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Design and cost analysis of perovskite oxygen permeable membrane reactors for hydrogen and syngas co-production

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***Abstract*—**Dense oxygen permeable membrane supported water splitting is a potential technology for high purity hydrogen production. It utilizes thermochemical energy to split water to hydrogen with the membrane separating the products so that the water splitting extent is not constrained by its thermodynamic equilibrium. Meanwhile, when methane partial oxidation is integrated into the other side of the membrane, syngas is co-produced with stoichiometry $H_2/CO = 2$. The carbon species will not mix with the H_2/H_2O mixture on the water side since the dense membrane is selective to oxygen permeation only. In this paper, the co-production of high purity hydrogen and syngas is studied in a monolith membrane reactor, and a computational model is developed to study the reactor performance and the associated material cost. Two types of membranes are investigated, i.e., $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF) and $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ) membranes. Results show that the required BCFZ membrane surface area for the production of 100 kmol H_2/h (from water splitting) is 5.3 times smaller than the required LCF area under base case conditions. Moreover, the cost study shows that the raw material cost depends on the price of the critical minerals such as cobalt, which are uncertain due to the demand and supply imbalance. Therefore, developing membrane materials with less critical minerals can benefit the implementation of the membrane reactor in an industry-scaled hydrogen production plant.

Keywords—oxygen permeable membrane, water splitting, high purity hydrogen, cost analysis, reactor design

I. INTRODUCTION

Hydrogen is an important chemical feedstock. The annual consumption of hydrogen is approximately 7.2 exajoules (EJ) globally [1], among which 53% is in ammonia production and another 31% in refineries [2]. Most of the hydrogen is produced from hydrocarbon reforming (e.g., 96% in 2012), among which half is from natural gas [3]. Using the conventional steam methane reforming (SMR) process as an example,

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H^0_{298} = 165\ kJ/mol, \quad (1)$$

more than 5.5 t CO_2 is generated per ton H_2 production. In addition, to produce high purity hydrogen, pressure swing adsorption (PSA) columns are usually used. However, the hydrogen recovery ratio using PSA is around 75 – 90%, and this value drops with increasing purity requirements [4]. The recovery ratio will further decrease to produce hydrogen fuel for the proton-exchange membrane fuel cells where the CO concentration standard becomes more stringent (< 0.2 ppm) [5]. This stringent CO standard also increases the capital cost of PSA. Therefore, hydrogen produced from water splitting is more desired for the applications with stringent CO standards.

In this paper, we discuss a potential technology that uses an oxygen permeable membrane to facilitate water splitting for hydrogen production. Methane partial oxidation is integrated in the membrane reactor to use the permeated oxygen to co-produce syngas (with stoichiometry $H_2/CO = 2$). A schematic is shown in Figure 1. The overall reaction is endothermic, and renewable or low-carbon heat source can be used as thermal input.

This technology is in the category of **clean energy conversion technologies**: Conversion of petroleum/gas/coal to high-valued materials and chemicals (A), and multienergy carrier energy systems (A or B). Understand the reactor design and costs can guide the development of lower cost membrane materials and expedite the deployment of this membrane-based co-production technology.

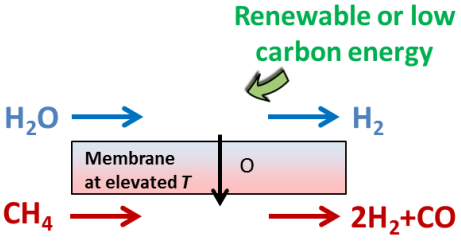

Figure 1 Schematic shows co-production of hydrogen and syngas from water splitting on the feed side and methane partial oxidation on the sweep side, respectively, in an oxygen permeable membrane reactor at elevated temperatures

II. Membrane Model

Two types of membrane materials, i.e., $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF) [6-11] and $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ) membranes [12-15] are proposed and their properties are well reported for oxygen permeation. In recent developments, due to the volatility of cobalt price [16, 17] and instability of Co cations under reducing environments [18], membrane materials without Co are more desired for large scale applications. Here, we compare the membrane reactors made of BCFZ and cobalt-free LCF membranes in the aspects of material consumptions and raw material costs. The results can guide the development of cobalt-free membrane materials to enhance hydrogen and syngas co-production.

The monolith membrane reactor design is investigated, which has high surface-area-to-volume ratio and can be readily produced and modularized in industry scale. We developed a 1D isothermal reactor model to compare the reactor design and the costs of the required mineral salts to fabricate the BCFZ and LCF membranes. The 1D monolith reactor model is shown in Figure 2.

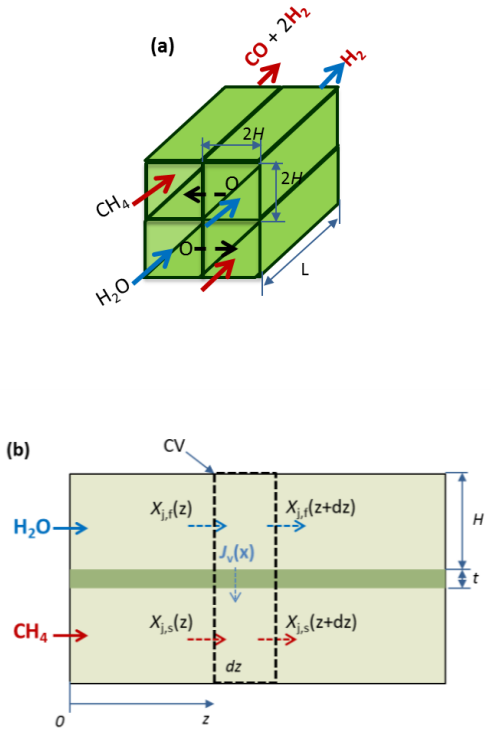

Figure 2 A monolith reactor is modelled in this study. (a) The channels are with dimensions: $2H \times 2H \times L$; (b) the control volume (CV) of the plug-flow reactor model. X_j is the molar concentration of species j, and the subscripts f and s represent feed and sweep sides, respectively.

The resistant-network oxygen flux model is used to simulate the oxygen transport process [7, 18]. This flux model considers both the surface reactions and ion diffusion kinetics in the membrane, and gives better description of the oxygen transport process in the membrane reactor than the previous models that assume the thermodynamic equilibrium in the gas phase [19]. The kinetics for the oxygen flux model are fitted using the least-squares method, and the fitted oxygen fluxes are compared with the experimental values, as shown in Figure 3. The mass transfer between the gas bulk and the membrane surface is also considered in the monolith reactor model.

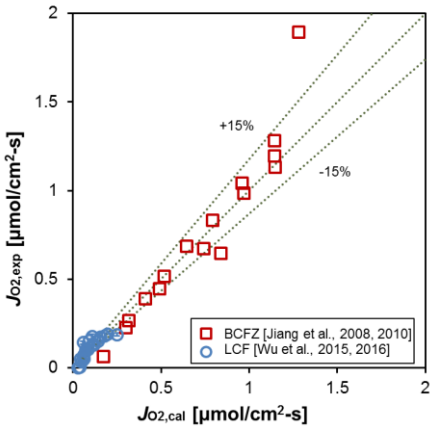

Figure 3 Comparison between the experimental data and the calculated values using the fitted kinetic parameters. The BCFZ data are from Jiang et al. 2008 [13] and Jiang et al. 2010 [15]; the LCF data from Wu et al. 2015 [7] and Wu et al. 2016 [6]

III. Results

A. Base model results

A base case with operating conditions similar to the solid oxide electrolysis cell (SOEC) is modeled (TABLE 1). The required channel length is defined as the length for 90% methane conversion, and results show that BCFZ membrane can co-produce more hydrogen and syngas per m^2 membrane area than the LCF membrane due to its high oxygen fluxes. As a result, the required BCFZ membrane surface area for the production of 100 kmol H_2/h (from water splitting) is 5.3 times smaller than the required LCF area.

TABLE 1 GEOMETRY, OPERATING CONDITIONS AND THE PERFORMANCES OF THE MEMBRANE REACTORS

	LCF	BCFZ
Channel height $2H$ [mm]	2	
Channel length L [mm]	7.81	7.35
Membrane thickness [mm]	0.9	
Porous catalytic layer thickness [mm]	Negligible (washed-coated)	
Temperature T [°C]	990	
Feed side flow rate [sccm/cm^2]*	4.2	21
Feed water concentration [-]	80%	
Sweep side flow rate [sccm/cm^2]	4.2	21
Sweep methane concentration [-]	5%	
Flow rates [sccm]	4.2	21
L [cm]	7.81	7.35
R_{CH_4} [-]	90%	
R_{H_2O} [-]	5.57%	
H_2 production [mol cm^{-2} s^{-1}]	1.782×10^{-7}	9.465×10^{-7}
Total membrane area for production of 100 kmol H_2/h [m^2]	1558.9	293.5
Total cost of raw materials for the membrane reactor	70153	29843
* Standard condition: 1 atm, 273 K		

B. Costs

We also compare the costs of the mineral salts required to manufacture the membranes for a small-scaled hydrogen

plant (100 kmol H_2/h from water splitting). The costs of mineral salts (industrial grade, purity > 98%) used in this study were quoted from the Alibaba website in the first quarter of 2018. The prices are the Free on Board (FOB) price from various major ports in China. The average price of each material is the mean value of all the available quotations. Based on our model, the raw materials required to produce 1 m^2 BCFZ membrane (stoichiometry is estimated as $BaCo_{1/3}Fe_{1/3}Zr_{1/3}O_3$) are 2.3 times more expensive than those for the LCF membrane. However, as the required LCF membrane area is larger, the cost for the LCF reactor is 2.4 times more expensive than that for the BCFZ reactor, which is shown in Figure 4. This means that the performance of the cobalt-free LCF membranes should be improved by more than 2.4 times compared with the literature reported values in [6] and [7], so that its cost can be lower than the BCFZ reactor.

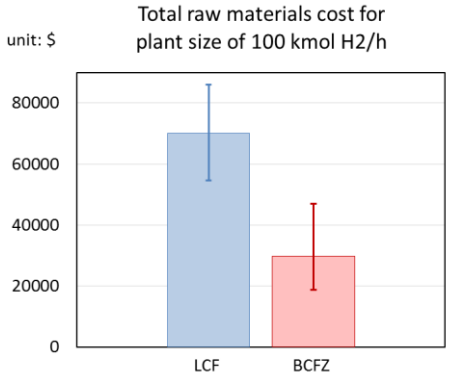

Figure 4 Total raw materials cost for a hydrogen plant (size: 100 kmol H_2/h from water splitting)

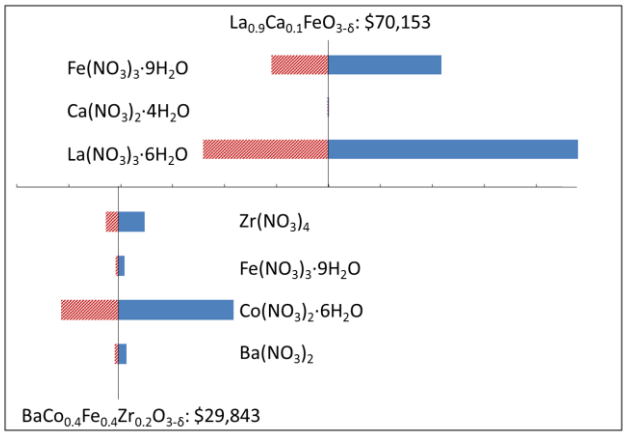

Figure 5 Sensitivity of material cost to the raw materials cost. The blue solid bars are results with +100% changes of the base case price, while the red patterned bars are results with -50% changes. The raw material next to each bar is the one with price changes

The sensitivity of the raw material costs to the prices of different mineral nitrate salts is also examined, and the results are shown in Figure 5. The positive change represents the cases doubling the raw material prices, while the negative change means half of the base case prices. We can see that LCF depends greatly on the lanthanum nitrate and iron nitrate costs, while BCFZ membrane reactor depends the most on the cobalt nitrate cost. The average cobalt price is expected to keep rising [17] (e.g., the cobalt price in US in 2017 was about 2.2 times of that in 2016) [16], while the lanthanum price is predicted to maintain low and drop slightly beyond 2019 [20]. Based on the sensitivity analysis, if cobalt price increases 2.82 times, the cost for the BCFZ reactor will be the same as that of the LCF reactor. Using cobalt-free membrane materials has more economic incentives for an industry-scaled co-production membrane reactor in the near future.

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