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Ion transport membrane reactors for oxy-combustion—Part II: Analysis and comparison of alternatives

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ABSTRACT

In order to design ITM-based oxy-combustion power cycles, various reactor engineering analyses must be conducted with detailed modeling and simulation. An intermediate-fidelity ITM model is used to explore the dependence of ITM performance on reactor geometric structure, flow configuration, operating conditions, membrane material properties, and uncertainty in key modeling assumptions, such as the dominant fuel conversion mechanism. Many operational constraints are presented that are usually overlooked by black-box modeling strategies, and the implications of these constraints are explored. Further, a comparison is made between reactive and separation-only ITMs to assess the relative merits and disadvantages of each. The results show that although a reactive ITM significantly improves the partial pressure driving force, practical reactor engineering considerations indicate that this concept is not superior to counter-current separation-only ITMs, mainly because of the stringent temperature limitations of the membrane material. A Second Law assessment of certain ITM configurations is performed to evaluate the potential of ITM technology to reduce the air separation penalty, and to provide insight for effective systems-level integration. Overall, the results of our analyses capture the essential characteristics of ITM air separation systems for power cycles, and enable detailed systems-level studies to be performed.

1. Base-case results and discussion

In order to understand how an ITM reactor depends on the operating conditions and flow configuration, simulations are performed for reactive vs. separation-only and co-current vs. counter current ITMs for two distinct cases. The results of all simulations are presented first, followed by detailed explanation of important state variables and their axially-distributed profiles. The first case represents a design problem, where the oxygen separation requirements of the ITM reactor are specified, and then the reactor is designed to meet them. In order to capture the scale of a large power plant, the requirements are to either oxidize 1 kmol/s of methane in a reactive ITM, or separate sufficient oxygen for an external combustor to oxidize the same amount of methane. These specifications would produce power in the range of 300–500 MWe depending on the cycle First Law efficiency.

The second case, a “rating” problem, compares co-current and counter-current separation-only ITM reactors with identical inlet temperatures, pressures, and flow-rates. In contrast, the first case allows for the approximate comparison of penalty for a given amount of oxygen required via the pressure drop, whereas the second case illustrates the importance of flow configuration and distributed profiles of key state variables such as temperature. The ITM reactor size and geometric structure are fixed for all simulations, allowing for comparison on an equal economic basis. That is, ITMs with the same size and geometric structure require the same amount of membrane material, and also will have identical manufacturing cost. This allows for a rough comparison of oxygen separation vs. capital cost for different ITM configurations. The ITM monolith reactor volume is 1000 m^3 or with 100,000 total square channels (50,000 per stream), each with a channel width of 1.5 cm, resulting in 266,700 m^2 of surface area and an overall reactor height of 4.75 m and length of 44.44 m, roughly the size of a typical heat recovery steam generator in large power plants [1]. Restricted equilibrium is assumed for simplicity (the effects of this assumption are explored later), and because it provides upper-bound estimates on the wall temperature and reactive ITM performance in general.

Table 1 gives the inlet conditions for the first case study where an oxygen requirement of 2.5 kmol/s is specified, slightly more than required for complete oxidation of 1 kmol/s of methane since most conventional combustors run slightly lean, and to avoid bulk

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Nomenclature

Latin letters

A	Preexponential [mol × m^{-2} × s^{-1} × Pa^{-n}]
B	Effective activation energy [K]
B^*	Modified effective activation energy [K]
J_{CH_4}	Methane flux [mol × m^{-2} × s^{-1}]
J_{O_2}	Oxygen flux [mol × m^{-2} × s^{-1}]
$La_2NiO_{4+\delta}$	LNO [−]
$La_{1-x}SrCo_{1-y}Fe_yO_{3-\delta}$	LSCF [−]
n	Partial-pressure curve-fit constant [−]
P''_{O_2}	Oxygen "permeate" partial pressure [Pa]
P'_{O_2}	Oxygen "feed" partial pressure [Pa]
V_R^*	Reactor Volume Required for Complete Fuel Conversion [K]
CCS	Carbon Capture and Sequestration [−]
ITM	Ion Transport Membrane [−]
NTU	Number of Transfer Units [−]

convective transport limitations. The inlet temperature of the feed stream is set to the lower bound of ITM operating temperature, whereas the permeate or sweep stream is set to the upper bound. This assumption is made based on power cycle concepts such as the AZEP [2], where the permeate or sweep stream comes from an oxy-combustor, and the feed stream originates from ambient conditions, and thus is typically minimally preheated. This last point is not necessarily always the case, and thus the effect of preheating both the feed and the permeate is addressed later. It should be noted that for a fixed thermal input, or "heat rate", prescribing a minimum inlet temperature results in a minimum flow-rate through the reactive ITM, and hence pressure drop is also a minimum.

The two separation-only ITM reactors have identical ratios of permeate to feed molar flow-rates (the sweep ratio), but are the magnitude of the flowrates are modified to obtain the specified oxygen separation (see Table 1). The reactive ITM however does not have the same ratio of permeate to feed flow-rates for two reasons. First, the permeate stream has an upper-bound on diluent flow-rate because the inlet methane concentration should not fall below roughly 5% for mass transfer and combustion stability reasons (explored in detail later). Second, the extremely narrow operating temperature range of the ITM ($\approx$200 K) dictates a large amount of diluent for a fixed thermal energy input, and so the feed stream flow-rate must be increased relative to the separation-only ITMs.

Table 2 gives the results of the design case study for three of the four simulations, omitting the counter-current reactive ITM. The reactive counter-current ITM temperature profiles cannot effectively be controlled, and full details are provided in the following section. As explained previously in Part I [3], the oxygen flux is a strong function of the local membrane temperature, and so the average membrane temperature is given for each simulation. Interestingly, the counter-current separation-only ITM has the highest average temperature due to the well-balanced heat exchange between the streams. The reactive co-current ITM has the lowest average wall temperature because of the nature of the combustion process and the narrow temperature operating constraints. That is, to maintain the temperature below the failure point of roughly 900−950 °C, the diluent flow-rate must be high, and since the oxygen enters the reactive stream slowly, the temperature rises gradually from the inlet condition to the maximum temperature-in contrast to the separation-only ITMs. As will be shown, the temperature profiles are quite important, and careful selection of the inlet conditions could lead to large improvements in ITM performance.

The pressure drop is one of the most important results from an ITM simulation because it represents the primary (practical) thermodynamic penalty associated with ITM oxygen separation. The counter-current separation-only ITM has the lowest pressure drop by a large margin, mainly because of the high average wall temperature, but also because of the oxygen partial pressure profiles that requires much lower flow-rates. The average difference in oxygen partial pressure can be used to estimate the potential for chemical expansion stress failure, and the average partial pressure driving force indicates how effective a particular ITM design is at maintaining a low permeate partial pressure. The counter-current ITM appears to be least likely to exhibit chemical expansion failure, i.e., material fracture due to expansion stresses, whereas the reactive co-current ITM displays the highest partial pressure gradients and thus would be most likely to fail.

Interestingly, the counter-current has the lowest average partial pressure driving force, but an analogy to heat exchangers explains this apparent contradiction. Essentially, having a fixed oxygen separation is equivalent to having a fixed heat duty. Usually, the heat transfer coefficient and area are identical for these sorts of comparisons, but here, the overall mass transfer coefficient (essentially the flux) is a much stronger function of the local flow properties than in typical heat exchangers. That is, the overall mass transfer coefficient depends both on the average wall temperature and average partial pressure driving force. Thus, since the average

Table 1
Inlet and operating conditions: fixed total oxygen separation.

Parameter	Separation-only co-current	Separation-only counter-current	Reactive co-current
Permeate T_{in} [K]	1173	1173	973
Feed T_{in} [K]	973	973	973
Feed $\dot{n}_{O_2,in}$ [kmol/s]	10.18	3.30	12.00
Feed $\dot{n}_{N_2,in}$ [kmol/s]	38.28	12.41	45.12
Feed $\dot{n}_{H_2O,in}$ [kmol/s]	1.00	1.00	10.00
Permeate $\dot{n}_{CH_4,in}$ [kmol/s]	0	0	1
Permeate $\dot{n}_{CO_2,in}$ [kmol/s]	24.68	8.34	10.00
Permeate $\dot{n}_{H_2O,in}$ [kmol/s]	24.68	8.34	10.00
Feed P_{tot} [bar]	10	10	10
Permeate P_{tot} [bar]	10	10	10

Table 2
Base case results: fixed total oxygen separation.

State variable	Separation-only co-current	Separation-only counter-current	Reactive co-current
O_2Separated [kmol/s]	2.5	2.5	2.5
Avg. Flux [mol/m^2/s]	0.0187	0.0187	0.0187
Avg. T_{memb}[K]	1091	1157	1071
Avg. $P'_{O_2} - P''_{O_2}$ [bar]	1.434	0.636	1.465
Avg. $P'^{0.5}_{O_2} - P''^{0.5}_{O_2}$[Pa$^{0.5}$]	258.3	102.3	354.3
Feed ΔP [bar]	1.670	0.228	2.878
Permeate ΔP [bar]	1.99	0.318	0.384
Feed T_{out} [K]	1092	1173	1199
Permeate T_{out} [K]	1092	1047	1210
Recovery Ratio (%)	25.8	74.9	22.2
Work Lost [kWh/ Metric Ton O_2]	237.8	30.1	N/A