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FABRICATION OF POROUS 3-YSZ TUBULAR SUPPORTS FOR OXYGEN TRANSPORT MEMBRANES

Astri Bjørnetun Haugen, Jonas Gurauskis, Simona Ovtar, Peter Vang Hendriksen and Andreas Kaiser
Department of Energy Conversion and Storage, Technical University of Denmark
Frederiksborgvej 399, DK-4000, Roskilde, Denmark
Email: ahua@dtu.dk

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Pure oxygen gas supplied by ceramic oxygen transport membranes can facilitate reduced CO_2 emissions through more efficient gasification processes, partial oxidation reactions and CO_2 capture and storage. Tubular membranes have some advantages compared to planar membranes, such as better resistance to thermal gradients and a more straightforward sealing. The active oxygen separation layer in the membrane should be as thin as possible and therefore supported on a highly porous tubular substrate. The aim of this project is to produce oxygen transport membrane components for integration in a biomass gasifier. A component has been developed that consists of a 3 mol% yttria-stabilized zirconia (3-YSZ) porous support, dense Sc_2O_3-doped YSZ + Al_2O_3-doped ZnO as the composite membrane, and porous Sc_2O_3-doped YSZ infiltration layers on each side of the dense membrane. The requirements for the porous 3-YSZ support are gas permeability of 10^{-14} m^2, mechanical strength of 50 MPa and sufficient sintering shrinkage for densification of the membrane layer.

This work focuses on the manufacture of tubular porous supports of 3 mol% yttria-stabilized zirconia using thermoplastic extrusion. Two types of poreformers (spherical graphite (d_{50} 18 µm) and polymethyl methacrylate (PMMA, d_{50} 10 µm)) have been used as sacrificial fugitives to form connected macropores, since their spherical geometry limits preferential orientation during extrusion. Their difference in decomposition temperatures also allows a high volume fraction of pore formers without deformation during de-binding. The influence of the amount of pore formers (relative to the amount of ceramic and thermoplastics) on the microstructure of sintered samples, as well as the extrudability and ease of de-binding of the feedstock, has been studied. Combining both spherical graphite and PMMA pore formers was necessary to obtain the highest permeability and a feedstock with a viscosity suitable for extrusion. Ceramics with 1-20 µm pore size, pore neck size up to 1.2 µm, open porosities exceeding 55 % and gas permeabilities exceeding 10^{-14} m^2 were then produced (Figure 1). Poor connectivity and small pore neck size is the main limitation for the pore connectivity and therefore also the gas permeability. Still, these results demonstrate that porous tubes with sufficient gas permeability can be fabricated by thermoplastic extrusion.

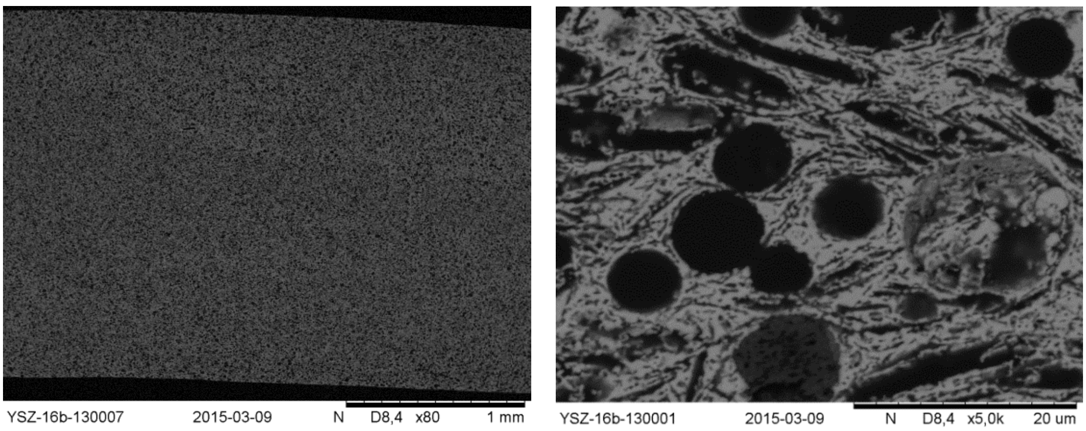

Figure 1. Microstructure of the most permeable 3-YSZ feedstock composition after sintering at 1300 ˚C. Left: cross-sectional view demonstrating a homogeneous porous structure. Right: High magnification of the microstructure demonstrating spherical pores from PMMA pore formers and elongated pores from spherical graphite pore formers.