9th International Conference on Applied Energy, ICAE2017, 21-24 August 2017, Cardiff, UK

Simulation of Oxygen Transport Membranes for CPO Reactors in Small-scale Hydrogen or Syngas Production Applications

Luca Mastropasqua*, Gioele Di Marcoberardino, Paolo Chiesa, Stefano Campanari

Department of Energy, Politecnico di Milano, Via Lambruschini 4, 20156, Milan - Italy

Abstract

The proposed work aims at presenting a 1D finite volume steady state simulation model of an Oxygen Transport Membrane for Catalytic Partial Oxidation (OTM-CPO) reactor developed at the Group of Energy COnversion Systems (GECOS) at Politecnico di Milano. The model is able to simulate supported and unsupported perovskite-based reactive membranes by means of a lumped mass and energy transport method; the active ceramic layer is modelled throughout a generalised O_2 permeation equation, which depends on the micro-structure characteristics and mixed-ion conduction properties of the material. The supporting porous structure is represented by a mass diffusion model dominated by gas-gas, porous and surface exchange transport processes. The model also includes a global chemical reaction kinetic mechanism of CPO on Rh-based catalysts. The model is applied to simulate the behaviour of a membrane reactor operated upstream the Hydrogen Transport Membrane for Methane Steam Reforming (HTM-MSR) installed at the Laboratory of Micro-Cogeneration (LMC) at Politecnico di Milano. The test bench is focused on testing fuel pre-processing systems for low temperature fuel cells (PEM) applications. The simulation object of this work would allow obtaining a feasibility assessment of the system and a preliminary design of the OTM-CPO reactor.

Keywords: Oxygen Transport Membrane; Catalytic Partial Oxidation; H_2 production; PEM; fuel cell

1   Introduction

The production of pure H_2 and H_2-rich syngas is nowadays becoming always more important for small scale power generation applications, such as in fuel cell-based µ-CHP systems or in micro-grid-powered communities. In order to foster the downsizing of H_2-rich syngas fuels production systems, Catalytic Partial Oxidation (CPO) reactors are usually considered a valuable alternative to the more conventional Steam Reforming (SR) of hydrocarbons. In

* Corresponding author. Tel.: +39 022399 3842.
  E-mail address: luca.mastropasqua@polimi.it

particular, catalytic membranes (both Hydrogen and Oxygen Transport Membrane – HTM and OTM) are currently being studied for this application thanks to the potentialities of process layout simplification compared to conventional solutions and improved scalability of the components due to their modularity. For instance, *Ji et al. 2004* [1] have reported a comparative thermodynamic analysis of three H_2/syngas production systems for fuel cells applications: i) a conventional MSR+WGS process; ii) an OTM reactor + WGS; iii) an HTM reactor. They concluded that both membrane-based systems could achieve a second law efficiency higher by 3-5% than the conventional process.

This study will focus only on OTMs reactors for syngas production. Their technology level is mostly still glued at the lab scale and their development is hindered mainly by the long-term thermo-mechanical phase stability of the ceramic and sealant material [2], the possibility of decomposition in reducing gas environments [3] and the research on new more performing materials for low temperature operation [4,5]. However, many are the recent experimental [6,7] or modelling [8–10] analyses for both reactive and non-reactive membranes in which new materials or process integration configurations are explored and the applications range suggest a promising development. Moreover, especially the USA R&D activities are actively supporting the commercialisation of OTMs for fuel conversion and air separation processes for CCS systems throughout important industrial alliances [11–13].

The main goal of a CPO-OTM reactor is to perform a fuel conversion by means of a catalytic process in which one of the reactants (O_2) is supplied throughout a non-galvanic electrochemical mechanism occurring within the O_2-ion transport membrane. In fact, the driving force of the process is solely dependent on the difference of chemical potential of O_2 between the two sides of the membrane.

Nomenclature

OTM	Oxygen Transport Membrane
HTM	Hydrogen Transport Membrane
CPO	Catalytic Partial Oxidation
MSR	Methane Steam Reforming
WGS	Water Gas Shift
ATR	Auto-Thermal Reforming
FBMR	Fluidised Bed Membrane Reactor
CHP	Combined Heat and Power
CCS	Carbon Capture and Storage

The objectives of this study can be summarised as follows:
- Development of a 1D finite volume model of a co-flow planar reactive OTM
- Calibration of the model for intermediate and low temperature operation
- Design and simulation of an OTM reactor for laboratory-scale H_2 and syngas production

2   OTM-CPO Reactor Modelling

The model proposed in this work is developed in Fortran 90 programming language using the Visual Studio 2012 graphic interface. The model performs a one-dimensional axial discretisation of a co-flow planar reactive OTM into control volumes. Each volume resolves the mass and energy transport in the bulk phase and the mass transport mechanism in the ceramic membrane and porous support (when present). A schematic representation of the simulated reactor is depicted in Figure 1, which highlights the main seven steps of the permeation process.
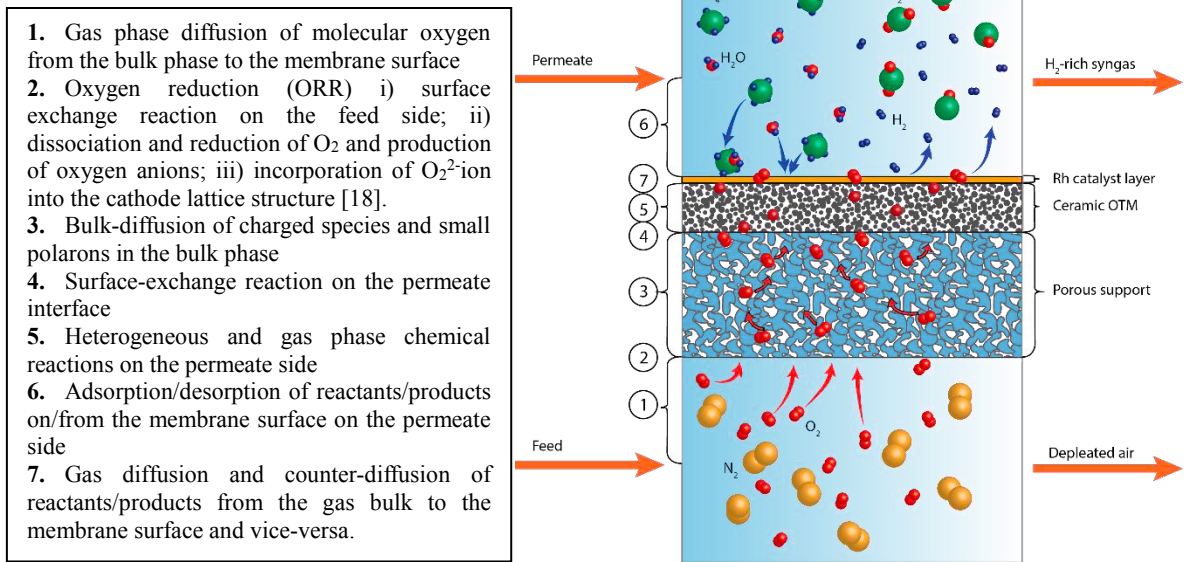
1. Gas phase diffusion of molecular oxygen from the bulk phase to the membrane surface
2. Oxygen reduction (ORR) i) surface exchange reaction on the feed side; ii) dissociation and reduction of O_2 and production of oxygen anions; iii) incorporation of O_2^{2-}ion into the cathode lattice structure [18].
3. Bulk-diffusion of charged species and small polarons in the bulk phase
4. Surface-exchange reaction on the permeate interface
5. Heterogeneous and gas phase chemical reactions on the permeate side
6. Adsorption/desorption of reactants/products on/from the membrane surface on the permeate side
7. Gas diffusion and counter-diffusion of reactants/products from the gas bulk to the membrane surface and vice-versa.

Figure 1 – Simplified representation of main physical and chemical phenomena involved in a non-galvanic O_2 membrane

3   Discussion

The reference membranes considered herein are those developed during the FP7 European funded DEMOYS project [7,14] in which Politecnico di Milano and GECOS participated. The membranes are characterised by a 30 µm $La_{0.6}Sr_{0.4}Co_{0.2}FeO_{3-\delta}$ (LSCF) as the active layer which included a 15 µm porous catalytic layer of BSCF+5%wt. Pd., supported on a metallic porous support of a NiCoCrAlY alloy.

The calibration of the model is performed minimising the square of the differences between the experimental and calculated O_2 flux between 650°C and 1000°C. This procedure gives the permeation parameters reported in Table 1, according to the O_2 transport equation reported. The metallic support is characterised by the following structural properties: porosity = 35%, pore diameter = 28 µm, support thickness = 2 mm, density = 4.3 g/cm³, thermal conductivity = 4.3 W m⁻¹K⁻¹. The value of tortuosity of the porous material is calibrated upon the permeability performances provided by the manufacturer and results in a tortuosity factor of 0.08. The calibrated O_2 flux is reported in Figure 2 in comparison with the experimental data.
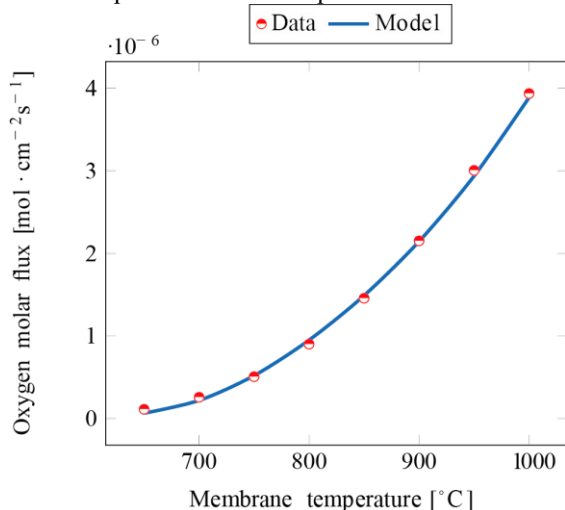
$$min \sum_{i=1}^{8} \left(j_{O_{2_i}}^{data} - j_{O_{2_i}}^{model} \right)^2 = 1.44$$

Figure 2 – Result of the calibration methodology

Table 1 – Calibration parameters for the membrane bulk diffusion and superficial reactions model

$$j_{O_2} = \frac{D_{V_O^{\bullet\bullet}} k_r (p_{O_2}'^{0.5} - p_{O_2}''^{0.5})}{2L k_f (p_{O_2}' p_{O_2}'')^{0.5} + D_{V_O^{\bullet\bullet}} (p_{O_2}'^{0.5} + p_{O_2}''^{0.5})}$$

Parameter	Units	Value
$D_{V_O^{\bullet\bullet}}^0$	cm²/s	1.47E-02
k_f	cm/atm$^{0.5}$s	7.92E-05
k_r	mol/cm²s	2.89E-03
E_{act}^D	J/mol	211.59
E_{act}^f	J/mol	51.09
E_{act}^r	J/mol	69.83

4   Hydrogen Production – Case Study

The preliminary design of a laboratory scale hydrogen production test stand for fuel cell applications is presented herein. Currently the LMC is equipped with a test stand based on a tubular three-end hydrogen membrane which can either operate as a pure H_2 separator or as a membrane WGS reactor [15]. The separated H_2 can be stored or supplied to a low temperature fuel cell (i.e., PEM). Figure 3 represents the current test stand simplified layout.
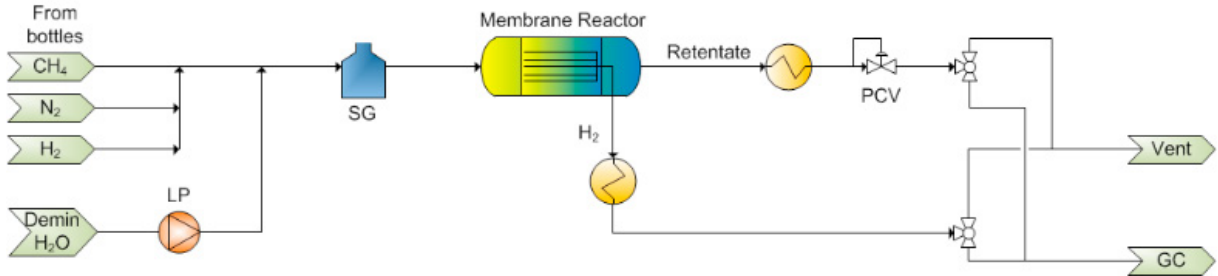

Figure 3 – Simplified layout of the current test bench for H_2 production at the Laboratory of Micro-Cogeneration

The active membrane is supported on a ceramic layer and the active material is made up of Pd, which guarantees high H_2 selectivity. The membrane operates between 350°C and 700°C at a maximum pressure of 11 bar. The system is isothermal and maintained at the operating temperature by means of an electric furnace.

The separation efficiency of these systems is usually hindered by the limited methane conversion which is obtainable from the MSR and WGS reactions; therefore, in order to compensate for this limitation, the system is pressurised to increase the H_2 partial pressure on the retentate side and thus the required H_2 flux through the membrane. It is proposed here to include an OTM-CPO reactor upstream the HTM with the purpose to increase the H_2 recovery with respect to a system which performs the entire reaction process in the HTM. The new configuration is represented in Figure 4. The concept of a series of OTM and HTM reactors has already been proposed in the DEMOYS project, for CCS purposes, since the retentate composition, subsequently to an appropriate water separation process, is typically rich in CO_2. In this application, the layout is proposed and designed for a micro-scale application.
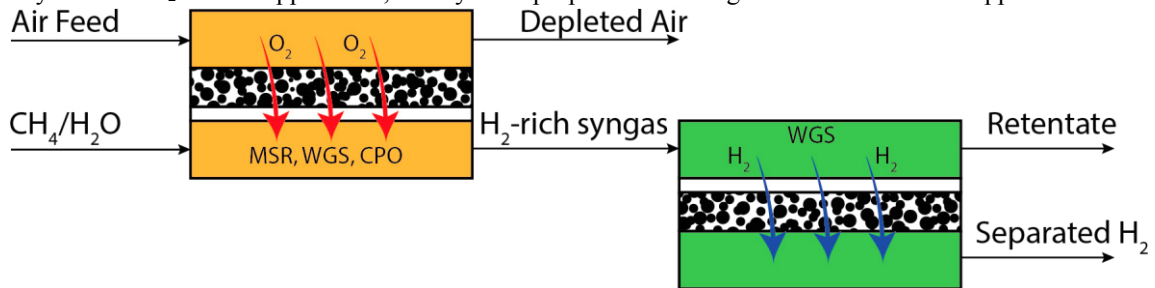

Figure 4 – New proposed configuration comprising an OTM-CPO reactor (yellow) upstream a H_2-selective membrane (green)

In the new proposed configuration reported in Figure 4 the output of the OTM reactor is directly fed into an HTM-based component, following the required heat recovery sections. The HTM shall either be characterised by a catalytic activity towards WGS and MSR reactions or simply operate as a pure permeator. These two scenarios are assessed employing a mono-dimensional Fluidised Bed Membrane Reactor (FBMR) two-phase model present in *Deshmuckh et al., 2005* [16] and the results of the integrated OTM-HTM system are compared with a more conventional membrane-based Auto-thermal Reforming (ATR) reactor for H_2 production, as reported in Table 2.

Table 2 – H2 production performance parameters, compared between a H_2-membrane ATR reactor and an OTM-HTM system

	Units	ATR-HTM	OTM-HTM	
			H_2 permeator	Reactive HTM
H_2 production	Nl/min	4.52	9.93	9.98
CH_4 conversion	[%]	80.51	93.20	79.56
H_2/CO	-	4.23	0.550	2.63
HRF	[%]	49.85	63.80	64.17
H_2 Separation factor	[%]	-	86.93	87.43

The three layouts are compared at constant inlet conditions, with the exception of the ATR reactor whose inlet composition is diluted with a stream of air in order to impose an oxygen-to-carbon ratio at the feed inlet of 0.25, as suggested in *Fernandez et al., 2015* [15]. Moreover, the HTM reactor operates in all cases at an inlet temperature of 600°C and at a pressure of 6 bar and 1 bar, respectively on the feed and permeate side. The H_2-selective membrane surface area is also kept constant, assuming the installation of 6 tubular components of 173 mm length and 10.5 mm diameter. Notice that in all three cases considered the H_2 production is in line with the test stand requirements and would be adequate to partially feed a small PEM fuel cell system [17] and a H_2 storage for future uses.

Table 2 also reports the most important dimensionless performance parameters for H_2 production of the combined OTM-HTM system, namely methane conversion, H_2/CO outlet ratio, H_2-selective membrane Separation Factor (SF) and overall Hydrogen Recovery Factor (HRF), namely:

HTM separation factor:
$$SF_{HTM} = \frac{\dot{n}_{H_2}^{out}}{\dot{n}_{H_2}^{in}}$$

Hydrogen Recovery Factor (HRF):
$$HRF = \frac{\dot{n}_{H_2}^{out}}{n_{CH_4}^{in} \times 4 - \frac{1}{2}\dot{n}_{O_2}^{in}}$$

It is noticeable how the overall H_2 production (i.e., the system HRF) is higher in the OTM-HTM cases with respect to the ATR one; moreover, the non-reactive HTM scenario allows for a higher methane conversion compared to the reactive one since, when MSR reactions is activated, kinetics favours the reverse process (i.e., methanation), hence entailing a higher CH_4 fraction in the retentate stream.

A drawback of the non-reactive solution is the missed conversion of an important fraction of CO, present at the OTM outlet; in fact, the H_2/CO ratio in the retentate outlet stream is the lowest among the considered cases. This aspect could be addressed in a more thorough design of the OTM reactor.

5   Conclusions

This study aims at presenting the application of a new dimensional model for the design and simulation of reactive O_2 transport membranes. The model takes into account the fundamental physical and chemical phenomena involved in OTM reactors: gas bulk diffusion, charged particle transport and chemical reaction equilibrium and kinetics.
The model is then applied to design an OTM reactor and to assess the feasibility of its installation upstream of an H_2-selective membrane currently installed at the Laboratory of Micro-Cogeneration at Politecnico di Milano for micro-scale H_2 production in fuel cell applications. The main conclusions shall be summarised as:

- The model is calibrated against experimental data available from the DEMOYS FP7 project, focusing mainly on the permeation and structural parameters of the metallic support and the membrane
- The newly proposed system for H_2 production allows achieving higher HRF and CH_4 conversion factors compared to a more conventional ATR system, due to the higher H_2 concentration which the HTM operates at.
- The main drawbacks of the system concern the high operating temperature and the general more complex layout compared to a single component configuration, such as a reactive HTM

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