Computational analysis of an O2-separating membrane for a CO2-emission-free power process

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ABSTRACT

The increased demand for clean power in recent years has led to the development of various processes that include different types of CO₂ capture. Several options are possible: pre-combustion concepts (fuel de-carbonization and subsequent combustion of H₂), post-combustion concepts (tail-end CO₂ capture solutions, such as amine scrubbing), and integrated concepts in which combustion is carried out in pure O₂ or oxygen-enriched environment instead of air. The integrated concepts involve the use of oxygen-, hydrogen-, or CO₂-separating membranes resulting in exhaust gas containing CO₂ and water, from which CO₂ can easily be separated. In contrast to traditional oxygen pumps, where a solid oxide electrolyte is sandwiched between two gas-permeable electrodes, a dense, mixed ionic-electronic conducting membrane (MIECM) shows high potential for oxygen separation without external electrodes attached to the oxide surface. Models for oxygen transport through dense membranes have been reported in numerous recent studies. In this study, an equation for oxygen separation has been integrated into a steady-state heat and mass transfer membrane model. Oxygen transfer through a porous supporting layer of membrane is also taken into account. The developed FORTRAN code has been used for numerical investigation and performance analysis of the MIECM and the oxygen transport potential over a range of operating conditions. Preliminary results indicate that a non-uniform temperature distribution, for a given set of oxygen inlet boundary conditions has considerable impact on the oxygen flux and membrane efficiency. Since the implementation of detailed membrane models in heat and mass balance calculations for system studies would result in excessive calculation time, results from this study will be utilized for the generation of correlations describing the oxygen transfer as a function of operating parameters such as temperature and partial pressure. This modeling approach is expected to improve the accuracy of system studies.

INTRODUCTION

Integration of MIECMs into power processes is a fairly new concept. In contrast to high-temperature catalytic processes, such as deep and partial oxidation of methane, fuel combustion, etc., which are now the most rapidly developing fields in heterogeneous industrial catalysis, the use of MIECM in power processes has not been mentioned in the literature to any great extent. The development of MIECMs has been driven primarily by the desire for energy-efficient and environmentally benign power generation technologies. Several research groups have reported on the use of MIECMs for various applications, including CO₂ separation, hydrogen production, and fuel cell applications. The aim of this study is to develop a comprehensive model for the performance analysis of MIECMs in power processes. The model will be used to investigate the effects of various operating parameters on the membrane efficiency and oxygen transport potential. The preliminary results indicate that the non-uniform temperature distribution has a significant impact on the oxygen flux and membrane efficiency. Future work will focus on the development of detailed membrane models and the generation of correlations describing the oxygen transfer as a function of operating parameters.
extent. Their use in power processes, where O\textsubscript{2} is separated from air permits combustion in a nitrogen free environment, while at the same time facilitating CO\textsubscript{2} removal as the exhaust gas contains only CO\textsubscript{2} and water. Such concepts can be found in an oxy fuel processes such as the Advanced Zero-Emission Power Plant (AZEP) [1, 13, 14] and other similar processes [12, 17]. The AZEP concept is illustrated in Figure 1. The combustor in an ordinary gas turbine is replaced by a membrane reactor which contains MIECM. The membrane reactor must to have high oxygen permselectivity, which is achieved in dense (nonporous) membranes at elevated temperatures.

These membranes have attracted much interest in recent years as a clean and efficient means of producing oxygen by separation from air or from other oxygen-containing gas mixtures. The separation of oxygen is enabled by the driving force, which is the differential oxygen partial pressure applied across the membrane. Since MIECMs are made of a dense material, there is no direct passage of the oxygen molecules, instead oxygen ions migrate selectively through the membrane. Dissociation and ionization of oxygen occur at the surface on the feed side, where electrons are picked up from near-surface electronic states. The flux of oxygen ions is charge compensated by a flux of electronic charge carriers in order to sustain charge neutrality. On the permeate side, oxygen ions implies again with electrons to form oxygen molecules which are released into the permeate stream. [2]

The major resistance to this complex oxygen transport depends on the bulk conduction properties of the membrane material and the rate of oxygen reduction at the surface of the membrane. Several researchers have attempted to determine the influence of these two kinds of resistance for a number of various promising membrane materials. The membrane materials studied most extensively are the oxygen-ionic-conducting perovskite-structured lanthanum cobaltite (LaCoO\textsubscript{3}), titanium-doped YSZ and SrFeO\textsubscript{3-δ} [5-7, 18]. These studies showed that even if there is no surface oxidative reaction, oxygen-ion surface-exchange kinetics may exert partial or dominant control over oxygen permeation [16].

In a membrane reactor for an integrated power process (AZEP, [1]) one side of the ionic or mixed-conducting ceramic membrane is exposed to air and the other side to a mixture of carbon dioxide and water vapor (sweep), i.e., the gas turbine effluent in Figure 1. Oxygen from the air permeates through the membrane and is released into the bulk stream on the permeate side. Although it is generally agreed that the driving force for oxygen permeation is the oxygen potential gradient across the membrane, it is important to investigate how the temperature gradient along the length of the membrane reactor affects the oxygen permeation rate.

The objective of this paper is to present a simple mathematical model for an oxygen-separating MIECM and to investigate the effects of a non-uniform temperature distribution on the oxygen permeation rate. Further more, the impact of permeation resistance on membrane performance has been analyzed. The reactor chosen for the investigation of heat and mass transfer contains extruded monolithic elements. Such monolithic elements offer the advantages of having thinner walls, high geometric surface area, low pressure drop, and good mass transfer [3].

**THE MATHEMATICAL MODEL**

A multichannel, monolithic, “honeycomb” element with multiple passageways extending from one end (1) to the other (2) is considered, [see Figure 2].

The channels are chosen to be square where the length of the channel is much greater than its width. The membrane is composed of a thin active layer for separation and a mechanical
supporting layer to prevent mechanical failure of the active layer when applying a pressure difference. To minimize the mechanical load, the process operating conditions were assumed to be a medium-pressure air feed stream, typically 7-20 bar, and low-pressure permeate stream, typically at a fraction of an atmosphere [17].

The temperature of the gases passing through the channels and their mass fractions vary significantly from inlet to outlet. However, in this model we assume that these variations are negligible in the x- and y-directions (see Figure 3). It is then possible to investigate the behavior of the reactor using a two-dimensional (x-z) cross section. Figure 4 shows the calculation domain for steady-state heat and oxygen transfer with laminar, fully developed gas flows through the reactor. The total pressure drop in the gas flows has not been included in this model and will be a task for future studies.

**Governing equations**

The following transport phenomena are considered:
- Oxygen diffusion through the membrane and oxygen surface exchange,
- Heat transfer by diffusion in the membrane and support,
- Heat transfer in gas flows,
- Material balance for oxygen.

**Oxygen diffusion through the membrane and oxygen surface exchange**

The oxygen permeation rate across the perovskite membrane is governed by the flux of oxygen vacancies, and was described by Kofstad in 1972 [4-7]:

$$j_v = -\frac{\sigma_v}{4F^2}\left(V\mu_v + 2F\nabla \varphi\right)$$

(1)

where $\sigma_v$ is the oxygen vacancy conductivity, and $V\mu_v$ and $\nabla \varphi$ are the gradients of the chemical potential and the electric field, respectively. If we assume that a steady-state electric potential gradient has not been established because of the fast movement of electron holes inside the membrane, and that the concentration of oxygen vacancies at both surfaces of the membrane is also governed by surface exchange kinetics, then equation (1) can be expressed assuming ohmic behavior with an extra term ($d/D_{eff}$) added to total permeation resistance which represents resistance in support material [5]:

$$J_{O_2} = \frac{k_f}{k_f}\left(p_{O_2}^{0.5} - p_{O_2}^{0.5}\right)$$

(2)

Here, $t$ is the membrane thickness (between 0 and 1 in Figure 4) and $d$ is the thickness of the supporting material (between 1 and 2 in Figure 4), $k'$ and $k''$ are the surface exchange coefficients on the high and low oxygen pressure side of the membrane and are introduced in equilibrium conditions as [5]:

$$k' = k_f p_{O_2}^{0.5}$$

(3)

$$k'' = k_f p_{O_2}^{0.5}$$

(4)
where \( k_f \) and \( k_r \) are forward and reverse reaction rate constants and \( D_V \) the diffusion coefficient of oxygen vacancies. These are defined as [5]:

\[
k_f = k_{f,0} \exp\left(-\frac{E_f}{RT}\right) \tag{5}
\]

\[
k_r = k_{r,0} \exp\left(-\frac{E_r}{RT}\right) \tag{6}
\]

\[
D_V = D_{V,0} \exp\left(-\frac{E_D}{RT}\right) \tag{7}
\]

where the pre-exponential factors \( k_{f,0}, k_{r,0} \) and \( D_{V,0} \), and the activation energies \( E_f, E_r \) and \( E_D \) can be experimentally estimated. The membrane and porous support are made of the similar material as similar thermal and chemical behavior is desirable [9]. This involves the use of a support material with very small pores so that the governing mechanism for oxygen diffusion in the bulk support material can be approximated to Knudsen diffusion. Two-dimensional, steady-state diffusion in the support bulk material is defined as:

\[
\frac{\partial}{\partial x}\left(D_{\text{eff}} \frac{\partial C_{O_2}}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_{\text{eff}} \frac{\partial C_{O_2}}{\partial z}\right) = 0 \tag{8}
\]

where \( D_{\text{eff}} \) is the effective diffusion coefficient and \( C_{O_2} \) is concentration of oxygen in the support material. The effective diffusion coefficient is defined as [8]:

\[
D_{\text{eff}} = \frac{2}{3} \varepsilon \tau \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{9}
\]

where \( \varepsilon \) is the porosity or volume void fraction, \( \tau \) is the tortuosity factor, and \( r_e \) is the effective pore radius. Figure 5 shows the profile of the oxygen partial pressure assumed in the model.

**Heat transfer by diffusion in membrane and support**

Two-dimensional steady state heat diffusion is defined by:

\[
\frac{\partial}{\partial x}\left(k_{\text{eff}} \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_{\text{eff}} \frac{\partial T}{\partial y}\right) = 0 \tag{10}
\]

where \( k_{\text{eff}} \) is the effective thermal conductivity of the material. An additional equation for wall heat flux \( (q_w) \) is defined as:

\[
q_w = h_{\text{c}} (T_\infty - T_w) = -k_e \frac{\partial T}{\partial x} \tag{11}
\]

where \( h_{\text{c}} \) is the channel-membrane heat transfer coefficient, \( T_\infty \) represents the mean temperature of the main flow, and \( T_w \) is the wall temperature.

**Fig.5. Oxygen partial pressure profile across the membrane and support.**

**Heat transfer in gas flows**

The following energy balance is applied to the gas flows (air and sweep):

\[
d\dot{Q} = m c_p dT \tag{12}
\]

where \( m \) and \( c_p \) are the mass flow rate and constant-pressure specific heat, respectively, for the gases.

**Material balance for oxygen**

Simple molar balance is used to calculate the \( O_2 \) fluxes in gases:

For the \( O_2 \)- rich side:

\[
F'_{O_2,\text{out}} = F_{O_2,\text{in}} - J_{O_2} A \tag{13}
\]

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For the O₂-lean side:
\[ F_{\text{O}_2, \text{out}} = F_{\text{O}_2, \text{in}} + J_{\text{O}_2, \text{A}} \] (14)

**Boundary conditions**

The mathematical formulation is completed by specifying four conditions at each of the boundaries of the calculation domain. Figure 6 shows the sign convention and co-ordinate system for heat and molar fluxes.

**Heat transfer boundary conditions**

Both the upper and lower boundaries are insulated \((q=0)\). At the left and right boundaries (Figure 6.), heat is transferred from hot gases by convection, Eq. (11) Equation (11) applied to the left and right boundaries is given below:

\[ h_c(T_x - T_w)_{\text{feed}} = -k_c \frac{\partial T}{\partial x} \]  \(h_c(T_x - T_w)_{\text{permeate}} = \)  \(h_c(T_x - T_w)_{\text{permeate}} \) (15)

\[ -k_c \frac{\partial T}{\partial x} = h_c(T_x - T_w)_{\text{permeate}} \] (16)

Estimation of the convective heat transfer coefficients is usually based on a constant value of the Nusselt number, assuming established laminar flow in the channels. The heat transfer coefficient can then be calculated from the following expression for the average Nusselt number:

\[ \overline{N_u} = \frac{h_s D_h}{k_{\text{gas}}} = \frac{q_w D_h}{k_{\text{gas}}(T_x - T_w)} \] (17)

where \(k_{\text{gas}}\) is the thermal conductivity of the gases.

To obtain an approximate value of the Nusselt number for fully developed flow at a specified axial wall heat flux, standard correlation has been used for a duct with constant axial wall heat flux with uniform peripheral wall heat flux, Eq. (18). This gives \(N_u=3.091\) for a quadratic duct [10].

**Oxygen transfer boundary conditions**

Both top and bottom boundaries are non-permeable \((j=0)\). The oxygen flux through the MIECM is calculated (Eq.2.) and used as the boundary condition for the adjacent supporting material (see Figure 6). This is given as:

\[ J_{\text{O}_2} = -D_{\text{eff}} \frac{dC_{\text{O}_2}}{dx} \] (18)

---

**Fig.6.** Co-ordinate system and sign convention for the heat and mass flux boundary conditions.

**Numerical technique**

An approximate solution of Eqs. (8) and (10) subject to the boundary conditions (15-16) and (18) is obtained numerically using a finite volume method. The solution domain is rectangular and is discretized using a rectangular grid with different sizes in the x and z directions. The partial derivatives in the governing equations are approximated using central differences; see Versteeg & Malalasekera [11].

General form of the steady state two-dimensional diffusion equation of the property \(\phi\) is given below:

\[ \frac{\partial}{\partial x} \left( \Gamma \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial z} \left( \Gamma \frac{\partial \phi}{\partial z} \right) + S = 0 \] (19)

When Eq. (19) is integrated over the control volume, each of the governing equations is then written in the general form and applied at each node:

\[ a_p \phi_p = a_p \phi_{WP} + a_E \phi_E + a_N \phi_N + a_S \phi_S + S_{up} \] (20)
Figure 7 shows the iteration algorithm used for calculation of the solid temperature and oxygen concentration in support material. The coefficients in Eq. (20) are functions of the variable $\phi$. The coupling between the diffusion through the MIECM and convective transport in the channels has been taken into account.

RESULTS AND DISCUSSION

The numerical simulations presented in this paper deal mainly with the effects of the temperature and oxygen permeation resistance coefficient on the oxygen permeation flux through the MIECM and the impact of inlet gas temperature on the efficiency performance of the membrane. The perovskite material, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, which has been used in experimental studies on oxygen permeation performed by Xu and Thomson [5], was chosen as the membrane material. The physical properties of the perovskite membrane were varied with the purpose of illustrating their impact on the membrane performance. The values of the operating parameters are given in Table 1.

In order to validate the oxygen permeation model the experimental data of Xu and Thomson [5] were used. Since the model developed in this paper differs somewhat from the experimental case some modifications have been made. The experiment was conducted with a circular membrane 1.7 cm in diameter and 1.68 mm thick, and uniform membrane temperature of 850°C was assumed. To simulate this uniform temperature isothermal channels were assumed. The resistance to the total permeation flux due to the porous support was also neglected. As shown in Figure 8, the model fits the experimental data well over a range of $P''O_2$ values. The model for oxygen permeation flux is itself a generic model for all ionic-conducting membranes. Different membrane materials will have different magnitudes of the oxygen permeation flux as different diffusion and surface coefficients would be used in Eq. 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_e$, Thermal conductivity</td>
<td>1.5 W/mK</td>
</tr>
<tr>
<td>$F_{O_2, air}$, Oxygen flow rate</td>
<td>4.76E-2 ml/min</td>
</tr>
<tr>
<td>$F_{O_2, sweep}$, Sweep flow rate</td>
<td>3.59E-2 ml/min</td>
</tr>
<tr>
<td>$\varepsilon$, Porosity (support)</td>
<td>0.5</td>
</tr>
<tr>
<td>$r_p$, Size of pores (support)</td>
<td>1.0E-6 m</td>
</tr>
<tr>
<td>$P''O_2$, Oxygen partial pressure oxygen-rich side</td>
<td>1 atm</td>
</tr>
<tr>
<td>$P''O_2$, Oxygen partial pressure oxygen-lean side</td>
<td>0.001 atm</td>
</tr>
<tr>
<td>$t$, Membrane thickness</td>
<td>1.0E-6 m</td>
</tr>
<tr>
<td>$d$, Support thickness</td>
<td>1.0E-3 m</td>
</tr>
<tr>
<td>$D_v$, Oxygen vacancy bulk diffusion coefficient</td>
<td>1.58e-2 cm$^2$/s</td>
</tr>
<tr>
<td>$k_f$, Forward surface exchange rate constant</td>
<td>5.90e6 cm/atm$^{0.5}$/s</td>
</tr>
<tr>
<td>$k_r$, Reverse surface exchange rate constant</td>
<td>3.45e4 mol/cm$^2$/s</td>
</tr>
<tr>
<td>$E_d$, Activation energy for $D_v$</td>
<td>73.6 kJ/mol</td>
</tr>
<tr>
<td>$E_f$, Activation energy for $k_f$</td>
<td>226.9 kJ/mol</td>
</tr>
<tr>
<td>$E_r$, Activation energy for $k_r$</td>
<td>241.3 kJ/mol</td>
</tr>
</tbody>
</table>

The total feed channel flows are calculated assuming a Reynolds number of 100. The thermal conductivity of the dense membrane and porous support is assumed to be the same and is set to a constant value (see Table 1). The computed temperature distribution shown in Figure 9 clearly illustrates a non-uniform temperature field in the gas channels of the MIECM. These results indicate that at a distance of 0.6 m in the $z$-direction there is a small temperature difference (about 3°C) between the outlet fluids.
Figure 8 shows a comparison of oxygen flux measurements with the oxygen flux model. Experimental data taken from [5].

Figure 9 illustrates temperature profiles for air and sweep gases.

Figure 10 demonstrates the influence of reverse pre-exponential factor on the oxygen permeation flux.

Comparing these results to the case with an increased pre-exponential factor for the forward reaction, it can be concluded that the impact of the reverse pre-exponential factor is greater. This phenomenon has been explained previously [5, 16], as the resistance exerted by surface exchange on the oxygen-rich side being relatively small, so that for this operating temperature regime, the oxygen permeation is mainly controlled by bulk diffusion and surface exchange on the oxygen-lean side.

Oxygen permeation resistance in the membrane support has been calculated for all cases (see Table 2). The difference between the oxygen flux calculated for the membrane support does not significantly influence the oxygen permeation flux.

Figure 11 and 12 display the oxygen flux through MIECM at different inlet air and sweep temperatures. The membrane material chosen for this investigation is La0.6Sr0.4Co0.2Fe0.8O3-δ [5]. Two different cases have been analyzed. The first case considers the same reverse pre-exponential factor as used in experimental investigation by Xu and Thomson [5] (k_0 = 3.45e4 mol/cm²/s). The second case uses k_0 = 3.45e5 mol/cm²/s. Maximum oxygen flux is achieved in all cases at high oxygen concentration and high gas temperatures. In the second case, (Fig. 11 b. and 12.b) the maximum point of the permeation flux is moved away from the edge. Since the surface resistance for the permeation flux is higher for the membranes with lower reverse pre-exponential factor, more energy is needed in the process to achieve the desired oxygen flux magnitude. This occurs downstream in the reactor where heat is transferred from the sweep gas and the air temperature is raised to the needed level.
The efficiency of the membrane is defined by Eq. (21).

$$
\varepsilon_{O_2} = \frac{y_{O_2, \text{sweep, out}} - y_{O_2, \text{sweep, in}}}{y_{O_2, \text{air, in}} - y_{O_2, \text{sweep, in}}} \tag{21}
$$

As can be seen in Table 2, the highest efficiency is achieved at highest sweep and air temperature (1000°C, 850°C) used in calculations and is approximately 49%. Lowest air temperature used in calculations (700°C) gives membrane efficiency of 2%. Of course, due to an uncertainty for the material constants in this work, the reported numbers should be treated as preliminary.

**FINAL REMARKS AND CONCLUSIONS**

A modeling method for simulating oxygen permeation through a membrane with the capability to account for the non-uniform temperature distribution along the gas channels has been presented. The primary application of the model would be in the simulation of a monolithic membrane reactor for a CO₂-emission-free process, AZEP.

Table 2: Results for membrane efficiency with varying gas temperatures. (Inlet oxygen molar fractions in gases used for calculations were: $y_{O_2}^\prime=0.20$, $y_{O_2}^\prime\prime=0.16$, $k_0=4.7E6$ mol/cm²/s)

<table>
<thead>
<tr>
<th>$T_{\text{sweep}}$ (°C)</th>
<th>$T_{\text{air}}$ (°C)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>700</td>
<td>38</td>
</tr>
<tr>
<td>1000</td>
<td>750</td>
<td>44</td>
</tr>
<tr>
<td>1000</td>
<td>800</td>
<td>47</td>
</tr>
<tr>
<td>1000</td>
<td>850</td>
<td>49</td>
</tr>
<tr>
<td>750</td>
<td>700</td>
<td>2</td>
</tr>
<tr>
<td>800</td>
<td>700</td>
<td>4</td>
</tr>
<tr>
<td>900</td>
<td>700</td>
<td>16</td>
</tr>
</tbody>
</table>

Due to a lack of experimental data for the integrated membrane performance, a complete comparison to such data was not possible. Part of the model describing the oxygen permeation through the membrane was compared to experimental data found in the literature and showed good agreement. Qualitative verification of the integrated membrane model was carried out by varying different operational parameters and comparing the model results to results available in the literature.
The simulation results confirmed that the oxygen permeation flux for this type of membrane, with very thin membrane thickness, depends strongly on the pre-exponential factor for the reverse reaction constant compared to the forward reaction constant.

Applying this model to the membranes with different surface morphologies would be possible by adjusting the pre-exponential factor on the oxygen recombination rate constant $k_r$.

The influence of the membrane support on oxygen permeation was negligible, as long as the effective pore radius of the support was small ($\leq 1\, \mu m$). Furthermore, an optimal channel length was found (0.6 m) at which the minimum temperature difference between the gases was observed.

Integration of this model into simulation tools for the analysis of combined systems will be a task for future studies. The identification of the best membrane material, which has significant oxygen flux at elevated pressures, will be of the greatest importance. Future work will concentrate further on the sizing of the reactor (channel height, channel length, number of channels, and the shape of the channels etc.), in order to find the optimum reactor design with respect to the performance (e.g. heat transfer, oxygen separation) and space requirements of the application.

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