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## Short Communication

# Rapid thermal processing of tubular cobalt oxide silica membranes



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## ABSTRACT

This work is the first demonstration of rapid thermal processing techniques as applied to metal oxide/silica membranes on tubular geometries. A procedure was developed which combined fast sol–gel synthesis, rapid calcination steps and a thermal annealing stage to reduce the membrane fabrication time by more than two-thirds, from a conventional process taking seven or more days to less than two. A significant aspect of this major development was the use of a pre-hydrolysed silica precursor ethyl silicate 40 (ES40), instead of the generally preferred tetraethyl orthosilicate (TEOS) which eliminated the need for the researcher specific and time consuming sol–gel reaction stages prior to membrane fabrication. As a result, modified-silica membranes containing cobalt oxides could be directly calcined at 600 °C, instead of conventional thermal process which require slow ramping rates of  $\leq 1$  °C min<sup>-1</sup> to avoid cracking. As-prepared membranes delivered H<sub>2</sub> permeances of  $5 \times 10^{-7}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> at 450 °C and H<sub>2</sub>/N<sub>2</sub> permselectivities of 54. The RTP techniques demonstrated in this work greatly reduced the production time and should both allow researchers to significantly increase their productivity and ultimately reduce the barriers for deployment of inorganic membranes into industrial applications.

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## 1. Introduction

The role of hydrogen (H<sub>2</sub>) in a sustainable energy and carbon constrained future is widely accepted [1], especially as an energy vector. H<sub>2</sub> can be produced from a variety of sustainable sources including biomass and water [2]; however, currently hydrogen is directly produced from fossil fuels by industrial processes such as gas reforming or coal gasification [3]. In these cases, H<sub>2</sub> is generated from syngas streams at high temperatures (>200 °C). In order to avoid the energy penalties associated with conventional gas separation technologies,

inorganic membranes, which operate within the required temperature and pressure ranges are a very attractive technology [4]. Modified-silica membranes have been at the forefront of inorganic membrane technology research for much of the last decade, where researchers have doped silica with metal oxides such as alumina [5,6], cobalt oxide [7], zirconia [8], nickel [9] and titania [10] to confer major improvements to both membrane performance and stability. Igi et al. [11] reported that cobalt oxide assisted the silica matrix in resisting the typical densification associated with pure silica membranes under hydrothermal conditions. Cobalt oxide silica

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membranes were also shown to be stable in the presence of hydrogen sulphide containing gas streams [12] which are typically fatal to other inorganic membranes such as pure palladium. More recently, cobalt oxide membranes were successfully tested for H<sub>2</sub> separation at temperatures up to 600 °C with mixed gas feeds [13] and have been scaled up to a multi-tube membrane module and tested for over 2000 h [14].

Yet despite these major developments to take silica derived membranes towards the requirements of industrial applications, the high cost price of production remains a substantial barrier to be overcome. This is due in a large part to the complex and time-consuming membrane fabrication techniques. Microporous silica-based membranes are typically fabricated either through sol–gel synthesis and dip-coating or chemical vapour deposition techniques [15]. Sol–gel techniques are commonly touted as the way to market due to their increased process flexibility, utilization of less costly precursors, and traditionally higher membrane fluxes; albeit with reduced selectivity as the trade-off. However researchers must typically coat multiple membrane layers, with a thermal calcination step following each coating, in order to ensure high quality membranes with no defects [16]. A major drawback of this technique is the slow thermal processing of each membrane layer, with heating and cooling rates typically  $\leq 1$  °C min<sup>-1</sup> [17]. Thus with calcination temperatures of  $\geq 400$  °C and holding times on the order of several hours, the processing time per coating is often more than 16 h and the total time to produce a high performance membrane in the range of several days to weeks. The slow calcination process is a generally accepted practice to reduce thermal stresses across the substrate, interlayers and membrane top layer which typically all possess different thermal expansion coefficients. However, membranes with production times of several days to weeks will be extremely costly and thus are not well-suited to scale up and industry acceptance.

In 2010 Schillo et al. reported for the first time a rapid thermal processing (RTP) technique inspired by the semiconductor industry whereby each coat was calcined in a matter of minutes using tungsten-halogen lamps with heating rates of  $>100$  °C s<sup>-1</sup> [18]. The authors showed that for sufficiently thin  $\gamma$ -alumina membrane layers, rapid heating and cooling did not cause cracking of the layers because the short processing times and directed heating only allowed the top layer to reach the desired temperature whilst the temperature of the substrate and interlayers remained relatively unchanged. In 2012, Kappert et al. [19] also reported considerable success for silica membranes (derived from tetraethyl orthosilicate (TEOS)) using rapid heating rates whereby the coated membrane was either placed directly into a preheated furnace or was placed on a hot plate. This reduced calcination times to  $\sim 3\%$  of conventional processes without compromising membrane performance. Yet, despite these promising results, conventional thermal processing techniques (CTP) still dominate the research landscape and significant work is still required to establish RTP as a credible alternative synthesis route. In particular, both studies employed small scale flat membrane geometries to ensure homogeneous heating rates prepared under special laboratory conditions. However, tubular membranes are more suited to industrial application

due to their larger surface area to volume ratios, which in turn translates to a reduced plant footprint.

In this work we report for the first time the rapid production of a cobalt oxide silica membrane on a tubular membrane support using a RTP approach that combines the rapid calcination of membrane layers with a conventional thermal annealing step. Furthermore, the successful membrane was produced using a pre-hydrolysed, industrial silica precursor (ethyl silicate 40 (ES40)), instead of the conventional TEOS precursor. ES40 was chosen as it eliminates the need for the unnecessarily complex and time-consuming hydrolysis and condensation stage of TEOS sol–gel preparation [20]. The combination of methods reduced the overall membrane fabrication time from an estimated 7 days, including  $\frac{1}{2}$  day sol–gel synthesis and at least 6 days of coating and calcination; to approximately 2 days for the same number of membrane layers. This is significant as it demonstrates the versatility of RTP techniques, which do not appear to adversely influence the metal oxide doping process. The final RTP membrane was examined by electron microscopy to characterise the membrane morphology and tested for single gas permeation and permselectivity for helium, hydrogen, nitrogen and carbon dioxide at temperatures ranging from 200 °C to 450 °C.

## 2. Experimental

### 2.1. Sol–gel preparation and membrane fabrication

Cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O; 98%, Alfa Aesar) and ethyl silicate 40 (ES40; Colcoat Co., Japan) were used without further purification. Absolute ethanol (EtOH; AR grade) was used. Tubular alumina support (10 mm i.d., 14 mm o.d., 100 mm length) consisting of  $\alpha$ -alumina substrate and  $\gamma$ -alumina interlayer was obtained from the Energy Research Centre of the Netherlands (ECN). The CoES40 coating solution was prepared using a simplified sol–gel method reported elsewhere [20]. Briefly, cobalt nitrate hexahydrate was dissolved in double distilled water, diluted with ethanol, and ES40 was slowly added under stirring to achieve a final molar ratio of 255:4:1:40 for the EtOH:ES40:Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O:H<sub>2</sub>O sol.

Each CoES40 layer was deposited onto the support using a dip-coater with a dwell time of 1 min and a withdrawal rate of 10 cm min<sup>-1</sup>. After the deposition of each layer, the membranes were calcined in an air atmosphere at 600 °C for 1 h per membrane layer. The furnace was preheated at 600 °C; hence the temperature ramping rate experienced by the membrane was on the order of  $>100$  °C s<sup>-1</sup>. After each calcination step the membrane was immediately removed from the hot furnace and allowed to cool on the bench top of a laminar flow cabinet to prevent dust contamination. The cycle of dip-coating and calcination was repeated six times for a total of six membrane layers. The membrane was initially coated with 3 layers and tested for gas permeation. Generally membranes require at least 3 layers to cover small surface or pin hole defects. Preliminary results yielded lower He/N<sub>2</sub> permselectivity  $< 6$ . Hence, further 3 layers were coated to cover any remaining defects. For the 3rd and the 6th layers, the membrane was

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