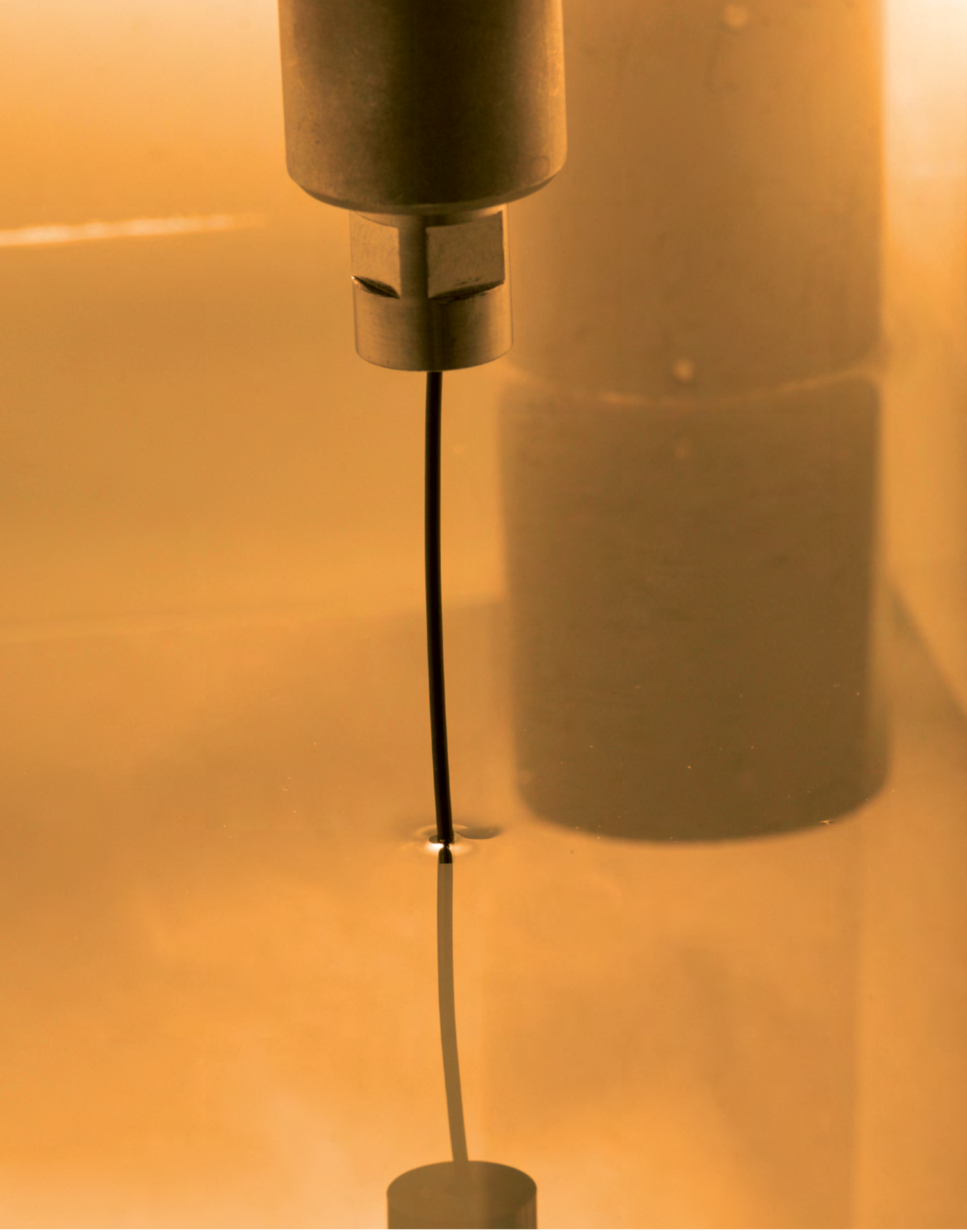
Fraunhofer IGB

Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB

Technical membranes

Materials, processing, applications

www.igb.fraunhofer.de/membranes



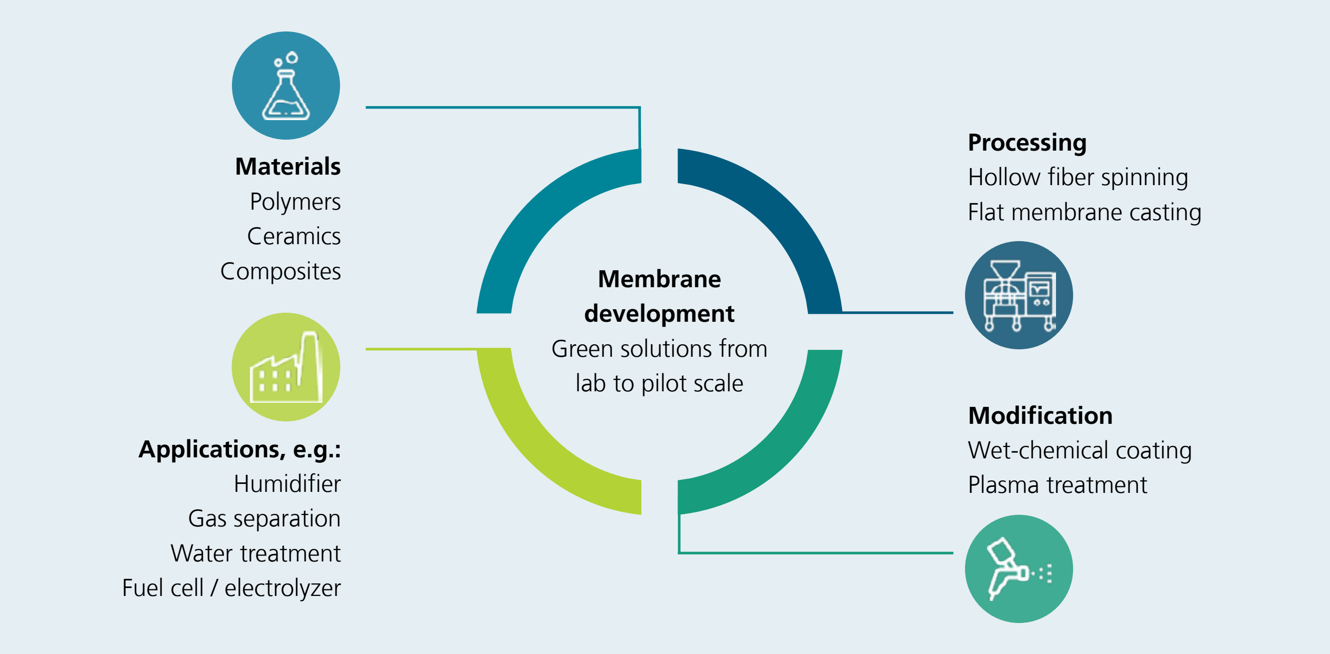
Wet-spinning of hollow fiber membranes

Fraunhofer IGB – partner for innovative membrane technology

Technical membranes are the tool of choice for the separation of complex mixtures. Depending on the various application areas, special requirements concerning structure, separation properties and stability must be fulfilled. At Fraunhofer IGB we develop innovative membranes for various applications in your business area.

R&D services offer

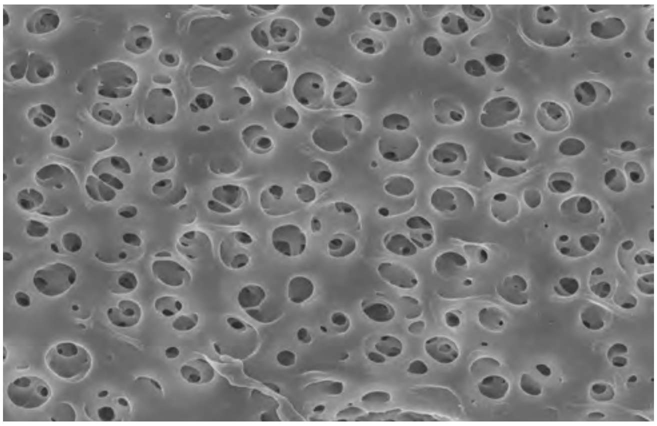
We offer various forms of cooperation, which can be individually adapted to suit your needs including long-term strategic partnerships. Individual solutions are elaborated in direct contact with our customers. We are ready to deal with projects ranging from short-term literature studies via feasibility studies up to product development and optimization. Our services include membrane development up to a pilot scale, analytical characterization of membranes as well as performing application studies.



Membrane materials

Polymer membranes

By far, most of the commercially available membranes are made of polymers. This class of materials offers convincing advantages, like cost, processibility and a broad range of applications. Polymers, we are working with, comprise commercially available ones, their modifications by e.g. sulfonation and self-made (block-co-) polymers by radical polymerization or anionic polymerization. We develop polymer membranes in flat and hollow fiber geometry starting from lab scale and going up to a pilot scale.



Polyethersulfon membrane by phase inversion process

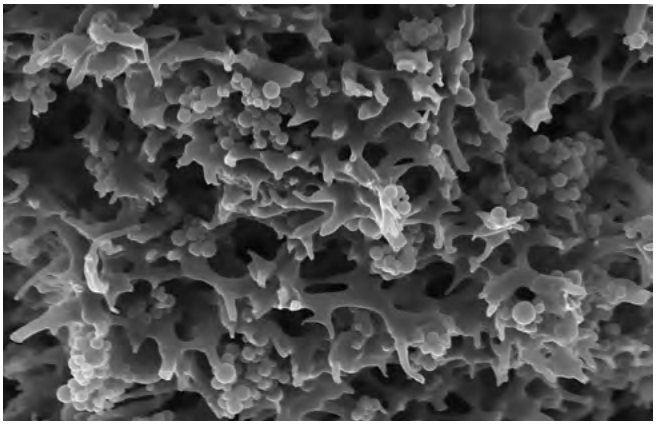
Processes for the manufacturing of porous membranes include both non-solvent and thermally induced phase inversion. We have established processes for e.g. cellulose derivates, polysulfone, polyethersulfone, polyacrylnitril, polyvinylidenfluoride and biopolymers.

For the manufacturing of dense membranes we use a solvent evaporation process and apply this process for e.g. Nafion®, sulfonated polyetheretherketone and polybenzimidazole membranes.

To control pore size or to introduce special properties we can use various additives like hydrophilic agents, conductivity enhancers, inorganic fillers and reinforcements. In addition, we have extensive expertise in the replacement of toxic solvents (e.g. NMP, methanol) by green solvents.

Mixed-matrix membranes

Mixed-matrix membranes (MMM) are made of hybrid materials, where defined internal interfaces exist with a discontinuous change in material properties. We are working with both organic-organic and organic-inorganic composite materials, where the membrane polymer is often filled with particles or fibers. The second phase can improve the membrane properties such as permeability and selectivity, can add completely new functionalities or can improve swelling behavior or the overall stability.



Porous mixed-matrix membrane

In case of organic-organic MMM we often use self-made polymeric sub-micron particles which are available with a broad range of different surface functions. These particles are completely compatible with the phase inversion process and the resulting membranes can be used as selective membrane adsorbers.

The inorganic particles used are commercially available or prepared at Fraunhofer IGB via precipitation or sol-gel chemistry. One kind of particles used are microporous systems, like zeolite or metal-organic frameworks, which are suitable for the separation of gases by size exclusion. Due to further modification of the inorganic phase by means of silanes bearing functional groups, tailor-made membranes can be prepared for various kinds of application (e.g. fuel cells).

Ceramic hollow fiber membrane in a microwave plasma

Ceramic membranes

We have established a wet-spinning process for the production of asymmetric ceramic capillary membranes. Capillaries with outer diameters in the range of 0.5 to 4 mm and wall thicknesses from 50 to 500 µm are available. In a first step microfiltration membranes are obtained which can be further modified by a coating with selective layers. Beside oxide ceramics also other ceramics (e.g. SiC) and even metals (e.g. stainless steel) can be processed. Production capacities range from just a few meters on laboratory scale to pilot plant application.

If functional ceramics, like perovskites are used, dense capillary membranes can be obtained after sintering. The geometry of the capillaries can be influenced both by different spinnerets as well as spinning parameters. High oxygen permeation can be achieved by such mixed ionic and electronic conducting materials. Due to the lattice transport of oxygen in the dense material the selectivity of O_2 to N_2 is infinite. Therefore dense perovskite capillaries are of interest as membranes for syngas production (gas partial oxidation), as a provider for pure O_2 or for the oxyfuel process.

Membrane processing

Wet-spinning of hollow fiber membranes

Wet-spinning of hollow fiber membranes

Hollow fiber membranes offer the advantage of a large specific separation area. Spinnerets are available to manufacture fibers with outer diameters in the range of 0.5 to 4 mm and wall thicknesses from 50 to 500 µm. Such fibers can be made from small lab scale to pilot scale where the fiber is continuously taken-up by a coiler. We have a huge experience with different polymers, like e.g. polysulfone, polyethersulfone, polyacrylnitril, polyvinylidenfluoride, polylactide and even self-made polymers. Special knowledge exists for the processing of dispersions to come to mixed-matrix membranes. Both polymer particles, ceramic and even metallic powders can be used. These particles are homogeneously distributed into the polymer matrix during the phase inversion process. Thereby special functionalities can be introduced into such mixed-matrix membranes. In addition, full ceramic and metal membranes can be obtained after sintering.

Casting of flat membranes

Flat membranes with thicknesses between 20 and 200 µm and a width of 300 mm can be manufactured by a roll-to-roll process. Both temperature and atmosphere can be controlled during casting. Precipitation baths with temperatures between 4–90°C are available. The main focus at Fraunhofer IGB lies in the processing of mixed-matrix systems. Both dense and asymmetric porous membranes can be obtained by solvent evaporation and phase inversion processes respectively. In addition, several functional layers can be calendered to complex systems.

Melt-spinning of capillary membranes

Hollow fibers (< 0.5 mm), capillaries (0.5 – 3 mm) and tubes (up to 10 mm) can be processed with our piston spinning equipment. The parameters of extrusion can be varied from RT up to 320°C and from 1 to 300 bars. Material amounts ranging from 10 to 500 g can be processed into membranes. By using suitable material combinations thermally induced phase separation can be performed to manufacture capillary membranes with a controlled pore size. Due to low material consumption expensive materials like biopolymers, noble metal-doped materials or valuable ceramics can be processed.

Wet-chemical modification

We have developed a variety of different polymers for the wet-chemical coating of membranes. These polymers are thermally or photo-chemically cross-linkable and therefore the resulting coatings are long-term stable. The properties are ranging from hydrophilic to hydrophobic, and also functional groups (e.g. amines) can be introduced which are good starting points for a further chemical modification. We have the infrastructure to make continuous roll-to-roll coatings both for hollow fiber and flat membranes. By controlling the wetting of the membranes it is possible to control whether the coating is on the surface of the membrane or inside the pores. In addition, there are coating systems available which are also suitable for a coating inside hollow fibers.

Besides the coating with polymers, other technologies, like interfacial polymerization or grafting-from are also available. Doing so thin film composite membranes are available with favorable properties for forward osmosis applications.

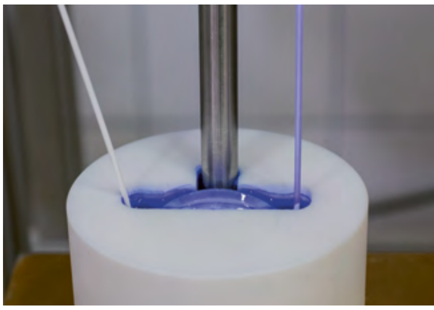
Plasma modification

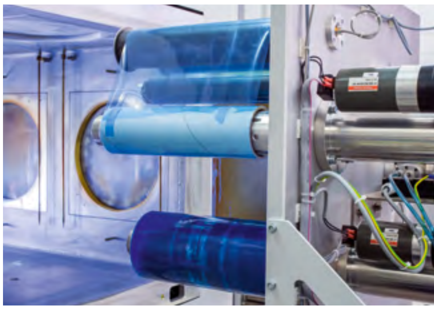
Plasma glow discharge is a versatile tool especially suitable for the chemical surface modification of polymeric membranes. Using this technique, etching, (regioselective) functionalization or deposition of a thin film in the nanometer range is possible with only a very tiny consumption of precursor chemicals. In this way the pore size of asymmetric membranes can be influenced in a defined manner by etching or plasma polymerization to adjust the filtration characteristics or to create a closed pinhole-free thin film with an adjustable crosslink density to create a solvent-stable permselective layer for the separation of organic vapors or solvents. Continuous roll-to-roll processes are possible for both hollow fiber and flat membranes.

Top:
Continuous wet-chemical coating of hollow fiber membranes

Center:
Casting of flat membranes

Bottom:
Plasma coating of flat membranes





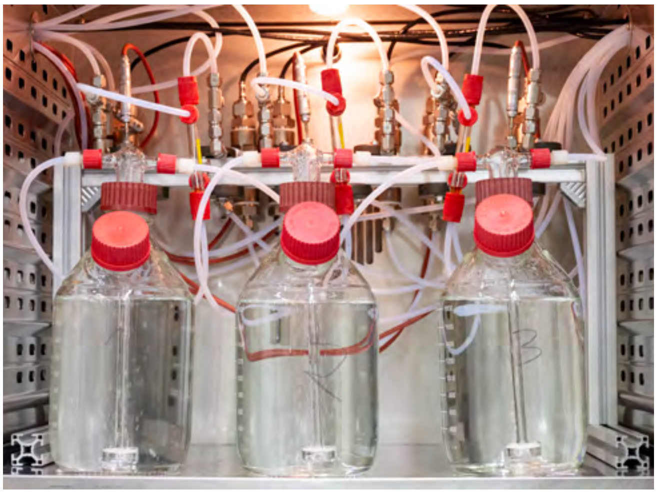
Pilot plant for casting and coating of flat membranes

Membrane applications

Humidification

The control of humidity in buildings or industrial process streams plays a key role in overall energy efficiency or in the reduction of corrosion. We have developed hydrophilic membranes with a high water vapor transfer rate and a low air leakage which can be used for fuel cells or drying applications. Therefore we apply thin polymer coatings on flat or hollow fiber membranes (both outside and inside coating possible).

We have built up excellent infrastructure for the characterization of such membranes. The water transfer rate can be automatically measured at different temperatures, pressures and humidities. In addition, air leakage or mechanical properties can be determined.



Parallel characterization of three humidifier membranes

Gas separation

Gas mixtures can be separated by different types of membranes. In comparison to the cryogenic methods for gas separation, membranes offer higher gas selectivities and are more energy-efficient. For hydrogen separation we have developed Pd-coated alumina capillary membranes. If the operating temperature is high, dense perovskite capillaries can be implemented in the process e.g. for oxygen separation from air, CO_2 capture and storage or catalytic reactions such as syngas production. In addition, we have polymer membranes in our portfolio which show high CO_2 permeation and a good selectivity against other gases.

(Electro)chemical membrane reactor

Polymer electrolyte membranes (PEM) consist of ionomer materials where acidic or basic functionalities account for the ion flow through the material. Our specialty is the introduction of an additional inorganic phase into the polymer to enhance chemical, mechanical and thermal stability and to increase the barrier function for other substances e.g. fuel, oxidant and intermediates. We are working in the field of fuel cells, electrolyzers and in the electrochemical transformation of carbon dioxide into valuable products.

Of special importance is the interface between the electrode, the catalyst layer and the membrane. E.g. for direct alcohol fuel cells we have developed an aqueous sPEEK-based binder system to optimize compatibility of these layers and we apply these layers by a screenprint technique. Thereby requirements range from an appropriate porosity for the supply and removal of reactants to low electrical resistance.

Besides the coupling to electrochemical processes membranes can also directly be used to shift thermodynamic equilibria as in the case of water splitting or to decrease kinetic hindrance as in the case of greenhouse gas nitreous oxide splitting. Reactants can be dosed by the membranes e.g. for selective hydrogenation, or micropollutants can be degraded effectively on catalytic active membrane surfaces.

Water treatment

For the filtration of water a variety of different types of membranes ranging from micro- to nanofiltration are already commercially available. Goals of our research are to improve the properties of membranes by a modification of the surface or by embedding additional functions, like adsorption sites into the membranes. In the first case the (bio)fouling behavior could be controlled and this allows for an e.g. improved back flushing behavior of the membranes.

The second case leads to so-called membrane adsorbers where filtration and adsorption are directly integrated into one system. In contrast to pure adsorbers the adsorption capacity of membrane adsorbers is independent from flow velocities and therefore allows for a high throughput. Meanwhile we have systems with different functionalities at hand for the selective adsorption of micropollutants, heavy metals or the recovery of valuable metals.

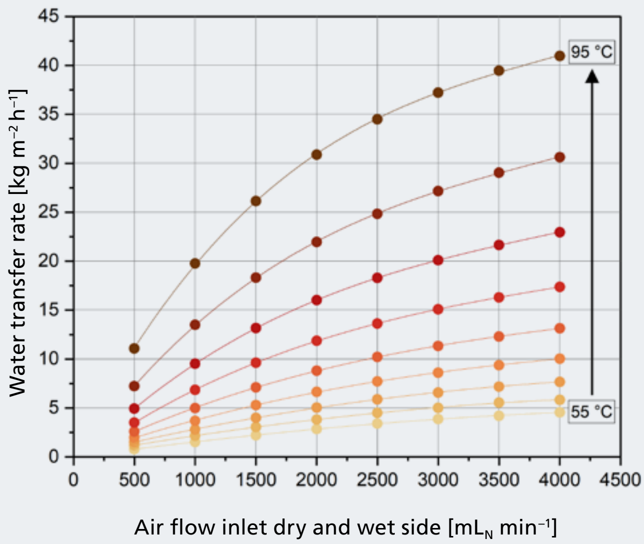
Forward osmosis

In forward osmosis (FO) two liquids of different osmotic pressure are contacted via a semi-permeable membrane. Water transfers towards the chamber with high osmotic pressure while solutes are retained. Most current membranes, developed and optimized for pressure-driven processes, do not perform in FO due to excessive concentration polarization. Major applications are the recovery of drinking water from contaminated water sources, the production of energy from salt concentration differences (e.g. river to seawater) by pressure-retarded osmosis (PRO) or the reduction of fouling in the concentration of landfill leachate. We develop FO membranes which are stable against solvents like butanol, aceton and ethanol and which can be used to enrich butanol from ABE fermentation broth.

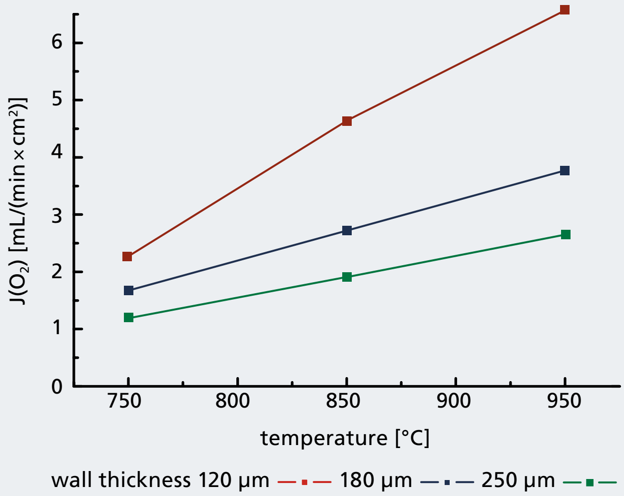
Biomedical applications

We modify your medical membrane device (e.g. for dialysis) to optimize the contact to body fluids, to separate toxins or to reduce fouling. The surface of our membranes can be optimized to enhance sticking and growth of cells or to diminish the adherence of unwanted microbes. Forming membranes from biodegradable polymers is part of our expertise.

Water transfer as a function of temperature and air flow

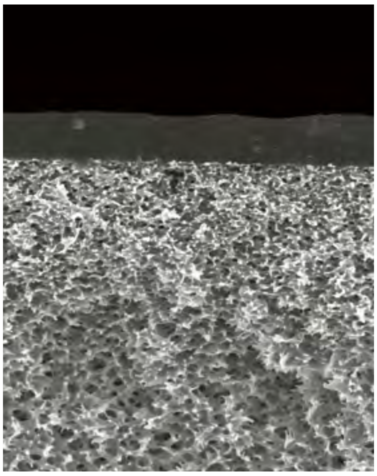


Gas separation: oxygen permeation through dense pervoskite capillaries



Left:
Hydrophilic PVA coating on HF membrane for humidification

Right:
Cellulose acetate membrane on a fabric for forward osmosis applications




Services

Membrane development

- Polymer, mixed-matrix, ceramic membranes
- Hollow fiber, capillary and tubular membranes
- Flat sheet membranes
- Membrane modification (wet-chemical, plasma, sol-gel, continuous roll-to-roll processes)

Module development

- Polymer modules
- Full ceramic modules
- Static potting
- Centrifugal potting

Application studies

- Humidifier
- Gas separation (RT up to 1000°C)
- Reverse osmosis (RO), forward osmosis (FO), pressure-retarded osmosis (PRO)
- Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF)
- Membrane adsorber

Membrane characterization

- Microscopy (SEM, FESEM, AFM)
- Flux, permeability and selectivity
- MWCO determination
- Pore size and pore size distribution (BET)
- Conductivity (ion, electron)
- Gas cross-over at high pressure
- Mechanical properties
- Thermal properties (TGA, dilatometry)
- Surface analysis (ESCA, XPS, wetting)
- Membrane swelling
- Membrane degradation
- Post mortem analysis (membranes and modules)

Glass module for hollow fiber membranes

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