Mathematical Modeling and Optimization of Ion Transport Membranes for Oxygen Separation from Air

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Introduction and Background on Air Separation

- There is a growing demand for high purity oxygen (oxy-combustion) as a replacement for air in combustion and gasification processes
- Energy-related emission awareness has been growing recently as such emissions account for roughly 68% of greenhouse gas emissions
- In comparison to air-combustion, oxy-combustion processes have exhibited lower harmful CO_2 and NO_x emissions and higher overall combustion efficiency, due to reduced heat loss (as a result of lower mass flow rates) out of the stack
- The main air separation technologies used currently to produce high purity (>99%) oxygen are cryogenic air separation, pressure or vacuum swing adsorption (PSA or VSA, respectively), as well as, ion transport membrane (ITM) technologies
- In comparison to cryogenic air separation, ITM technologies exhibit lower electricity costs attributed to external electrical loadings to drive the separation process
- Approximately 1520 mol/s of oxygen is required for a 620 MWe IGCC power plant

Ion Transport Membrane Modeling and Optimization

- An Ion Transport Membrane (ITM) consists of a shell and tube setup where surface ion exchange reaction/permeation occur simultaneously

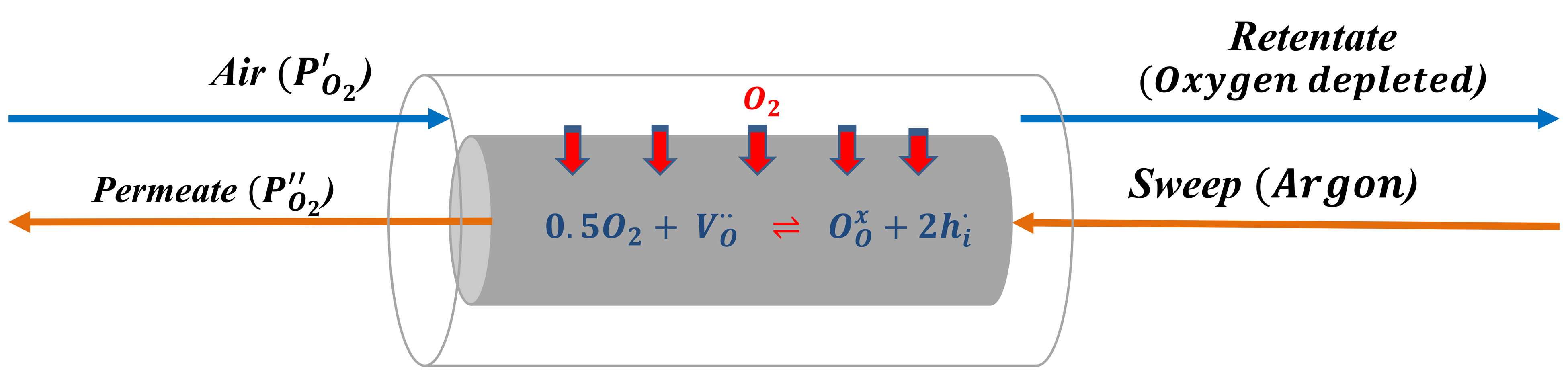

Figure 1: Ion Transport Membrane

- Oxygen permeation rate equation for perovskite ITM material $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\alpha}$ (LSCF)[1]

$$\frac{\partial N_{O_2}}{\partial l} = \frac{k_r\left[\left(p'_{O_2}\right)^{0.5} - \left(p''_{O_2}\right)^{0.5}\right]}{\frac{(p''_{O_2})^{0.5}}{2\pi R_O} + \frac{k_f \ln\left(\frac{R_O}{R_i}\right)(p'_{O_2})^{0.5}(p''_{O_2})^{0.5}}{\pi D_V} + \frac{(p'_{O_2})^{0.5}}{2\pi R_{in}}}$$

- The governing equations for the countercurrent operation of the ITM model are as follows[1]
- Shell side for oxygen

$$\frac{\partial (p'_{O_2})}{\partial l} = -m\frac{RT}{\dot{V}_s}\frac{\partial N_{O_2}}{\partial l}$$

- Tube side for oxygen

$$\frac{\partial (p''_{O_2})}{\partial l} = -m\frac{RT}{\dot{V}_t}\frac{\partial N_{O_2}}{\partial l}$$

p'_{O_2} = Oxygen partial pressure in shell side (Pa)
p''_{O_2} = Oxygen partial pressure in tube side (Pa)
P_t = Pressure in tube (Pa)
$\dot{V}_t$ = Volumetric flow rate of tube side gas stream (m^3/s)
$\dot{V}_s$ = Volumetric flow rate of shell side gas stream (m^3/s)

- Objective function:

$$\boldsymbol{\varphi} = \min_x \{\boldsymbol{cost_m} + \boldsymbol{cost_{Air}} + \boldsymbol{cost_{Ar}} + \boldsymbol{utility_{FH}} - \boldsymbol{credit_{O_2}}\}$$

$$cost_m = 2\pi \times R_O^2 \times L \times \$_m$$
$$cost_{Ar} = N_{Ar} \times \$_{Ar} \times Op$$
$$cost_{Air} = N_{Air} \times \$_{Air} \times Op$$
$$credit_{O_2} = N_{O_2} \times \$_{O_2} \times Op$$
$$cost_{FH} = N_{NG} \times LHV_{NG} \times \$_{NG} \times Op = Q_{FH}$$

- Decision variables

$$\boldsymbol{x} = \left[\boldsymbol{T_2}, \frac{\boldsymbol{N_{Air}}}{\boldsymbol{N_{Ar}}}, \boldsymbol{P_{shell}}, \boldsymbol{P_{tube}}, \boldsymbol{L_{membrane}}\right]'$$

- Constrained nonlinear multivariable optimization method: **Sequential Quadratic Programming**
- Function utilized for optimization in MATLAB: **FMINCON**

Table 1: Values for cost parameters objective function[2]

$\$_{Ar}$ (\$/kmol)	8.92
$\$_{Air}$ (\$/kmol)	0.11
$\$_{O_2}$ (\$/kmol)	960
$\$_{NG}$ (\$/GJ)	3.95
$\$_m$ (\$/m^2)	100
Op (hours)	7880

*Based on LHV of natural gas of 0.7935 GJ/mol ** Price at pressure of 3.3 barg[2]

Optimization Results

Table 2: Based case versus optimized case parameters

Parameter	Base Case	Optimized Case
Feed Ratio (Air / Sweep)	0.75	0.90
Inlet Temperature (K)	1150	1185
Inlet Shell Side Pressure (Pa)	2.026×10^5	2.535×10^5
Inlet Tube Side Pressure (Pa)	1.013×10^5	1.022×10^5
Membrane Length (m)	15.5	0.75
$\boldsymbol{\varphi}$	70.268	6.174

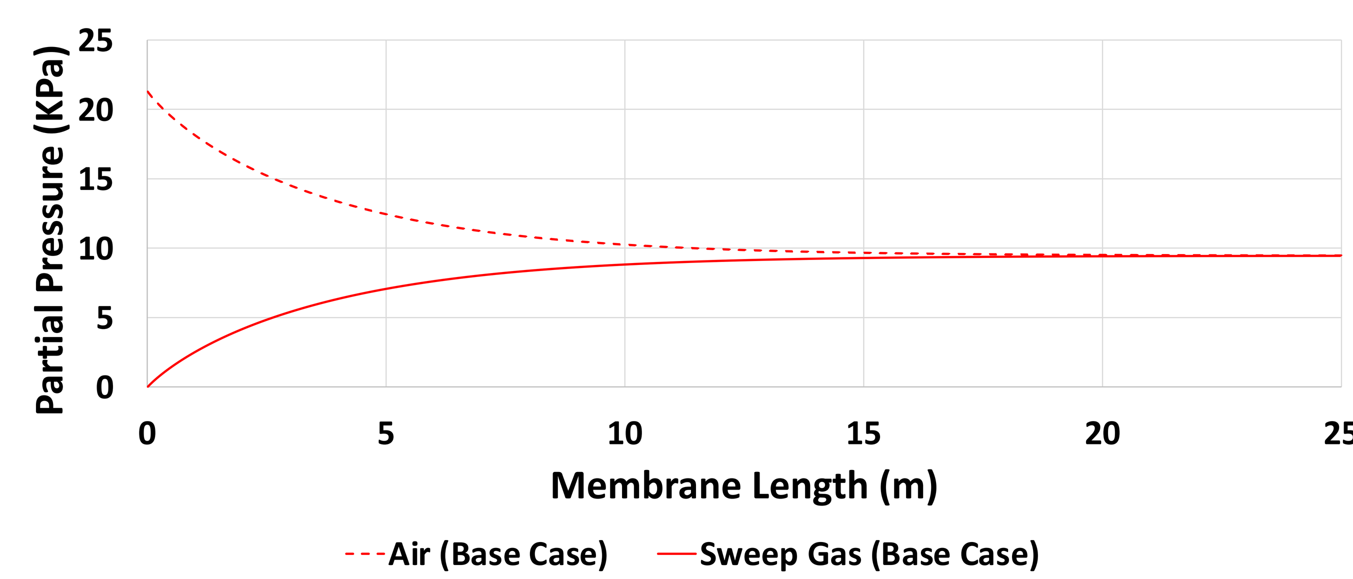

Figure 2: Base Case Oxygen partial pressure profile in air and sweep gas

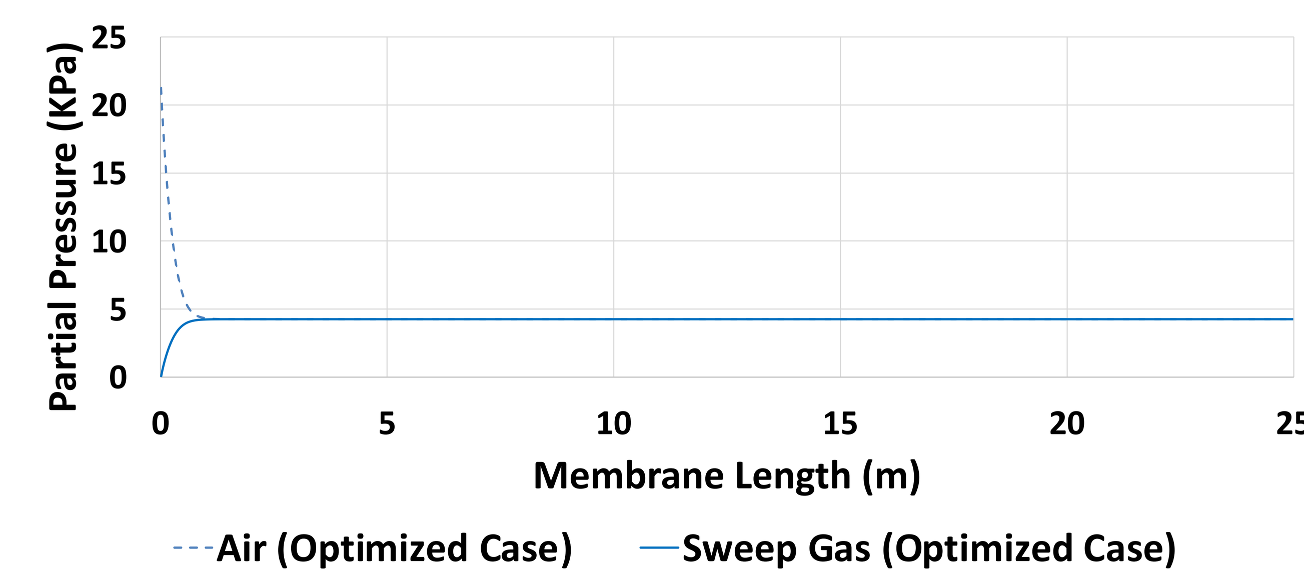

Figure 3: Optimized Case Oxygen partial pressure profile in air and sweep gas

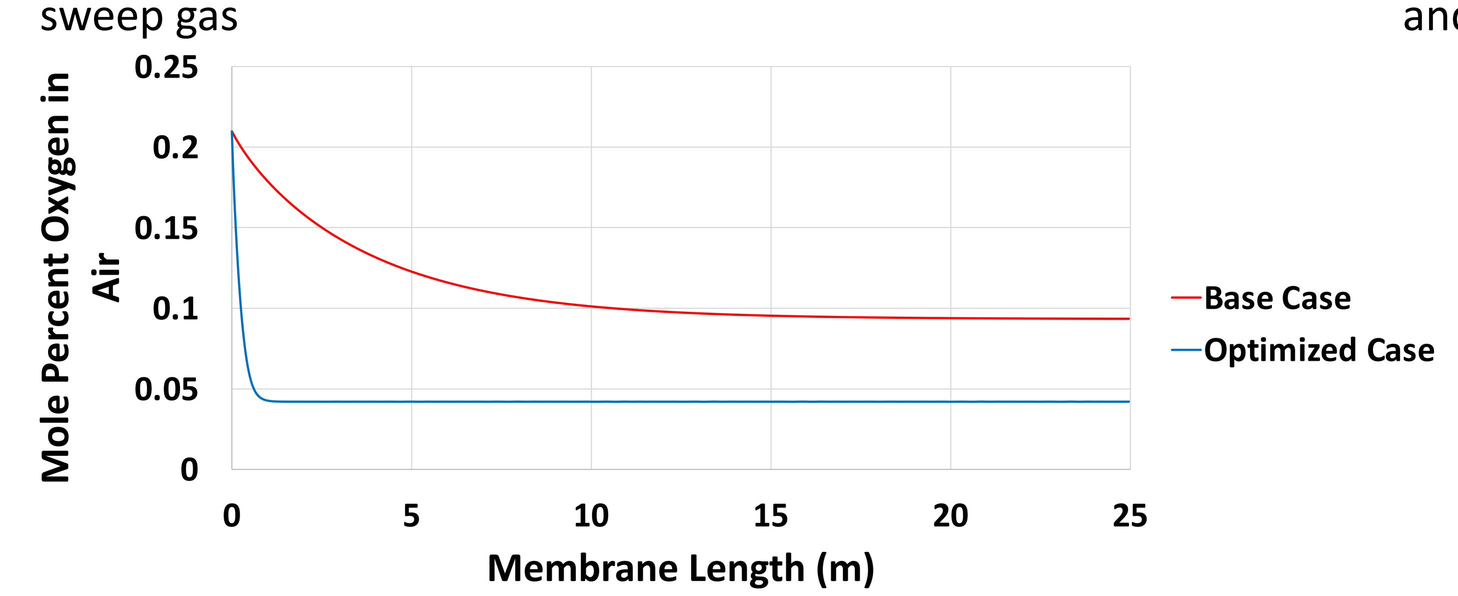

Figure 4: Base case versus optimized case oxygen separation over length of membrane

- The molar feed ratio of the air stream to the sweep steam was able to be raised to 0.9 before it began to significantly affected the oxygen permeation
- Due to the extreme temperature conditions of the module the ITM technology is best suited for high temperature processes such as gasification power plants and the optimal temperature could vary based off of downstream conditions
- Based off of the simplified economic model an optimal temperature for ITM oxygen separation was found to be 1185 K
- At the optimal length of 0.75 and optimized process conditions the cost was reduced by approximately 91.2 %

Conclusion and Future Directions

- A perovskite ITM model was developed and evaluated at a range of process conditions while maintaining set performance constraints
- A constrained optimization problem was formulated and minimized, permitting efficient selection of optimal reactor design conditions to improve membrane utilization
- As new membrane materials emerge and the membrane capital cost continues to decrease, the ITM air separation technology is it will become a highly competitive option for the production of high purity oxygen in IGCC power plants
- Future work will consider application to operability and process control studies

References

(1) Tan, Xiaoyao, et al. "Mixed Conducting Ceramic Hollow-Fiber Membranes for Air Separation." AIChE Journal, vol. 51, no. 7, 9 May 2005, pp. 1991–2000.
(2) Armstrong, Phillip A, et al. ITM Oxygen: The New Oxygen Supply for the New IGCC Market. Edited by Ted Foster, 2005 Air Products and Chemicals, Inc., 9 Oct. 2005.

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