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Highly permeable and mechanically robust silicon carbide hollow fiber membranes

Patrick de Wit [a], Emiel J. Kappert [a], Theresa Lohaus [b], Matthias Wessling [b,c], Arian Nijmeijer [a], Nieck E. Benes [a,*]

[a] Inorganic Membranes, Department of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[b] RWTH Aachen University, AVT.CVT – Chair of Chemical Product and Process Engineering, Turmstr. 46, 52064 Aachen, Germany
[c] DWI – Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

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ABSTRACT

Silicon carbide (SiC) membranes have shown large potential for applications in water treatment. Being able to make these membranes in a hollow fiber geometry allows for higher surface-to-volume ratios. In this study, we present a thermal treatment procedure that is tuned to produce porous silicon carbide hollow fiber membranes with sufficient mechanical strength. Thermal treatments up to 1500 °C in either nitrogen or argon resulted in relatively strong fibers, that were still contaminated with residual carbon from the polymer binder. After treatment at a higher temperature of 1790 °C, the mechanical strength had decreased as a result of carbon removal, but after treatments at even higher temperature of 2075 °C the SiC-particles sinter together, resulting in fibers with mechanical strengths of 30–40 MPa and exceptionally high water permeabilities of 50,000 L m^{-2} h^{-1} bar^{-1}. Combined with the unique chemical and thermal resistance of silicon carbide, these properties make the fibers suitable microfiltration membranes or as a membrane support for application under demanding conditions.

1. Introduction

The outstanding mechanical integrity and chemical stability of silicon carbide has resulted in its use in various applications in which the material has to resist harsh conditions, such as diesel particulate filters [1], catalyst carriers [2], and sensors that are used at extreme pHs [3]. Whereas silicon carbide membranes have also been proposed for gas separation [4–8], the application of silicon carbide membranes for liquid applications has received little attention in literature. In 2011, Hofs et al. demonstrated the superb fouling resistance of silicon carbide membranes in the treatment of surface water [9]. Several companies claimed that this low-fouling behaviour extents to the harsh conditions of oil/water separations [10–12].

Until now, silicon carbide membranes have been limited to flat [13], tubular [14,4] and multichannel [5] geometries. All these geometries have a comparatively low surface-to-volume ratio in comparison with hollow fibers. The synthesis of inorganic hollow fibers has seen increasing attention during the last decade [15–18], but the few silicon carbide fibers that have been produced so far have showed an undesirable pore structure [19,20] or poor mechanical stability [21].

In the present paper, we developed a procedure for the fabrication of mechanically robust, porous silicon carbide hollow fibers via dry–wet spinning. The paper elaborates on the effects of the thermal treatment on the structure and properties of the obtained fibers, demonstrating that a felicitous thermal treatment is of key importance for the successful synthesis of highly permeable and mechanically robust silicon carbide hollow fibers.

2. Experimental

2.1. Materials

α-Silicon carbide powders with a mean size of 0.4 and 0.6 μm were supplied by Liqtech International AS (Denmark). Polyethersulfone (PES, Ultrason® E 6020 P, BASF), N-methyl-2-pyrrolidone (NMP, < 99.5%, Sigma Aldrich) and de-ionized water (< 18.2 MΩ cm^{-1}, Milli-Q Advantage A10, Millipore) were used for dry–wet spinning. Prior to use, PES was dried overnight at 80 °C; all other chemicals were used as received. Sintering was

* Corresponding author.
E-mail address: N.E.benes@utwente.nl (N.E. Benes).

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carried out in argon (4.5) or nitrogen (2.8) gas atmosphere (Praxair).

2.2. Dry–wet spinning

The spinning dope composition was based on prior work [22]. Silicon carbide powders were mixed in a 1:5 weight ratio (0.4 : 0.6 μm), added to NMP and treated ultrasonically for 30 min. PES was added in multiple steps to this mixture, allowing the PES to dissolve before the next amount was added. The resulting spinning mixture was composed of 36 wt% of SiC, 50 wt% of NMP and 14 wt% of PES. After stirring overnight, vacuum was applied for 30 min and the mixture was left overnight to degas.

For the dry–wet spinning, the mixture was forced through a spinneret by pressuring a stainless-steel vessel with nitrogen. The spinning conditions are given in Table 1; full details on the spinning setup can be found elsewhere [21]. After spinning, the fibers were stretched (1 cm m^{-1}) and dried prior to sintering.

2.3. Thermal treatment

Thermal treatments up to 1500 °C were carried out in a STF 16/610 tubular furnace (Carbolite) equipped with an alumina working tube. Samples were loaded in SiC crucibles and thermally treated according to the programs given in Table 2. Prior to sintering, the system was evacuated and refilled with either argon or nitrogen three times, followed by sintering under a sweep flow of 100 ml min^{-1}.

High-temperature sintering (1500–2075 °C) was carried out at Liqtech Industries A/S, Denmark, where the fibers were co-sintered with a running production batch. All high-temperature sintering was carried out under argon; prior to shipping for high-temperature sintering, the samples were pre-sintered at 1500 °C for 2 h in argon.

Fiber mass (m), length (l) and diameter (d) were determined per fiber prior to and after thermal treatment to allow for paired comparison.

Table 1
Spinning conditions.

Condition	Value
Bore liquid	H_2O
Coagulation bath	H_2O
Extrusion pressure	2 bar
Air gap	3 cm
Bore liquid flow rate	7 ml/min
Diameter spinneret	OD/ID=2.0/0.8 mm

Table 2
Overview of the used sintering programs. For all experiments, a 5 °C min^{-1} heating rate was employed.

Name	Sintering	Atmosphere
300-N_2	1 h at 300 °C	Nitrogen
1000-N_2	1 h at 300 °C, 3 h at 1000 °C	
1500-N_2	1 h at 300 °C, 3 h at 1500 °C	
300-Ar	1 h at 300 °C	Argon
1000-Ar	1 h at 300 °C, 3 h at 1000 °C	
1500-Ar	1 h at 300 °C, 3 h at 1500 °C	
1790-Ar*	6 h at 1790 °C	
2075-Ar*	0.75 h at 2075 °C	

* Sample sintered at Liqtech, Denmark. Samples were pre-sintered according to program 1500-Ar.

2.4. Characterization

2.4.1. SEM-EDS

The cross section morphology, the wall thickness and semi-quantitative elemental analysis of green and sintered fibers were obtained with a JSM-6010LA scanning electron microscope equipped with an energy dispersive spectrometer (Jeol). To obtain a clean fracture, the green compacts were soaked in liquid nitrogen before fracturing. The samples were gold-sputtered (13 mA, 3 min) before SEM photos were taken. The EDS spectra were obtained from a cross-section of the non-sputtered fibers in low-vacuum mode.

2.4.2. TGA-MS

Thermogravimetric analysis (TGA) was performed on a STA 449 F3 Jupiter® (Netzch) fitted with a TG-only sample holder. Measurements were performed under 70 ml min^{-1} argon at a heating rate of 20 °C min^{-1} from room temperature to 1500 °C. Temperature correction by melting standard and a blank correction with an empty cup were carried out prior to the measurements. Small fragments of dried fibers were used as sample and their mass was determined externally.

Gases evolving during the thermogravimetric analysis were transferred to a mass spectrometer (MS, QMS 403 D Aëolos ®, Netzsch) by a glass capillary. TGA and MS start times were synchronized; no correction was applied for the time offset caused by the transfer line time (estimated < 30 s, systematic offset). First, a bar graph scan for m/z=1–100 amu was performed to determine the evolving m/z-numbers (data not included here). The detected m/z-numbers (2, 12, 14–18, 20, 26–30, 32, 36, 38, 40, 44, 48–52, 56, 60–61, 64, 67–68) were selected and recorded more accurately in multiple-ion-detection mode, with a dwell of 0.5 sec per m/z-value and a resolution of 50.

2.4.3. Clean water permeation

The clean water flux was measured using an OSMO Inspector 2 (Convergence, Netherlands). Experiments were carried out in dead-end mode under constant flux operation with three different flux settings for each fiber. Custom-made single-fiber modules were used made out of Plexiglass tubing and sealed with PUR435/PUR-N 2-component glue (Intercol, Germany).

The permeate flow Φ_v (Lh^{-1}) was recorded as a function of the transmembrane pressure. The pressure drop over the fiber is assumed to be negligible. The permeability was calculated using Eq. (1), where A is the effective membrane area:

$$\Pi = \frac{\Phi_v}{(p_{\text{feed}} - p_{\text{permeate}}) \cdot A}. \quad (1)$$

2.4.4. Conductivity

Electrical conductivity was measured using a home-build 4-probe conductivity meter. Current was applied at the outer probes that were 7 cm apart; the voltage drop was measured with two inner probes 3 cm apart. Measurements were performed at room temperature on three different spots at each fiber.

2.4.5. Mercury intrusion porosimetry

The volume of mercury intruded was measured as function of the pressure using a Poremaster PM-33-14 (Quantachrome®). The helium density was measured using an AccuPyc II 1340 gas displacement analyzer (Micromeritics). Pressure p and volume mercury intruded V_{Hg} were recorded and data processing was performed using Matlab® [23]. The pore diameter corresponding to a certain pressure is calculated using Washburn's equation [24] (Supplementary Information). The volume based pore size