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- [12] a) Single crystals were obtained by slowly concentrating a solution of **2** in Et_2O at -15°C by solvent evaporation. Crystal dimensions $0.37 \times 0.20 \times 0.10$ mm³, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.4062(1)$, $b = 19.1825(1)$, $c = 14.2169(2)$ Å, $\beta = 92.462(1)^\circ$, $V = 2562.85(5)$ Å³, $\rho_{\text{calcd}} = 1.240$ g cm⁻³, $2\theta_{\text{max}} = 55.0^\circ$, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $0.3^\circ \omega$ scans, $T = 200$ K, 26061 reflections collected, 5883 unique, 4379 observed with $I > 2\sigma(I)$. Corrections for absorption were applied (program SADABS), $\mu = 0.795$ mm⁻¹, $T_{\text{min}} = 0.75$, $T_{\text{max}} = 0.94$. The structure was solved by Patterson methods and refined by full-matrix least-squares methods on F^2 (program SHELXTL (5.10)), 271 parameters refined.
- Np hydrogen atoms not localized but considered at calculated positions. Final agreement factors $R(F) = 0.040$, $wR(F^2) = 0.089$ for observed reflections. Largest peak and hole in the final difference map: 0.70 and -0.70 e Å⁻³. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148676 (**2**), CCDC-148678 (**3**), CCDC-148677 (**6**), and CCDC-148679 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). c) Structural data for **5**: C. Meier, PhD thesis, Technische Universität München (Germany), **1991**.
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YBa₂Cu₃O_{6+δ} as an Oxygen Separation Membrane**

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High- T_c superconducting oxides exhibit fast oxygen transfer across the interface between gas and solid phase and diffusion in the bulk at elevated temperatures.^[1,2] This is of crucial importance to the fine-tuning of the superconductivity by intercalating oxygen into the oxides to oxidize the copper ions. The fast oxygen transport kinetics may also be used to develop oxygen-semipermeable dense membranes, which have potential applications in oxygen production and oxy-

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gen-based industrial processes.^[3, 4] When oxygen activity in the gas phase is greater than that in the bulk of the oxide, oxygen is intercalated into the oxide, and the reverse process occurs when the oxygen activity in the gas phase is less than that in the oxide. Therefore, upon applying a differential oxygen partial pressure p_{O_2} across the oxide membrane, a nonvanishing oxygen flux results and permeates from the high- to the low- p_{O_2} compartment; this results in separation of oxygen from oxygen-containing mixed gases. With $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ as a dense membrane, an appreciable oxygen flux is obtained at elevated temperatures.^[5] This prompted us to examine the possibility of using $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ as an oxygen-permeable membrane.

The oxygen permeability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ was determined by using a permeation cell in which a dense oxide disk (1.2 mm thick and 1.2 cm in diameter) acts as a membrane (Figure 1). The chromatograms of the feed and permeate streams at 850 °C are shown in Figure 2. The permeate contains a significant amount of oxygen, while nitrogen is hardly detectable. This clearly demonstrates that $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ is permeable to oxygen but impervious to other gas components such as nitrogen. Further quantitative analysis revealed that the oxide allows oxygen to be transported at a rate of $3.1 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$ at 850 °C, and $2.0 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$ at 750 °C, under a relatively small oxygen

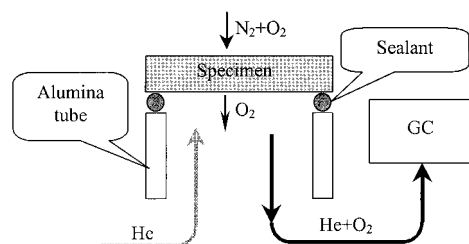


Figure 1. Schematic representation of a $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ -based permeation cell.

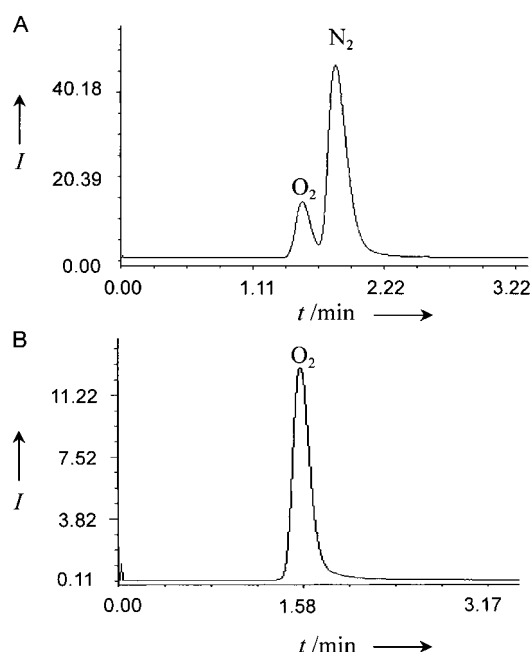


Figure 2. Chromatograms of A) feed stream (air) and B) permeated stream for the permeation cell. I = intensity.

partial pressure difference ($p_{\text{O}_2}(\text{high}) = 0.209 \text{ atm}$, $p_{\text{O}_2}(\text{low}) \approx 10^{-3} \text{ atm}$). Figure 3 shows the Arrhenius plot of the steady-state oxygen flux; the apparent activation energy is 44 kJ mol^{-1} . Compared with oxygen-deficient perovskite oxides such as $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$,^[6] the decrease in the oxygen permeability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ with decreasing temperature is less pronounced.

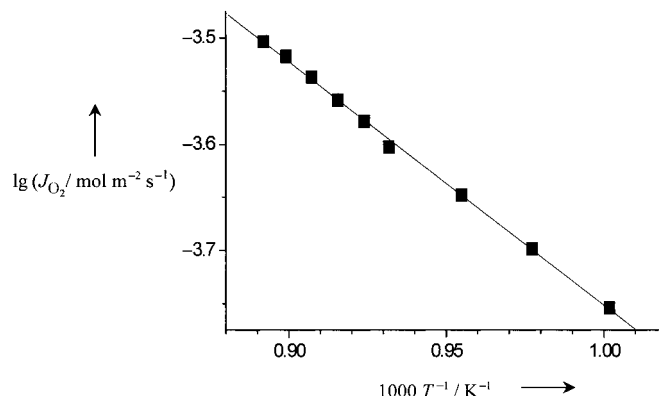


Figure 3. The temperature dependence of oxygen permeation flux through a $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ membrane of 1.2 mm thickness.

Oxygen permeation consists of two processes, namely, transfer of oxygen across the gas/solid interface and transport of oxygen in the bulk oxide membrane. The latter process is phenomenologically described by Fick's first law: $J_{\text{O}} = -D_{\text{chem}} \frac{\partial C_{\text{O}}}{\partial x}$. From the measurements of the oxygen permeation flux (J_{O_2}), J_{O} is available by virtue of $J_{\text{O}} = 2J_{\text{O}_2}$. The oxygen concentration gradient $\partial C_{\text{O}} / \partial x$ across the $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ membrane can be estimated by $\frac{\delta(\text{low}) - \delta(\text{high})}{V_{\text{m}} L}$, where $\delta(\text{low})$ and $\delta(\text{high})$ are the oxygen nonstoichiometry of the oxide corresponding to low and high oxygen partial pressure, respectively; V_{m} is the molar volume of the oxide, and L the thickness of the sample. From the oxygen nonstoichiometry data^[7] at $p_{\text{O}_2} = 0.209$ and 0.001 atm and the oxygen permeation flux from Figure 3, the oxygen chemical diffusion coefficient D_{chem} can be calculated. Figure 4 shows the Arrhenius plot for D_{chem} ; the apparent

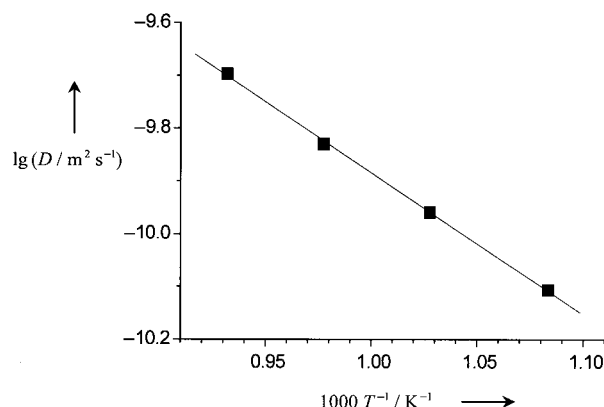


Figure 4. Temperature dependence of the chemical diffusion coefficient of oxygen for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$.

activation energy is $(51 \pm 0.9) \text{ kJ mol}^{-1}$. The value of D_{chem} is in the order of $10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the temperature range of $650\text{--}850^\circ\text{C}$, while the oxygen tracer diffusion coefficient, determined by the method of Rothman et al.,^[1] is in the order of $10^{-13} \text{ m}^2 \text{ s}^{-1}$. Hence, the thermodynamic factor in our case is around 10^3 . The oxygen diffusion coefficients reported in the literature are widely scattered,^[8] and our present data are comparable to those reported by Mitberg et al.^[2]

Oxygen diffusion in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ is generally assumed to take place in the CuO basal plane. To examine this assumption, oxygen permeation measurements were performed on $\text{LaYBa}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$,^[9] which can be regarded structurally as derived from $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ by substitution of the CuO basal plane by a $\text{TiO}_2\text{--LaO--TiO}_2$ sheet. The oxygen permeability, if any, is too small to be detected (less than $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$). The sharp difference in oxygen permeability between these two oxides suggests that the CuO basal plane is the structural origin of fast oxygen transport. It is known that at temperatures above about 650°C , oxygen atoms are equally distributed on O1 and O5 positions in the basal plane, the occupancy being $\delta/2$. It is likely that oxygen transport occurs by jumping between O1 and O5 positions. The oxygen flux should be proportional to the product of the mobility and concentration of the basal-plane oxygen atoms. As oxygen transport is a thermally activated process, lowering the temperature results in a lower mobility and hence a lower flux. However, the concentration of mobile oxygen increases with decreasing temperature and thus partially compensates the loss in mobility. These two opposing effects result in a weak temperature dependence of oxygen permeation flux. It is also known that grain boundaries can enhance the oxygen transport.^[10] Our work demonstrates the role of the CuO basal plane in transporting oxygen and can help to understand the effects of grain boundaries. If oxygen ions encounter grains oriented along the c axis, they will bypass the grains and travel through grain boundaries.

Oxygen in the basal plane of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ lattice has been suggested to have different oxidation states namely, O^0 , O^{1-} , and O^{2-} .^[8, 11, 12] Unlike the movement of O^{1-} and O^{2-} , that of O^0 does not contribute to the flow of electrical charge. Since relative contributions of neutral oxygen atoms and charged oxygen ions to oxygen permeation remain unknown, it is inappropriate to derive oxygen ionic conductivity from oxygen permeation data by using the Wagner equation.^[4, 13] Instead, we can only give a phenomenological treatment of oxygen transport in terms of Fick's first law. Note that to maintain electrical neutrality, the movement of oxygen ions O^{1-} and O^{2-} in the oxide must be accompanied by movement of electrons in the opposite direction, which is termed ambipolar diffusion.^[13] $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ should be very suitable for oxygen transport by an ambipolar mechanism, because Cu(1)O and Cu(2)O_2 planes in the lattice can conduct oxygen ions and electrons (holes), respectively.

In summary, $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ exhibits good oxygen permeability at elevated temperatures. Further research topics are clarifying the oxygen transport mechanism in relation to the structure, and improving the oxygen permeability by optimizing the composition and microstructure.

Experimental Section

Single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ samples were prepared by a standard ceramic method. Appropriate amounts of reagent-grade Y_2O_3 , BaCO_3 , and CuO powders were weighed, mixed in a mortar for 2 h, and calcined in air at 920°C for 24 h. The calcined powder was uniaxially pressed into compacts and sintered at 950°C for 24 h. The density of the sintered compacts was measured by the Archimedes method. The phase composition of the calcined and sintered sample was determined by X-ray diffraction with $\text{CuK}\alpha$ radiation ($D/\text{Max-}\gamma_{\text{A}}$, Rigaku).

Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ disks with relative density greater than 90% were machined to 1.2 mm in thickness and 1.2 cm in diameter, and then sealed to an alumina tube at 860°C to form a permeation cell (see Figure 1). Air was fed into the upper compartment, and a stream of high-purity helium was introduced into the lower compartment to sweep away the permeated gas components. The gas compositions were analyzed by GC (Varian 3400). The oxygen permeation flux was calculated from the concentration of the oxygen in the effluent stream and the flow rate of the helium.^[14]

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