

CVD of thin oxygen permeable membrane films

R.Muydinov, M.Novojilov, O.Gorbenko, I.Korsakov,
A.Kaul

Chemistry Department, Moscow State University,
119899, Moscow, Russia

D.Stiens, S.Samoilenkov, G.Wahl

IOPW, TU Braunschweig, 38108 Braunschweig,
Germany

Membranes with high mixed oxygen-ionic and electronic conductivity are of great interest for oxygen separation and catalytic membrane reactors for partial oxidation of hydrocarbons. In diffusion regime, oxygen flow through a membrane is proportional to its reciprocal thickness, therefore, dense thin films of the functional material on porous substrates are very promising for such applications.

Present work describes a method to produce tight thin layers on porous Al_2O_3 substrates with an average pore size of 4 μm . $(\text{La},\text{Sr})(\text{Ga},\text{Fe})\text{O}_3$, $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3$, and La_2NiO_4 ceramic layers were investigated. The oxygen permeability of 1.5 mm-thick pellets of these oxides at 900°C is the range of $3 - 10 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$ [1]. Thus, for a 10 μm -thick membrane, the oxygen permeability as high as $10^{-4} \text{ mol cm}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$ can be reached. The aim of the work was therefore to obtain gas tight layers of afore-mentioned materials.

The deposition experiments were carried out in a stagnation flow arrangement with a cold-wall reactor. The deposition temperature was in the range of 500–700°C. A powder flash evaporation and an ultrasonic nebulization systems were used. The precursors used were thd-chelates of corresponding metals. Diglyme was used as a solvent for the aerosol feeder. Argon and oxygen were used as carrier and oxidation gases. Depositions were carried out at 6–10 mbar. The samples obtained were investigated by SEM and EDX (CamScan 4M electron microscope, EDAX9800 analysing system) and XRD (Siemens D5000 diffractometer). The permeability at room temperature was measured with a gas diffusion equipment, where the pressure vs. time dependence was measured for the container filled with nitrogen up to 2.5 bar and separated from ambient by the sample.

The deposition rates have been calculated and experimentally determined for $(\text{La},\text{Sr})(\text{Ga},\text{Fe})\text{O}_3$ layers. The deposition rate of $9.14 \cdot 10^{-6} x_{\text{tot}} \cdot \text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ corresponding to $5 x_{\text{tot}} \cdot \text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ (x_{tot} is the molar fraction of precursors in gas) has been calculated. This value was very close to experimentally determined, $dm/dt = 7 x_{\text{tot}} \cdot \text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$.

Further, the systematic analysis of the film composition and its dependence on corresponding gas phase concentrations has been done. In this analysis, the transfer coefficient of element A, α_A , is determined as the molar deposition rate of this element divided by the concentration of the corresponding precursor in the gas phase. The following relations have been found: $\alpha_{\text{Sr}} / \alpha_{\text{La}} = 0.6$; $\alpha_{\text{Ga}} / \alpha_{\text{La}} = 1.0$; $\alpha_{\text{Fe}} / \alpha_{\text{La}} = 1.0$; $\alpha_{\text{Ni}} / \alpha_{\text{La}} = 1.5$. The deviation of these ratios from 1 can be explained by incomplete evaporation of particular precursors, different gas diffusion coefficients, side reactions or decomposition processes in the gas phase.

XRD analysis of prepared coatings revealed the formation of polycrystalline material with a desired (perovskite or K_2NiF_4 -type for La_2NiO_4) structure. However, the as-prepared films were not tight, the flow rate of nitrogen through the sample was only by a factor of approx. 2 lower than that through the uncoated substrate.

In order to increase the coatings tightness, an aftertreatment procedure has been proposed and tested. Gorbenko et al. [2] have observed that the surface diffusion can be enhanced by treatment of the layers in Bi_2O_3 or PbO containing atmospheres. It is suggested that these oxides form a flux, in which the diffusion processes are faster and a material with better crystallinity and higher density can be formed [3]. In order to produce these oxide layers, the as-prepared films were infiltrated with a gel obtained by hydrolysis of Bi nitrate or by reaction of Pb nitrate with ammonium bicarbonate in alcohol. These infiltrated samples were then annealed in air at temperatures above the melting point of PbO or Bi_2O_3 (800–900°C) for 1–2 h. XRD analyses showed that the crystal structure was not affected by the annealing in the case of PbO , but the change of the lattice parameters was induced by Bi_2O_3 . Also, some amount of Bi (a few at. %) in the layer and also a diffusion of Al into the layer (a few at. %) have been detected by EDX. It is still to be verified if these processes can disturb the oxygen ion diffusion. First experiments have shown that the aluminium diffusion can be reduced by deposition of CeO_2 interlayers made by MOCVD from $\text{Ce}(\text{thd})_4$.

The gas permeability was measured for after-treated samples. The permeability was reduced by a factor of approximately 100 in comparison with the uncoated material.

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