Development of Thin-Film Manufacturing Technologies for Solid Oxide Fuel Cells and Gas Separation Membranes

N.H. Menzler, F. Han, T. van Gestel, W. Schafbauer, F. Schulze-Küppers, S. Uhlenbruck, W.A. Meulenberg, H.P. Buchkremer

Forschungszentrum Jülich GmbH,
Institute of Energy and Climate Research
52425 Jülich, Germany
Phone: ++49-2461-613059, Fax: ++49-2461-612455, Email: n.h.menzler@fz-juelich.de

Abstract

The development of solid oxide fuel cells (SOFCs) and gas separation membranes for fossil (fuel?) power plants has previously suffered from cost issues like the manufacturing of the core components including i) the ceramic fuel cell and ii) the ceramic membrane, and from insufficient power density (current density or flow rate) on the stack, module or system level. Forschungszentrum Jülich has been working on SOFC development for 20 years, and on membrane development for 6 years. Both energy-related applications are based on similar materials systems, similar micro-structural features (porous-dense, coarse-fine), comparable application parameters (e.g. high temperature) and are manufactured with similar technologies. In the past the focus laid mostly on basic materials research and proving the functionality of the membranes or fuel cells. Meanwhile, one key topic has been the application of low-cost thin-film high-throughput manufacturing technologies. This includes the fabrication of the supports (mostly tape-casting), the coating with functional layers by ceramics technologies (screen printing, roll coating) and the reduction of sintering steps and temperatures. Additionally special thin-film technologies like sol-gel technique and electron beam evaporation / sputtering have also been applied for functional layers, depending on the functional necessities. The presentation gives an overview regarding the state-of-the-art in SOFC and gas separation membrane development at Forschungszentrum Jülich with an emphasis on the manufacturing technologies, resulting in optimized layer micro-structures and thickness. Additionally it summarizes the electrochemical and permeation data obtained so far.

Keywords: solid oxide fuel cells, gas separation membranes, thin films, ceramic manufacturing

Solid Oxide Fuel Cell Development

Forschungszentrum Jülich has developed planar anode-supported SOFCs aimed at high power density, low-cost manufacturing and minimized degradation for long-term operation. In Figure 1 a typical microstructure of a single cell is presented. A thick coarse anode support consisting of NiO and yttria-stabilized zirconia (8YSZ) is covered with a fine structured anode (~ 7µm) of the same composition and a 10µm thin electrolyte of 8YSZ. To build up a complete cell, a diffusion barrier layer composed of gadolinia-doped ceria is applied, followed by a high power-density cathode made of La-Sr-Co-Fe perovskite. The support is tape-cast and all layers were applied by screen printing.

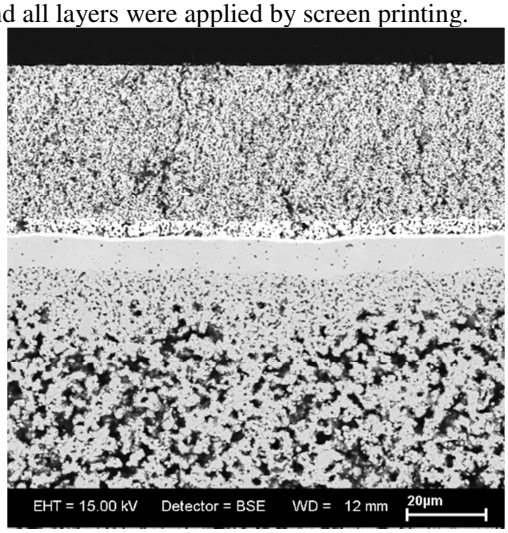

Fig. 1: SEM micrograph of a typical high power density SOFC cross section

In Figure 2 a single cell measurement of such a SOFC is presented. Typical current densities are approx. 2.0 A/cm² at 800°C and at 0.7 V (at 700°C 1.2 A/cm²). With such single cells in a stack environment, the current density is about 1.3 A/cm² at the same operational conditions (a little bit less due to contact limitations). A short-stack with two cells of 10x10 cm² each is currently running, with nearly 40,000 h of operation with an overall degradation rate of approx. 1 % voltage drop per 1,000 h (Figure 3).

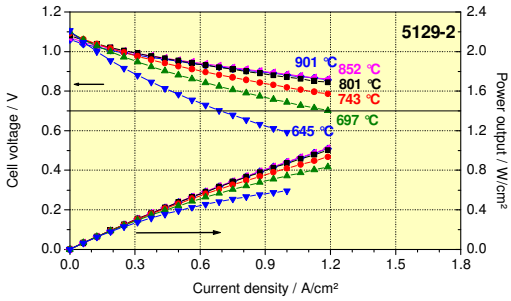

Fig. 2: I-V curve of a single cell (5x5 cm²) in ceramic housing

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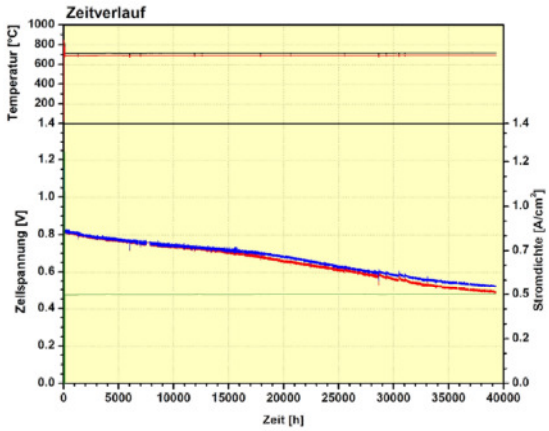

Fig. 3: Time-voltage (curr.dens., temp.) plot of a short stack running with the cells presented in Fig. 1; operated at 700°C and 0.5A/cm²

A comparable stack, consisting of a different type of protection layer on the metallic parts, has been operating for 10,000 h with a degradation rate of less than 0.2 %/1,000 h.

To enhance the power density of the cells (and thus to reduce costs; less repeating units per kW) the focus lies on reducing the layer thicknesses, and therefore to reduce the ohmic losses. In Figure 4 two examples of thin film coatings are presented.

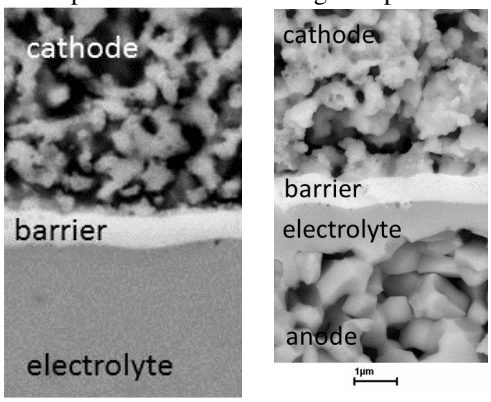

Fig.4: Left: thin-film barrier layer applied by PVD; right: thin-film electrolyte and barrier layer applied by sol-gel technique (magnification of both micrographs identical)

For the thinner functional layers different technologies like PVD, sputtering, ink jet printing/ dip-/spin-coating with sols are used. Additionally tests are ongoing to tape-cast the support, the anode and the electrolyte green-in-green and thus omitting one or two sintering steps. For further information, please refer to [1-4].

Gas Separation Membranes

Inorganic gas separation membranes can be divided into two different types, microporous membranes and dense membranes.

Microporous membranes

Microporous membranes are considered by many research groups as one of the candidates for separation problems involving small gas molecules (H_2, He, N_2, CO, CO_2, CH_4, …), because some of these materials hold the potential to combine an excellent selectivity with a high gas permeation. A microporous separation membrane can be defined as a graded multilayer porous ceramic material – with macroporous, mesoporous and microporous layers – in which the last membrane layer shows a pore size < 2 nm. The main classes of microporous membranes include amorphous SiO_2, doped SiO_2 membranes, templated SiO_2 membranes and zeolite membranes.

In our lab, microporous membranes are to date mainly developed for H_2/CO_2 separation in the so-called pre-combustion power plant application. As carriers for the functional gas selective membrane layer, mesoporous Al_2O_3, ZrO_2 and CeO_2 membranes have been developed. In a large series of permporosimetry-measurements, these meso-porous membranes show a reproducible pore size of ~2 nm for Al_2O_3, ~5 nm for ZrO_2 (type I) and ~3 nm for a finer ZrO_2 (type II) and ~4 nm for CeO_2. For power plant applications under harsh conditions (e.g. elevated temperatures, high water content, corrosive components), yttria-stabilized ZrO_2 (8YSZ) and gadolinia-stabilized CeO_2 (10GDC) mesoporous membranes, which show the same pore size of 3–5 nm in permporosimetry, have been developed.

In Figure 5, gas permeation results for a typical series of graded membranes, prepared with a sol-gel dip-coating process in a class 1000 cleanroom, are listed. The membranes consist of a thin film SiO_2 top layer with a thickness of ~100 nm and mesoporous γ-Al_2O_3 sublayers (Fig. 6). The observed gas permeation results (permeation He > H_2 >> CO_2 > N_2) and excellent average selectivity for H_2/CO_2 (~ 30) and H_2/N_2 (~ 175) were in fact in line with expectations. Similar membranes reported in the literature show a similar behavior – the size of the membranes showed here is ca. 40 mm – and have yielded also a relatively high selectivity. By optimizing all conditions in the membrane manufacturing procedure in our lab (e.g. support surface, sol composition, cleanroom coating) this result could also be achieved in a reproducible way. Further, in our research, we also discovered that for rapid production, the dip-coating process can be combined with a rapid thermal process (RTP), which gives an overall processing time of a few minutes for the membrane. Currently, all parameters in the preparation process are being further optimized in order to improve the reproducibility, and at the same time the coating process is being adapted for larger graded (commercial) membrane supports.

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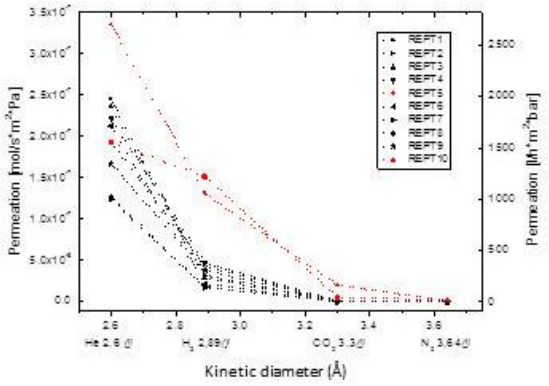

Figure 5: Gas permeation as a function of the kinetic diameter of the test gas for a series of 10 membranes with an amorphous SiO_2 toplayer.

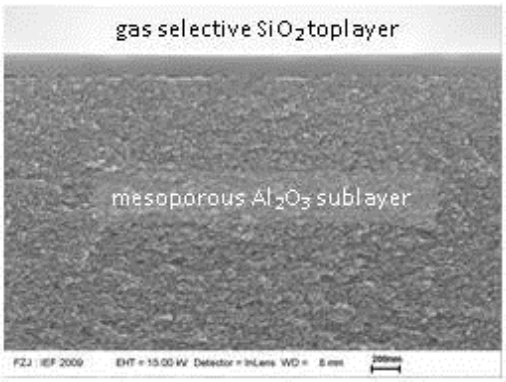

Figure 6: SEM micrograph of a graded membrane with a mesoporous γ-Al_2O_3 sublayer and an amorphous SiO_2 toplayer (bar = 200 nm).

Dense oxygen transport membranes

Depending on the gases that have to be separated, different types and materials are used. For the oxyfuel process where pure Oxygen is separated from air in a preliminary step before combustion, dense perovskite membranes, e.g LSCF or BSCF, are the materials of choice. Oxygen transport through dense ceramic materials under elevated temperature can be described by Wagner equation [8].

$$j = \frac{R\,T}{16\,F^2 \cdot L} \cdot \frac{\sigma_{ion} \cdot \sigma_{el}}{\sigma_{ion} + \sigma_{el}} \cdot \ln\left(\frac{p'_{O_2}}{p''_{O_2}}\right)$$

Oxygen flux can be mainly influenced by the membrane layer thickness L, material properties - electronic and ionic conductivity - and operation parameters T and O_2 partial pressures. In order to increase the flux for the use of pure oxygen in the combustion processes, the focus lies on the preparation of thin asymmetric membranes consisting of a porous support structure and a gas tight ion conducting membrane layer. [5] Comparative tests of 1mm bulk membranes and supported asymmetric BSCF and LSCF thin membranes are presented in Figure 7 [11]

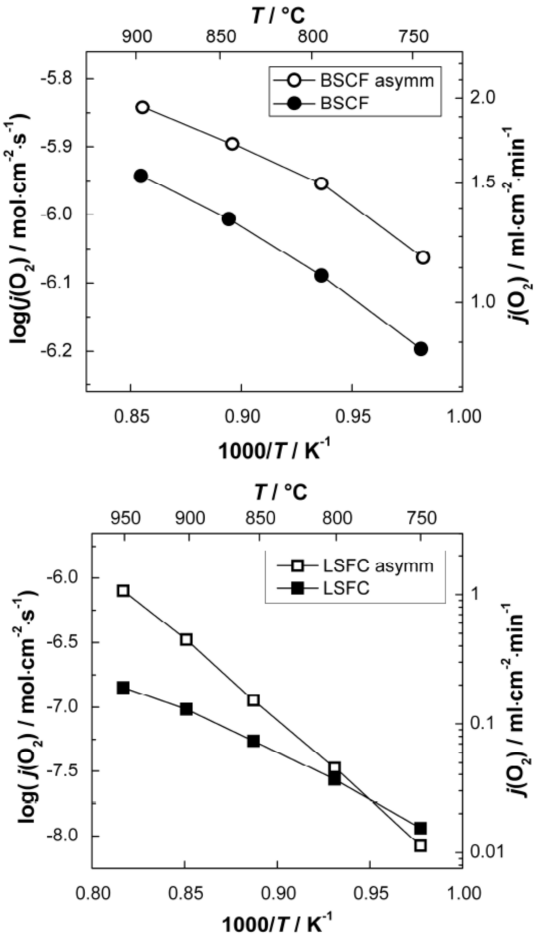

Figure 7: Oxygen flux versus temperature for BSCF (top) and for LSCF (bottom)

Variation of the support microstructure leads to significant changes in the oxygen flux. With the tape casting technology, porosity as a function of pore size and volume can be easily controlled by the use of different pore forming agents as shown in Figure 8 [10].

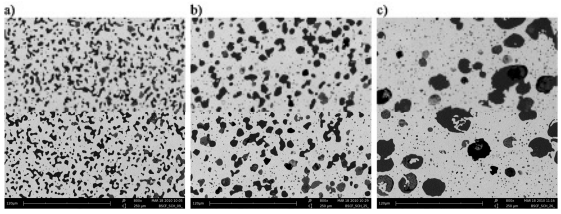

Figure 8: SEM micrographs of BSCF supports with different starch types used as pore forming agent.

Besides screen printing of the dense membrane layer on top of the porous support structure (similar to SOFC manufacturing) green-in-green tape casting technology is also under investigation. Beyond the avoidance of one sintering step, limitations in the relationship of the membrane layer thickness and the pore size can also be avoided. In Figure 9, asymmetric membranes using green-in-green tape casting technology are presented [10].

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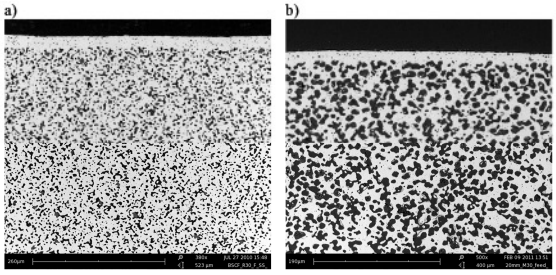

Figure 9: SEM micrographs of asymmetric BSCF membranes prepared by green-in-green tape casting with different support types

Recent development in the field of mixed ionic and electronic conducting membranes is focused to increase gas permeation, by either activating the surface with catalysts or by further reducing membrane layer thickness as well as gas diffusion limitations in the porous support structure.

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