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# Partial oxidation of methane using silver/gadolinia-doped ceria composite membranes



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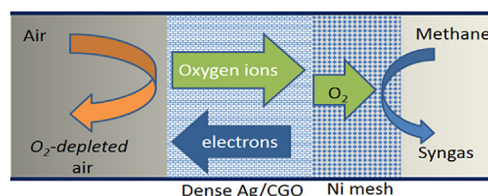
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## HIGHLIGHTS

- Novel Ag/CGO membranes fabricated with low metal content.
- Methane was partially oxidised using oxygen permeated through a Ag/CGO membrane.
- The membranes were stable in very low partial pressures of oxygen.
- No carbon deposition was observed in the membranes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Methane was partially oxidised to CO using oxygen permeated through a 1 mm thick silver/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-x</sub> (Ag/CGO) composite membrane operating at 500–700 °C with air at 1 bar pressure. The membranes were fabricated by sintering ultrafine nanoparticles of gadolinia-doped ceria (< 5 nm) coated with silver using Tollens' reaction. This unique combination led to dense composites with low content of silver (7 vol%), no reaction between the components and predominant metallic conductivity. When feeding 4% methane at 700 °C to a 1-mm thick Ag/CGO using Ni as reforming catalyst, the conversion reached 21% and the CO selectivity 92% with an estimated oxygen flux of 0.18 mL min<sup>-1</sup> cm<sup>-2</sup> (NTP). The samples were stable in carbon-containing atmospheres and under a large pO<sub>2</sub> transmembrane pressure difference at temperatures below 700 °C for 48 h.

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## 1. Introduction

Syngas, a mixture of carbon monoxide and hydrogen, is used for the production of synthetic fuels via the Fischer–Tropsch process or transformed into other chemicals, for example dimethyl ether (DME) (Sousa-Aguiar et al., 2011). Syngas is commonly produced on a large scale from methane by steam reforming, a method that requires large amounts of energy as the reaction is endothermic (Eq. (1)). The reaction also leads to a H<sub>2</sub>/CO ratio of 3, higher than the ideal H<sub>2</sub>/CO ratio of 2 necessary for further conversion to synthetic fuels (Sousa-Aguiar et al., 2011; Rostrup-Nielsen et al.,

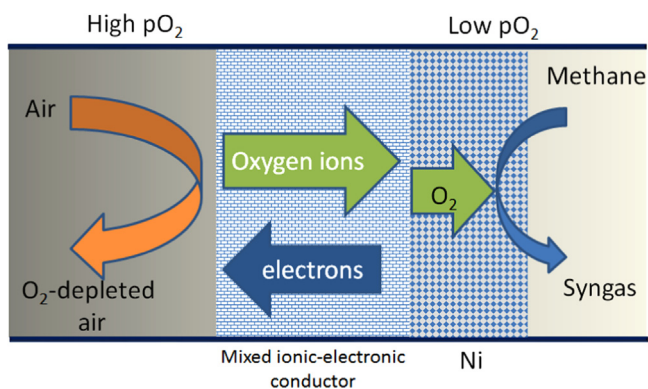
2002). Another method for the conversion of CH<sub>4</sub> is dry or CO<sub>2</sub> reforming, also an energy intensive process that yields a lower H<sub>2</sub>/CO ratio of 1 (Eq. (2)) [2].

An ideal process to achieve the preferred H<sub>2</sub>/CO ratio of 2 is the partial oxidation of methane. One way of achieving this is auto-thermal reforming, where a mixture of methane and oxygen is raised to a temperature of 1300 °C at which thermodynamic equilibrium favours the formation of syngas. The main disadvantages of this method are the high temperature and the need for high purity oxygen to hinder side reactions between nitrogen and the other components.

Catalytic partial oxidation on a mixed ionic–electronic membrane has been proposed to solve this problem (Yu et al., 2014; Balachandran et al., 1995). In practice, rather than direct partial oxidation, it is a two-step process. The first step is the complete

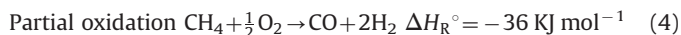
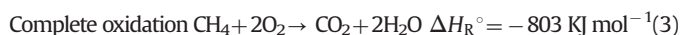
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**Fig. 1.** Using a mixed oxygen ionic–electronic membrane, oxygen from air is incorporated into the ionic crystal lattice. Oxygen diffuses across the gas-impermeable membrane driven by a gradient in the chemical potential of oxygen. In the case of a composite membrane, oxygen migrates as oxygen ions through the ionic material and electrons are transported in the opposite direction mainly through the electronic conductor network. On the reducing side of the membrane the permeating oxygen then reacts with methane in the presence of a reforming catalyst to form syngas.

oxidation of methane to  $\text{CO}_2$  (Eq. (3)) that provides the energy necessary for the second step, dry-steam reforming in the presence of nickel and excess methane. To be thermally efficient the energy released in the full oxidation step must be consumed in the reforming reactions. By combining Eqs. (1), (2) and (3), partial oxidation of methane to syngas produces the ideal  $\text{H}_2/\text{CO}$  ratio of 2 as shown in Eq. (4).



Previous literature reports have shown that methane can also be partially oxidised using the permeated oxygen from air in a gas separation membrane operating above  $800^\circ\text{C}$  in the presence of a reforming catalyst (Balachandran et al., 1995; Dyer et al., 2000; Shao et al., 2001), as illustrated schematically in Fig. 1.

Oxygen can be separated from air using a mixed ionic–electronic membrane that provides both oxygen transport and electronic conductivity (Yu et al., 2014; Dyer et al., 2000; Shao et al., 2001; Bouwmeester and Burggraaf, 1996; Dong et al., 2001; Teraoka et al., 1985; Ruiz-Trejo et al., 2014). A mixed ionic–electronic membrane can either be a composite, with separate electronically conductive and ionically conductive phases such as silver/ $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-x}$  (Ag/CSO) (Ruiz-Trejo et al., 2014), silver/copper oxide/gadolinia-doped ceria (Ag/CuO/CGO), CGO/ $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-d}$  (LSCF) (Samson et al., 2014), or a single phase material in which both electrons and oxygen ions are mobile, such as LSCF (Teraoka et al., 1985) or  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d}$  (BSCF) (Shao et al., 2000). Perovskite-based materials such as LSCF and BSCF have shown high permeation rates at high temperatures ( $800\text{--}1000^\circ\text{C}$ ).

BSCF, one of the materials that has attracted more interest, is nonetheless strictly limited to operation at  $p\text{O}_2$  above  $10^{-5}$  bar, therefore limiting its use in hydrocarbon atmospheres (Vente et al., 2006); it is also known that oxygen permeation is greatly reduced in the presence of  $\text{CO}_2$ , due to carbonate formation, and even though the carbonation process might be reversible, use in carbon-containing atmospheres is further restricted by the complexity of operation (Arnold et al., 2007; Bucher et al., 2008). Although a variety of strategies have been implemented to solve these problems, the stability of BSCF is the main challenge for its long term operation under highly reducing and carbon containing atmospheres.

Herein, we present a metal–ceramic composite for *in-situ* oxygen production or partial oxidation of methane operating in the temperature range:  $500\text{--}700^\circ\text{C}$  where economic heat sources can be used and with good tolerance to carbon containing atmospheres and good mechanical stability. The two main components are  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO) as the ionic conductor and silver as the electronic conductor, labelled hereafter as Ag/CGO.

CGO has been shown to be catalytically active for both steam and dry reforming (Ramirez-Cabrera et al., 2002; Ramirez-Cabrera et al., 2004) and it exhibits high oxygen ion conductivity. Doped ceria-based materials are stable in carbon containing atmospheres and their high oxygen storage capacity is useful in ceria–zirconia solid solutions for exhaust gas cleaning (Ozawa et al., 1993).

Silver is an excellent catalyst for the reduction of oxygen and its addition to CGO increases the oxygen surface exchange coefficient by orders of magnitude (Ruiz-Trejo et al., 2014; Seeharaj and Atkinson, 2011). Silver is also considerably cheaper than Pt, Pd or other metals used in similar membranes (Sunarso et al., 2008). Furthermore, silver is also catalytically active for partial oxidation reactions (Nagy and Mestl, 1999).

In this work the composite membrane was fabricated by coating ultrafine CGO particles (5 nm) produced by continuous hydrothermal flow synthesis (CHFS), with silver followed by careful sintering. We demonstrate the selective permeation of oxygen through such a membrane, confirming our earlier report (Ruiz-Trejo et al., 2014) and then further demonstrate the effectiveness of such a membrane for the partial oxidation of methane using nickel as a reforming catalyst.

## 2. Experimental

The nanoparticles from which the membranes were fabricated, were produced by CHFS. A single aqueous solution of ammonium cerium nitrate (0.45 M) and gadolinium nitrate (0.05 M) (pumped at a flow rate of  $200 \text{ mL min}^{-1}$ ) was mixed in line with an aqueous solution of KOH (0.5 M) at a flow rate of  $200 \text{ mL min}^{-1}$  before being mixed with a stream of water at  $450^\circ\text{C}$  and 24.1 MPa flowing at  $400 \text{ mL min}^{-1}$  in a co-current mixer as described elsewhere (Tighe et al., 2013). The CGO nanoparticles were precipitated instantly, and the stream was then cooled and the pressure reduced to ambient by passing the products through a back pressure regulator. The particles were then separated by centrifuging the initial solids and cleaning the concentrated sludge by placing it in a dialysis bag in a large plastic vessel and replacing with clean water several times in the vessel. Once cleaned, the wet sludge was freeze dried overnight.

The dried particles were then silver coated using Tollens' reagent (Ruiz-Trejo et al., 2014; Tollens, 1882). In a typical experiment concentrated  $\text{NH}_4\text{OH}$  was gradually added to a solution of  $\text{AgNO}_3$  (0.1 M), the addition was stopped when the black precipitate formed initially disappeared. The solution was then basified with KOH (0.8 M). The nanoparticles were suspended in this solution with the aid of an ultrasonic bath for 20 min. The initial ratio was 10 w% Ag and 90 w% CGO as this guarantees percolation in the final sintered sample. Finally, to initiate the reaction of reduction, 3 mL of dextrose solution (0.25 M) were added drop-wise to the mixture and left under stirring at room temperature for five minutes. The suspension was centrifuged and rinsed at least five times to eliminate all remaining reagents. The dry, clean, coated powders were pelletized (2.5 cm diameter) uni-axially and then cold-isostatically pressed (250 MPa) before being sintered at  $1100^\circ\text{C}$  for 4 h. The pellets were polished at both surfaces with metallographic paper down to the final 1 mm thickness. The density and open porosity was measured with Archimedes' method using deionised water as the immersion fluid. The samples were boiled for 1 h to ensure all open porosity was filled with water.

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