the year 2050. The capacity of hard coal fuelled plants with CCS is 7 GW (all retrofitted). **Figure 31** shows the installed power plant capacity using CCS technology (a) compared to the capacity without CCS (b) being introduced into the system.



**Figure 31:** Installed power plant capacity for a 69 % CO<sub>2</sub> reduction strategy a) with CCS and b) without CCS

To reach the reduction target the capacity without using CCS increases by 100 GW until 2050. About 57 % is renewable technology. Especially the amount of hard coal technology decreases drastically. The calculated capacity building rates for CCS are high and imply additional lignite supply infrastructure. Assuming an average membrane capacity of 1 m<sup>2</sup>/kW the calculated built up of capacity requires an annual membrane production of 2 Million m<sup>2</sup>.

To achieve the same 69% reduction target without CCS technology other measures (in other sectors) are necessary, which increase the total CO<sub>2</sub>-reduction costs for the total German energy system by about 27 Billion €/a in 2050. The specific CO<sub>2</sub> reduction costs for that scenario are 80 €/tCO<sub>2</sub>. Nevertheless, these results are strongly dependent on cost assumptions (investment costs, energy prices).