

Manufacturing of new nano-structured ceramic–metallic composite microporous membranes consisting of ZrO_2 , Al_2O_3 , TiO_2 and stainless steel [☆]

Tim Van Gestel ^{*}, Doris Sebold, Wilhelm A. Meulenber, Martin Bram, Hans-Peter Buchkremer

Forschungszentrum Jülich GmbH, Institute of Energy Research, IEF-1: Materials Synthesis and Processing, Leo-Brandt-Strasse, D-52425 Jülich, Germany

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Abstract

Frequently, the membrane employed in a traditional nano-filtration (NF) or gas separation (GS) membrane device consists of a polymeric material, having significant disadvantages including a restricted mechanical, chemical and thermal stability. As an alternative for the polymeric membranes, ceramic membranes with an improved stability have been introduced, but the current membranes still suffer from stability problems (e.g. brittle material, restricted chemical stability in water vapour). This paper reports the preparation of novel hybrid metallic–ceramic membranes, based on a porous 316L stainless-steel support material. The optimized membranes were made by deposition of a fine suspension with a particle size of ~180 nm, a colloidal sol with a particle size of ~30 nm and a nano-particle sol with a particle size of ~5 nm and show a comparable multilayer structure as current ceramic membranes for micro-, ultra- and nano-filtration and gas separation. The essential new features of the membranes include the use of an alternative metallic support material, which provides a high mechanical stability to the membrane, and the application of zirconia- and titania based functional membrane layers, which display a high chemical and thermal stability for potential filtration or gas separation applications.

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1. Introduction

When compared with organic polymeric membranes for microfiltration (MF), ultra-filtration (UF), nano-filtration (NF), gas separation (GS) and pervaporation (PV), a number of benefits have been frequently highlighted for ceramic membranes, including an improved mechanical, thermal and chemical stability [1]. In practice, however, an important problem hindering the establishment of membrane processes as a viable alternative to traditional separation methods often includes the lack of a selective and stable membrane able to withstand sustained exposure to real and sometimes harsh process conditions (e.g. corrosive liquids, water vapour, high pressure).

In our membrane research, novel hybrid metallic–ceramic membranes, with a comparable graded multilayer structure as conventional ceramic membranes and supported by a porous metallic material are developed. The functional layers of these membranes are made of ZrO_2 or TiO_2 and have pore sizes which are similar to those of current all-ceramic mesoporous and microporous membranes for e.g. UF, NF, GS or PV.

In literature, various articles can already be found reporting the development of tight mesoporous (pore size >2 nm) and open microporous membranes (pore size 1–2 nm) with a functional layer consisting of ZrO_2 or TiO_2 for UF and NF [1–4]. Membranes with a good chemical and thermal stability and as a consequence of these advantages, a long service-life have been developed. In order to optimize current ceramic filtration membranes further, the mechanical properties of the membrane support could be improved or — as shown in this paper — in an alternative concept the membrane layers can be applied on a metallic support material. From a practical point of view, the application of a metallic material appears also as an interesting alternative to the use of regular ceramic support materials, given

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^{*} Corresponding author. Tel.: +49 2461 615443; fax: +49 2461 612455.

E-mail address: t.van.gestel@fz-juelich.de (T. Van Gestel).

the possibility to house the membranes into a module by simple metal joining techniques such as welding or brazing.

Guizard et al. [5] already proposed two decades ago to use a metallic support for a conventional ceramic microfiltration (MF) membrane. They prepared macroporous ZrO₂ membranes with an average thickness of 15–25 μm and a pore size of 200 nm and 80 nm, respectively, on metallic filter disks and tubes, using slip-casting. Later, they used a porous flat support consisting of pressed stainless-steel fibers and deposited subsequently a ZrO₂ layer with a thickness of 30–35 μm from a suspension and a SiO₂ layer with a thickness of ~10 μm and a pore size of 10 nm by a colloidal sol–gel coating procedure [6]. Remarkably, up to now, there has been no interest to use a metallic support material as a substrate for the development of graded multilayer membranes with finer mesoporous and microporous layers for advanced membrane filtration or gas separation applications. This could be due to the lack of commercial porous metallic materials with the required quality and/or because the fabrication of ceramic membranes on a metallic substrate is more complex.

In the field of nano-structured ceramic membranes with a very tight microporous structure (e.g. for GS or PV applications) a number of articles can be found reporting membranes with ultra-thin SiO₂ based toplayers with a pore size <1 nm and a thickness in the range 50–200 nm [7]. The main drawback which is mostly reported for current ceramic (SiO₂ based) membranes includes a limited chemical resistance towards acids, bases and even water (vapour) during operation. Therefore, ultra-thin toplayers made from ZrO₂ or TiO₂ are proposed for the manufacturing of multilayer membranes on a metallic support.

2. Experimental

2.1. Preparation of steel support and macroporous membrane layer

The metallic support material was manufactured by tape-casting according to a procedure previously developed in our laboratory [8]. A macroporous membrane layer was produced by wet-powder spraying of a rutile-TiO₂ suspension (Kerr-McGee, TRONOX R-KB-3). The manufacturing procedure included ball milling of the commercial powder in ethanol, with the addition of dispersants and terpineol as coating regulating additive. The particle size of the suspension measured ~180 nm after ball milling for 20 h (measurement with dynamic laser light scattering (Horiba LB-550)). In all coating procedures, the suspension spraying quantity was set at 0.5 g/s with a spraying pressure of 0.5 bar and the coating was applied two times with overnight drying at 25 °C. No binders were used during the deposition process. After deposition, the membrane film was fired at 950 °C for 1 h in vacuum, using a heating and cooling ramp of 5 K/min.

2.2. Preparation of mesoporous membrane layers

Mesoporous membrane layers were made by a colloidal sol–gel coating procedure. In a first coating experiment, alumina membrane layers were prepared from sols containing γ-alumina colloidal particles with a size of ~30 nm. The sol preparation

was based on the well-known Yoldas process, which includes hydrolysis of a metal-organic precursor (Al(OC₄H₉)₃, Sigma-Aldrich) with H₂O and subsequent destruction of larger agglomerates with HNO₃ at elevated temperature (>80 °C) [9]. In a second coating experiment, a zirconia sol with a particle size of ~30 nm was prepared in a similar way by hydrolysis of Zr(OC₃H₇)₄ (Sigma-Aldrich). Titania doped zirconia sols were prepared by adding a titania sol prepared from Ti(OC₃H₇)₄, with a mole ratio of 25%.

Coating liquids were prepared from the sols by adding polyvinyl alcohol (PVA) as coating and drying controlling additive. Supported gel layers were formed on the membrane support by spin-coating in a clean-room. For coating, 2 ml sol was dropped onto the substrate, which was held to the spin-coating device by means of a vacuum pump. After 20 s, the substrate was then spun at high speed (1200 rpm, spinning time 1 min). In order to obtain a mesoporous γ-Al₂O₃ membrane layer, the alumina gel layer was fired at 600 °C for 3 h in vacuum. For the formation of a tetragonal-ZrO₂ membrane layer, firing was performed at 500 °C for 2 h. In all coating procedures, the coating–firing cycle was carried out twice.

The size of the sol particles (particle size distribution) was measured by a dynamic laser light scattering technique (Horiba LB-550). Scanning electron microscopy (FESEM, Zeiss Ultra55) and X-ray diffraction (Siemens D5000) were used to characterize the membrane microstructure and phase composition. The pore size of the substrate and macroporous membrane material was measured with Hg-porosimetry (Fisons Pascal 440); the mesoporous and microporous membrane material was characterized by means of N₂-adsorption/desorption (Sorptomatic 1990 Series).

2.3. Preparation of microporous membrane layers

For the manufacturing of an ultra-thin microporous toplayer with a pore size <1 nm, a polymeric type of sol–gel method was considered, analogous to the preparation procedure of state of the art microporous SiO₂ toplayers. In order to obtain a precipitate-free sol containing nanometer-sized particles, the reactivity of the precursor was reduced prior to the hydrolysis and condensation/polymerization reactions that are involved in the sol synthesis. The essential features of the method used here were the application of an alcohol amine (diethanol amine, DEA) as inhibitor for the polymerization reaction and as a coating and drying controlling additive during the critical deposition process. In a preferred preparation procedure, the amine was added to a solution of a zirconia precursor (Zr(OC₃H₇)₄) or a titania precursor (Ti(OC₃H₇)₄) and *n*-propanol (*n*-C₃H₇OH), after which a solution of a modified precursor was obtained. A stable sol containing nano-particles with a size of ~5 nm was obtained by hydrolysing these modified precursors with 5 to 10 mol of H₂O, in the presence of HNO₃.

In the first coating experiments, the prepared sols were used for spin-coating as described above. The obtained gel layers were fired at 500 °C in vacuum, to give a supported membrane layer on the previously deposited mesoporous membrane. In a second series of coating experiments, a sol spray-coating process was

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