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Mem-brain gas separation membranes for energy-efficient processes

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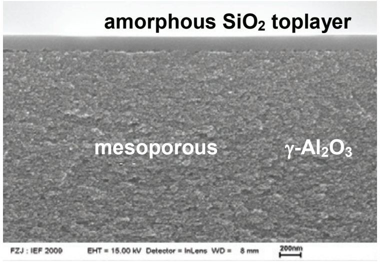
The objective of the Helmholtz Portfolio “MEM-BRAIN” is the development and integration of ceramic and polymeric gas separation membranes for advanced fossil power plants and other applications like biogas processing or processes in the chemical industry. This will be achieved using membranes with a high permeability and selectivity for either CO_2, O_2 or H_2, for the three CO_2 capture process routes in power plants, thus enabling CO_2 to be captured with high-purity in a readily condensable form.

Four types of membrane materials are developed and characterized:

- The **ceramic molecular sieving membranes** based on e.g. $SiO_2/ZrO_2/TiO_2$ or hybrid membrane materials like BTESE, BTESM are developed for H_2/CO_2 separation (pre combustion process). 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. Defect free sol-gel membranes could be prepared on flat substrates with a thickness in the range of appr. 50 -100 nm. A hydrothermal stable mesoporous intermediate layer was developed from yttria stabilized zirconia to replace the γ-alumina layer, Figure 1a, 1b.



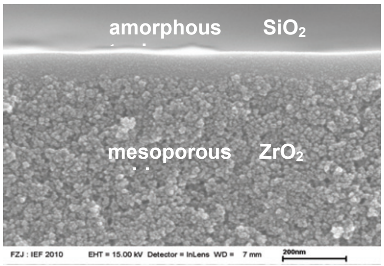


Fig. 1a: Graded molecular sieving membrane with a mesoporous □-Al_2O_3 sublayer (pore size 3 nm) and a gas selective amorphous SiO_2 toplayer (scale bar = 200 nm). Fig. 1b: Similar graded membrane with a mesoporous ZrO_2 sublayer (pore size 5 nm) and an amorphous SiO_2 toplayer (scale bar = 200 nm) [T. Van Gestel, Jülich].

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- The **dense ceramic proton-conducting** and **mixed proton-/electron-conducting membranes** are developed for H_2/CO_2 separation at elevated temperatures (400 – 700 °C), e. g. $Ln_{6-x}WO_{12-\delta}$ or $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$. Ceramic proton conducting membranes were prepared as monolithic discs, figure 2.

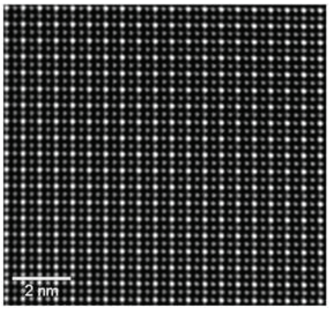

Fig. 2: High-resolution TEM image of the proton-conducting material La_6WO_{12} along the [001] direction. Atoms appear as bright spots on a dark background. The order of tungsten atoms generates a superstructure in the crystal lattice. [S. Roitsch, ER-C]

- **Dense ceramic mixed oxygen ionic-electronic conducting membranes** are developed for O_2/N_2 separation (Oxyfuel process) made by thin film wet coating, e. g. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), Zr-doped BSCF and $(Ce_{1-x}\ Pr_x)O_{2-\delta}$. At operating temperatures above 800 °C a stable window of application adapted to the oxyfuel process was identified. First time thin OTM were prepared on porous substrates confirming the expected rise of oxygen flux. A demonstration unit for oxygen mixed ionic-electronic conducting membranes containing 0.2 m^2 membrane area was built already in an early stage of the project. It was successfully operated over a long period. 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, figure 3.

Fig. 3: Demonstration unit for the oxygen separation from air [R. Kriegel, Fraunhofer-IKTS]

- **Polymeric** and **organic/inorganic hybrid CO_2-permeable membranes** and modules are developed mainly for CO_2/N_2-separation (post combustion process).

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.

One topic deals with the **system integration** of membranes for CO_2 capture into the three power plant process routes and also the design for a watergas shift membrane reactor with a test modul. The evaluation involves the comparison of the energy penalty, in contrast to conventional power plants without CO_2 capture and to conventional CO_2 separation methods like chemical CO_2-absorption or cryogenic air separation. Efficiency losses below 10 %-points could be achieved in oxyfuel and pre-combustion capture by means of membranes.

An accompanying **energy systems analysis** implies the analysis of the techno-economic requirements e. g. costs for transport and storage of CO_2, the Life cycle assessment (LCA) to compare membrane technology with other CCS technologies or energy systems model analysis of CCS.

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Keywords: Zero-emission power plants, gas separation, ceramic membranes, polymeric membranes, process engineering, system integration, energy systems analysis

Reference

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