

CERAMIC MEMBRANE DEVELOPMENT FOR MEMBRANE REACTORS AT FORSCHUNGSZENTRUM JÜLICH

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Introduction

Ceramic gas separation membranes have attracted high interest in energy applications due to its inherently high efficiency. Either oxygen or hydrogen permeable mixed ionic electronic conductors are feasible membranes for distributing or extracting oxygen or hydrogen to chemical reactions, respectively [1][2][3]. Another potential advantage is the provision of electrochemical active (ionic) species at the membranes surface. Besides the performance in terms of ionic flux the long term stability in operating conditions plays an important role for membrane reactor development. However, a typical trade-off between performance and stability exists. Hence, different material classes are investigated, which are the basis for material selection and tailoring for membranes dedicated to specific applications and its process conditions, i.e. temperatures and atmospheres.

Experimental

Materials synthesis is done by using different powder processing methods. Smaller quantities, i.e. 30-40 g batches, are prepared using the Sol-Gel based modified Pechini method. For larger quantities 0.5 – 10 kg solid state reaction or spray pyrolysis can be applied depending on targeted powder specifications.

The synthesized powders are characterized with regard to chemical composition and phase purity as well as processing related properties such as BET-surface, TEC, TGA etc.. Disc shaped small bulk samples are pressed and sintered in order to investigate performance in standard inert conditions as well as membrane reactor conditions.

Promising materials are processed into asymmetric membranes, i.e. thin (~20-50 µm) dense membrane layers on porous supports [4], [5], [6] using preferably tape casting. Also larger components, e.g. exhibiting gas flow channels, can be prepared by lamination and subsequent sintering [7].

Results and discussion

Single phase mixed oxygen ionic electronic conductors with perovskite structure show highest permeability [8] but suffers from limited stability both in acidic as well as reducing atmospheres. Therefore, its applicability is highly constrained. Nevertheless perovskite particularly titanate-based membranes have potential in certain application conditions. Another very promising alternative are dual phase composites combining a pure ion conductor with another electronic conducting ceramic phase, e.g. spinels or perovskites

[9]. Also for hydrogen permeable membranes in addition to single phase materials such as $\text{La}_{5.4}\text{WO}_{12-8}$ or doped Ba-zirconates the dual phase concept is feasible [10].

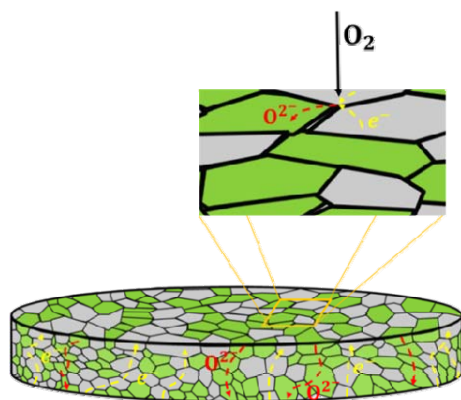


Fig. 1. Dual phase composite concept (exemplarily oxygen permeable) providing simultaneously high performance and high stability [8]

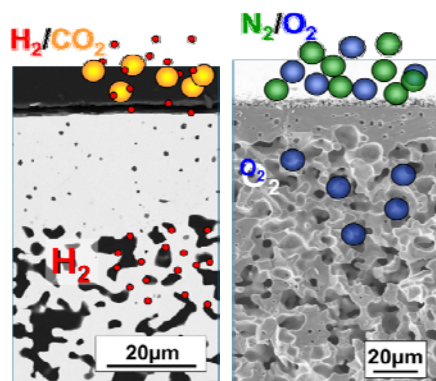


Fig. 2. Microstructure of asymmetric membranes composed of hydrogen permeable $\text{La}_{5.4}\text{WO}_{12-8}$ (left) and oxygen permeable $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (right)

Conclusions

Ceramic oxygen and hydrogen permeable membranes investigated at Forschungszentrum Jülich show high potential in membrane reactor conditions at several temperature levels ranging from 400 – 1000 °C.

References

- [1] Z. Cao, H. Jiang, H. Luo, S. Baumann, W.A. Meulenbergh, H. Voss, J. Caro, Simultaneous overcome of the equilibrium limitations in BSCF oxygen-permeable membrane reactors: Water splitting and methane coupling, *Catal Today* 193 (2012) 2–7
- [2] Z. Cao, H. Jiang, H. Luo, S. Baumann, W.A. Meulenbergh, J. Assmann, L. Mleczko, Y. Liu, J. Caro, Natural Gas to Fuels and Chemicals: Improved Methane Aromatization in an Oxygen-Permeable Membrane Reactor, *Angew. Chem. Int. Ed.* 52 (2013) 13794–13797
- [3] Z. Cao, H. Jiang, H. Luo, S. Baumann, W.A. Meulenbergh, H. Voss, J. Caro, An Efficient Oxygen Activation Route for Improved Ammonia Oxidation through an Oxygen-Permeable Catalytic Membrane, *ChemCatChem* 6 (2014) 1190–1194
- [4] S. Baumann, W.A. Meulenbergh, H.P. Buchkremer, Manufacturing strategies for asymmetric ceramic membranes for efficient separation of oxygen from air, *J Europ Ceram Soc* 33 (2013) 1251–1261
- [5] W. Deibert, M. E. Ivanova, W. A. Meulenbergh, R. Vaßen, O. Guillon Preparation and sintering behaviour of $\text{La}_{5.4}\text{WO}_{12-8}$ asymmetric membranes with optimised microstructure for hydrogen separation, *J Membr Sci* 492 (2015) 439–451
- [6] W. Deibert, F. Schulze-Küppers, E. Forster, M. E. Ivanova, M. Müller, W. A. Meulenbergh “Stability and sintering of MgO as a substrate material for LaWO membrane applications” *J Europ Ceram Soc* 37(2017) 671–677
- [7] P. Niehoff, F. Schulze-Küppers, S. Baumann, W.A. Meulenbergh, O. Guillon, R. Vaßen, Development and Manufacturing of Lab-Scale Planar BSCF Membrane Modules for Oxygen Separation, *Amer. Ceram. Soc. Bull.*, Vol. 94, No. 1 pp 28–31
- [8] S. Baumann, J.M. Serra, M.P. Lobera, S. Escolástico, F. Schulze-Küppers, W.A. Meulenbergh, Ultrahigh oxygen permeation flux through supported $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-8}$ membranes, *J Membr Sci* 377 (2011) 198–205
- [9] M. Ramasamy, S. Baumann, J. Palisaitis, F. Schulze-Küppers, M. Balaguer, D. Kim, W.A. Meulenbergh, J. Mayer, R. Bhawe, O. Guillon, M. Bram, Influence of Microstructure and Surface Activation of Dual Phase Membrane $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-8}$ - FeCo_2O_4 on Oxygen Permeation, *J. Am. Ceram. Soc.* 99 (2016) 349–355
- [10] M. E. Ivanova, S. Escolastico, M. Balaguer, J. Palisaitis, Y. J. Sohn, W. A. Meulenbergh, O. Guillon, J. Mayer, J. M. Serra, “Hydrogen separation through tailored dual phase membranes with nominal composition $\text{BaCe}_{0.8}\text{Eu}_{0.2}\text{O}_{3-8}$: $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{2-8}$ at intermediate temperatures” *Scientific Reports* 6 (2016) 34773