Membranes

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Perovskite Hollow-Fiber Membranes for the Production of Oxygen-Enriched Air**

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Oxygen-enriched air with 30–50 vol % O_2 is used in a number of industrial processes, for example, in the synthesis of ammonia, the Claus process, and the regeneration of the catalyst for the fluid-catalytic-cracking (FCC) process.[1,2] Another application of O_2-enriched air is the most efficient use of methane in high-temperature furnaces or cement kilns.[2] There are different methods for producing O_2-enriched air, mainly by mixing air with pure O_2 obtained from a cryogenic technique or pressure swing adsorption (PSA). However, these techniques require high capital investment and operational costs. Depending on the O_2 concentration and the amount of the O_2-enriched air needed, membrane technology can be competitive. As organic polymeric hollow-fiber membranes have a separation factor between 2 and 6, a single-stage membrane permeation gives an O_2 concentration typically of the order of 30–50 vol % under a pressure difference of about 10 bar.[3] Although higher O_2 concentration and permeability can be achieved by increasing the feed flow rate, by reducing the membrane thickness, or by increasing the pressure difference, these actions increase the separation costs. Furthermore, the organic polymeric membrane cannot be used for the recovery of heat from exhaust gas in high-temperature processes.

Herein we propose a new technique to produce O_2-enriched air by using a mixed-ion and electron-conducting (MIEC) perovskite membrane. The basic idea is shown in Figure 1. At elevated temperatures, under a slight difference in air pressure (1–2 bar) O_2 can be transported through a MIEC perovskite membrane in the form of oxygen ions from the side of high air pressure to the side of low air pressure. Simultaneously, electrons are transported in the opposite direction to maintain electric neutrality. The permeated O_2 increases the O_2 concentration to typically 30–50 vol % in the sweep air that forms the O_2-enriched air on the low-pressure side. Therefore, the perovskite membrane combines the in situ O_2 supply with permeated O_2 and air in one unit thus simplifying the process of O_2 enrichment and reducing the operational and capital costs.

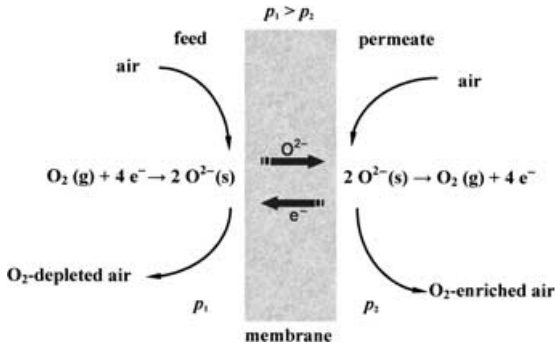

Figure 1. O_2 enrichment with perovskite mixed-conducting membranes.

The obvious advantage of using perovskite membranes is their 100 % selectivity for O_2. Usually, polymeric membranes also transport noble or inert gases such as Ar or CO_2, which can be disadvantageous depending on the process. Synthesis gas for ammonia production, for example, is prepared at a pressure level of about 30 bar and afterwards compressed to a pressure of typically 170–190 bar. Any inert gases contained within the synthesis gas are also compressed to a higher pressure and fed into the synthesis loop. This in turn increases the energy expenditure for compression, the necessary loop volume, and the purge flow used to get rid of the inert components in the synthesis loop.

Moreover, compared with hollow-fiber membranes made from organic polymers, the perovskite hollow-fiber membrane requires a lower pressure difference (1–2 bar) across the membrane and can work at elevated temperatures, thus allowing high-temperature heat exchange. O_2-enriched air is used mostly in high-temperature oxidation processes such as in the generation of synthesis gas for ammonia production in which O_2-enriched air is used to run a secondary reformer typically operated at 1000 to 1100 °C. Therefore, in this process the temperature required to operate the perovskite hollow fiber is already available and can be used by heat exchange. Furthermore, the heat used for the O_2 enrichment is not consumed, for example, in an endothermic reaction and can be regained by heat exchange with the product streams that leave the O_2-permeation-membrane module. A similar setup may also apply to other applications for O_2 enrichment with perovskite membranes, for example, the temperature increase of firing systems in power plants or industrial furnaces.

The perovskite of composition $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ; $x+y+z=1.0$) is a novel O_2-permeable membrane with high O_2 permeation fluxes and excellent thermal and mechanical stability.[4,5] BCFZ was used in a hollow-fiber configuration as

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the membrane, which showed an O_2 permeation flux of 6.5 $cm^3 min^{-1} cm^{-2}$ at 875 °C.[6] This flux is higher than those of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)[7] and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF)[8] hollow-fiber membranes under similar conditions with a nonreactive sweep gas. The preparation and characterization of the hollow-fiber membrane was recently reported.[6]

The performance of perovskite membranes for O_2 enrichment can be characterized by the O_2 permeation rate, the production rate of O_2-enriched air, and the O_2 concentration on the permeate side. The force that drives O_2 transport through perovskite membranes is the gradient of the chemical potential, that is, the difference between the O_2 partial pressures across the perovskite membranes. Instead of separating O_2 by using inert sweep gases, it is possible to obtain O_2-enriched air by using air as the sweep gas and applying a difference in air pressure as the driving force as shown in Figure 2. When the difference in air pressure

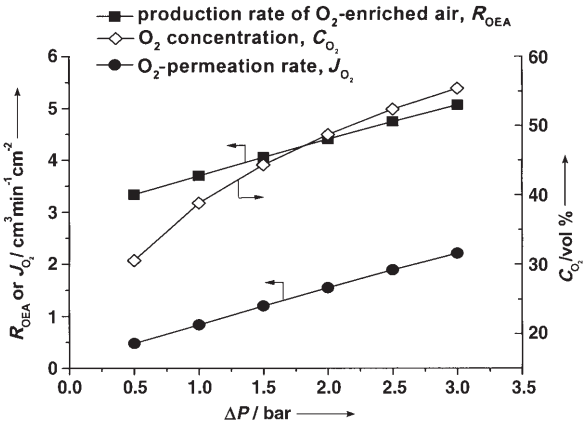

Figure 2. Influence of the pressure difference on the production of O_2-enriched air. Air flow rate: feed side = 100 $cm^3 min^{-1}$; permeate side = 10 $cm^3 min^{-1}$, membrane surface area = 3.50 cm^2, T = 950 °C.

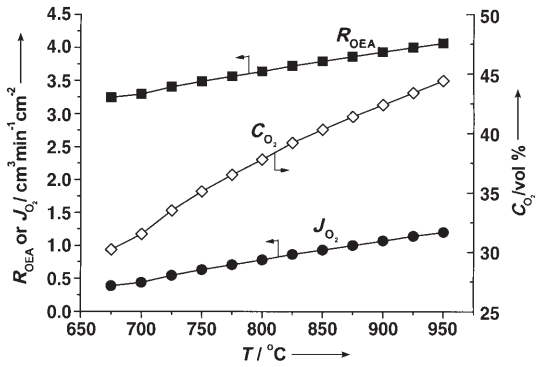

Figure 3. Influence of the temperature on the production of O_2-enriched air. Air flow rates: Feed side = 100 $cm^3 min^{-1}$; permeate side = 10 $cm^3 min^{-1}$, membrane surface area = 3.50 cm^2, pressure difference = 1.5 bar.

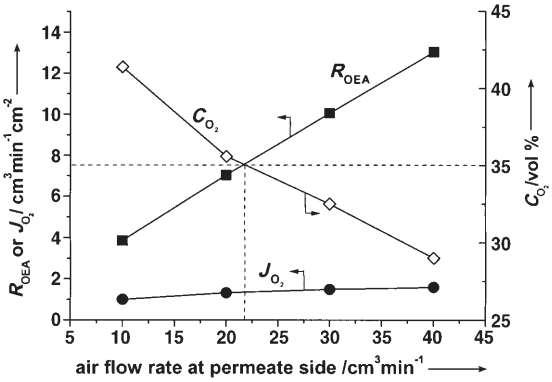

Figure 4. Influence of the air flow rate at the permeate side on the production of O_2-enriched air. Air flow rate: feed side = 100 $cm^3 min^{-1}$; permeate side = 10–40 $cm^3 min^{-1}$, membrane surface area = 3.50 cm^2, T = 875 °C, pressure difference = 1.5 bar.

increases from 0.5 to 3.0 bar, the O_2 concentration on the permeate side almost doubles from 30 to 55 vol %, and the O_2 permeation rates rise from 0.5 to 2.2 $cm^3 min^{-1} cm^{-2}$. Accordingly, the production rate of O_2-enriched air increases from 3.3 to 5.0 $cm^3 min^{-1} cm^{-2}$. Silicone rubber—the polymeric membrane used most often commercially—with a thickness of 25 μm shows an O_2 permeation flux of about 0.11 $cm^3 min^{-1} cm^{-2} bar^{-1}$ with an O_2 concentration of 35 vol % under a pressure difference of 9.0 bar.[9] However, the perovskite hollow-fiber membrane with a thickness of around 180 μm can give an O_2 concentration higher than 38 vol % with a production rate of 3.7 $cm^3 min^{-1} cm^{-2}$ by applying only a pressure difference of 1.0 bar.

Figure 3 shows the influence of the temperature on O_2 enrichment under a fixed pressure difference of 1.5 bar. As expected, the O_2 permeation rate increases with rising temperature, which leads to an increase in both the production rate of the O_2-enriched air and the O_2 concentration in the effluent air. Figure 4 shows how the rate of air flow on the permeate side affects the production of O_2-enriched air at a constant pressure difference of 1.5 bar at 875 °C. It was previously found that the O_2 permeation flux increases with raising the rate of He flow when He was fed to the permeate side as the sweep gas.[10] The reason for this increase is that the partial pressure of O_2 on the permeate side decreases with an increase in He flow.[10] As shown in Figure 4, the O_2 concentration decreases sharply when the air flow on the permeate side increases. This decrease leads to an increase in the rate of O_2 permeation when the air flow on the permeate side rises. Accordingly, the rate of production of O_2-enriched air increases. An air flow of about 22 $cm^3 min^{-1}$ on the permeate side gives a good compromise between the O_2 concentration ($\approx$35 vol %) and the rate of production of O_2-enriched air (7.5 $cm^3 min^{-1} cm^{-2}$).

Teraoka et al.[11,12] first reported O_2 permeability through perovskite membranes based on $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$. Since then, there have been numerous reports on perovskite membranes.[13–17] An attractive goal is the integration of perovskite membranes and the partial oxidation of methane (POM) to synthesis gas into a single reactor. Although a lot of effort has been made to apply perovskite membranes to an industrial POM process,[18,19] so far there are no plants using this methodology. The formidable problem for this technology lies in the poor stability of the perovskite membranes at elevated temperatures under a reducing atmosphere (e.g., a

mixture of hydrogen and carbon monoxide).[20] A further problem is the poor operational safety of such systems. In the event of a membrane leak, air, methane, and synthesis gas would mix at 800 °C, thus causing serious trouble if not handled properly. However, these stability and operational-safety problems are avoided in the above-proposed O_2-enrichment process because both sides of the perovskite membranes are exposed to an oxidizing atmosphere (air).

As expected, the perovskite membranes exhibit excellent stability (Figure 5). A perovskite membrane operated steadily

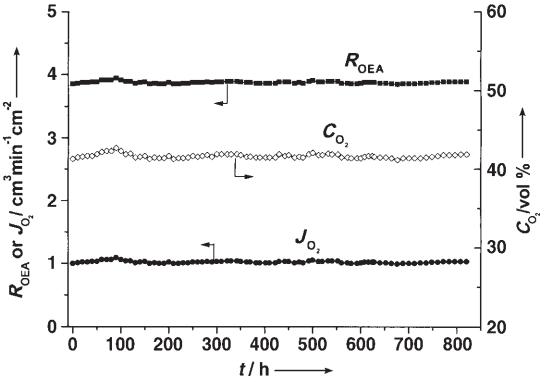

Figure 5. Long-term stability of perovskite hollow fibers for the production of O_2-enriched air. Air flow rate: feed side = 100 cm^3 min^{-1}; permeate side = 10 cm^3 min^{-1}, membrane surface area = 3.50 cm^2, pressure difference = 1.5 bar, T = 875 °C.

for more than 800 h at 875 °C under a constant pressure difference of 1.5 bar. During this operation, the O_2 concentration in the O_2-enriched air reached around 42 vol % with an O_2 permeation rate of about 1.0 cm^3 min^{-1} cm^{-2} and an O_2-enriched air production rate of about 4.0 cm^3 min^{-1} cm^{-2}. It should be pointed out that although we had to stop the test, the perovskite membrane was still working after 800 h. XRD and element maps obtained from scanning electron microscopy–energy-dispersive X-ray spectra (SEM–EDX) of the spent hollow-fiber membrane show no structural change and no significant element segregation (see Supporting Information).

In summary, the results presented here demonstrate the possibility of applying perovskite membranes to high-temperature O_2 enrichment. The O_2 concentration reached around 35 vol % with a production rate of 7.5 cm^3 min^{-1} cm^{-2} of O_2-enriched air at 875 °C under a pressure difference of 1.5 bar. The O_2 concentration and the rate of production can be adjusted by controlling the temperature, air pressure difference, and gas flow rates. It is important to note that hollow-fiber membranes can give very high values of the membrane area per unit volume (up to 5.000 m^2 per m^3 of permeator; based on the densest packing of fibers with outer diameters of 0.75 mm). Economic goals such as a price of well below 1000 € per m^2 of membrane area can be also met by using this perovskite membrane. We estimate that 700 tons of O_2-enriched air (35 vol %) can be produced per day in a permeator volume of about 1 m^3. The long-term stability found in our experiments indicates that perovskite membranes have the potential to replace the current O_2-enrichment systems for high-temperature applications because they can integrate O_2 separation and mixing in one application.

Experimental Section

BCFZ was obtained by simple hydrolysis of Ba, Co, Fe, and Zr nitrates in a solution of ammonium hydroxide. It was then mixed with a solution of polysulfone in *N*-methylpyrrolidone and ball-milled for 16 h. The resulting slurry was spun through a spinneret and the green BCFZ perovskite fiber, thus obtained, was cut into 0.5-m pieces before being sintered above 1200 °C. On sintering, the length shrank to 0.33 m and the outer diameter went from around 1.75 mm to around 0.90 mm.

O_2-enrichment experiments were carried out in a high-temperature permeator (Figure 6). The two ends of the hollow-fiber

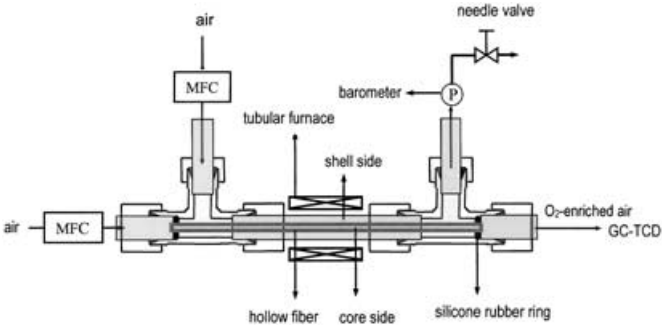

Figure 6. Scheme of the permeator for the O_2 enrichment at high temperatures.

membrane were sealed by two silicone rubber rings. Preheated air (100 cm^3 min^{-1}) was fed into the shell side and different air pressures were obtained by adjusting the needle valve on the air outlet. The air pressures on the shell side were between 1.5 and 4.0 bar. Preheated air (10–40 cm^3 min^{-1}) was fed to the core side and the air pressure was fixed at 1.0 bar. Due to the difference in air pressure between the shell side and the core side, the O_2 on the shell side permeates through the hollow-fiber membrane to the core side and mixes with air to form O_2-enriched air. The rate of O_2 permeation, J_{O_2} (cm^3 min^{-1} cm^{-2}), can be calculated with Equation (1) in which $F_{air,inlet}$ (cm^3 min^{-1}) is the rate

$$J_{O_2} = \frac{F_{air,inlet}\,(C_{O_2} - 20.9)}{S\,(100 - C_{O_2})} \quad (1)$$

of air flow at the inlet of the core side; C_{O_2} (vol %) is the O_2 concentration at the outlet of the core side, which can be determined by GC; S (cm^2) is the effective membrane surface area of the hollow fiber for O_2 permeation.

The O_2-enriched air production rate, R_{OEA} (cm^3 min^{-1} cm^{-2}), is defined in Equation (2) in which F_{outlet} (cm^3 min^{-1}) is the flow rate at

$$R_{OEA} = \frac{F_{outlet}}{S} \quad (2)$$

the outlet of the core side, which can be measured by soap film meter.

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