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**Hydrogen Production via Simultaneous Methane  
Reforming and Water Splitting Processes using  
Membrane Reactor**

By

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## Abstract

The main objective of this study is to investigate on the ability of a perovskite-based membrane reactor to produce hydrogen via simultaneous reforming and water splitting processes. Being able to perform such processes will confirm on the ability of the membrane system in performing an autothermal production of hydrogen. Initial experiments were conducted to evaluate the ability of two different types of hollow fibre membrane namely  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF6428) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF5582) in permeating oxygen in three different inlet configurations. All of the experiments were conducted at 900°C. The LSCF6428 membrane gives lower oxygen permeation rate comparing to BSCF5582 when inert gas argon was used as the sweep gas on the shell side of the membrane. The oxygen permeation rate into the shell side of LSCF6428 membrane reactor was at  $0.24\mu\text{molO}_2\text{s}^{-1}$  whereas for BSCF5582 was at  $1.50\mu\text{mol O}_2\text{s}^{-1}$ . The trend is similar when the shell sides were fed with 5% methane and the lumen sides were fed with 10% oxygen. In these experiments, both membranes were stable enough to perform oxygen permeation up to more than 100 hours of operation. BSCF5582 membrane however shows instability in performing oxygen permeation when the lumen side was fed with 4% water and shell side was fed with 5% methane. BSCF5582 membrane was only able to perform oxygen permeation for less than two hours before showing substantial amount of leaks upon breaking. In contrast, the

LSCF6428 membrane shows good stability in the same condition with the shell side oxygen permeation rate of  $0.04 \pm 0.01 \mu\text{molO}\cdot\text{s}^{-1}$ . The experiment operating time lasted for more than 90 hours. Based on its stability in performing oxygen permeation in the combination of highly reducing and highly oxidising environment, the LSCF6428 membranes were chosen to perform the simultaneous methane reforming and water splitting process in a multiple-membrane based reactor. The results obtained from this experiment proved that simultaneous methane reforming and water splitting can be achieved using a membrane reactor.

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# Nomenclature

## *List of acronyms*

ATR	Autothermal Reforming of Methane
BSCF5582	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{\delta-3}$
CPO	Catalytic Partial Oxidation
EDX	Energy Dispersive X-Ray Analysis
GC	Gas Chromatography
HEX	Heat Exchanger
HTS	High Temperature Shift
IGCC	Integrated Gasification Combined Cycle
LSCF6428	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{\delta-3}$
LTS	Low Temperature Shift
MFC	Mass Flow Controller
MIEC	Mixed Ionic and Electronic Conductor
OTM	Oxygen transport Membrane
PEM	Polymer Electrolytes Membrane
POM	Partial Oxidation of Methane
POX	Partial Oxidation
SEM	Scanning Electron Microscopy
SMR	Steam Methane Reforming
SOFC	Solid Oxide Fuel Cells
STP	Standard temperature and pressure (273.15 K, 1 atm)

TCD	Thermal Conductivity Detector
WGS	Water Gas Shift
YSZ	Yttrium Stabilised Zirconia

***List of symbols***

$ABO_3$	Perovskite structure
$CaTiO_3$	Calcium titanium oxide
$F$	Faraday constant ( $9.648\ 70 \times 10^4\ Cmol^{-1}$ )
$F$	Flowrate ( $mlmin^{-1}$ )
$J_{O_2}$	Oxygen permeation rate define by modified Wagner equation
$L$	Thickness of membrane
$P_A$	Permeability of A
$P_B$	Permeability of B
$p_{O_2}(feed)$	Oxygen partial pressure of feed side
$p_{O_2}(perm)$	Oxygen partial pressure of the permeated side
$r_A$	radius of the A-site cation
$r_B$	radius of the B-site cation
$r_O$	radius of the lattice oxygen anion
$R$	Ideal gas constant ( $8.314\ J\ K^{-1}\ mol^{-1}$ )
$T$	Temperature ( $^{\circ}C$ )
$V_m$	Molar volume of gas at STP ( $24\ 465\ mmlmol^{-1}$ at $25\ ^{\circ}C$ )
$\Delta H$	Heat of reaction ( $J\ mol^{-1}$ )
$\alpha_{A/B}$	Selectivity
$\sigma_{el}$	Electronic conductivity
$\sigma_{ion}$	Ionic conductivity

### **Kröger-Vink notation**

$V_{\ddot{O}}$	Oxygen vacancy site
$O_o^x$	Oxygen occupying site
$\delta$	Oxygen vacancies/deficiencies
$e^-$	electron
$h\cdot$	Electron holes

### **Material balance notation**

OP <sub>SS</sub>	Oxygen permeation on the shell side
OP <sub>LS</sub>	Oxygen permeation on the lumen side
$n_T^{L(x)}$	Total flowrate of lumen side x, where x is the number of lumen used in the experiment; x = 1 or 2
$n_T^{SS(y)}$	Total flowrate of shell side y, where y is the number of reactor; y= 1, 2 or 3
$CH_{4(in)}^{LS(x)/SS(y)}$	The inlet mole fraction of methane on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2 and y is the number of reactor used in the experiment; y = 1,2 or 3
$CH_{4(out)}^{LS(x)/SS(y)}$	The outlet mole fraction of methane on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2 and y is the number of reactor used in the experiment; y = 1,2 or 3
$CO_{(in)}^{LS(x)/SS(y)}$	The inlet mole fraction of carbon monoxide on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2 and y is the number of reactor used in the experiment; y = 1,2 or 3
$CO_{(out)}^{LS(x)/SS(y)}$	The outlet mole fraction of carbon monoxide on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2 and y is the number of reactor used in the experiment; y = 1,2 or 3
$CO_{2(in)}^{LS(x)/SS(y)}$	The inlet mole fraction of carbon dioxide on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2 and y is the number of reactor used in the experiment; y = 1,2 or 3
$CO_{2(out)}^{LS(x)/SS(y)}$	The outlet mole fraction of carbon dioxide on lumen side x or on shell side y, where x is the number of lumen used; x= 1 or 2

and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$H_{2(in)}^{LS(x)/SS(y)}$$

The inlet mole fraction of hydrogen on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$H_{2(out)}^{LS(x)/SS(y)}$$

The outlet mole fraction of hydrogen on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$H_2O_{(out)}^{LS(x)/SS(y)}$$

The inlet mole fraction of water on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$H_2O_{(out)}^{LS(x)/SS(y)}$$

The outlet mole fraction of water on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$O_{2(in)}^{LS(x)/SS(y)}$$

The inlet mole fraction of oxygen on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

$$O_{2(out)}^{LS(x)/SS(y)}$$

The outlet mole fraction of oxygen on lumen side  $x$  or on shell side  $y$ , where  $x$  is the number of lumen used;  $x = 1$  or  $2$  and  $y$  is the number of reactor used in the experiment;  $y = 1, 2$  or  $3$

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# Chapter 1 Introduction

## 1.1 Background of the Research

Hydrogen is the lightest substance in the periodic table. It is mainly being used in the production of ammonia, and as the reducing gas in stainless steel production, as a feedstock to the petrochemical industries and as the hydrogenation agent in the food processing industries [1]. It has the highest energy density with nearly three times the energy yield than other hydrocarbon fuels [2]. The fact that hydrogen when burned in air only produces water coupled with high amount of energy makes it easy to claim hydrogen is the cleanest, renewable alternative fuel available to date [3-5].

Globally the largest hydrogen production source is from natural gas followed by fossil fuels and coal [6]. Conventional hydrogen production processes that are widely used in the industries are the steam methane reforming, water gas shift and partial oxidation of methane processes[7]. As these processes are relying too much on the use of fossil fuels, efforts need to be made to find other alternatives for producing hydrogen in a cleaner environment and at a cheaper cost.

Perovskites-type mixed ionic and electronic conductor (MIEC) membranes were claimed to have great potential to be used in hydrogen production membrane

reactors because of their stability and good oxygen permeation attributes[8]. This hydrogen production system relies on the MIEC membranes' ability to separate oxygen from air and/or from other mixtures of gases only through partial pressure differences in the inlet streams.

Recently most of the studies on hydrogen production using MIEC membranes are focussed on the partial oxidation process [9, 10]. This kind of reaction is highly exothermic and energy intensive. It is only recently that a MIEC membrane was seen to have the potential to be used in a direct water splitting process[11]. Studies on combining both water splitting and methane oxidation in a MIEC membrane reactor however, are limited and not well described.

## **1.2 Scope of the Research**

The scope of the research will remain focussed on the ability of oxygen permeation using hollow fibre perovskites membranes to perform water splitting, partial oxidation of methane and full combustion of methane. The main aim of this thesis is to combine the methane oxidation and water splitting processes in the same reactor.

### **1.3 Objectives of the Research**

The objectives of this study are:

1. To solve membrane stability issues by redesigning the membrane reactor; having individual inlets and outlets for better gas analysis and monitoring purposes.
2. To investigate the performance of LSCF6428, BSCF5582 in performing oxygen permeation with and without reducing gas.
3. To investigate the ability of LSCF6428, BSCF5582 to perform the water splitting process with reducing gas on the other side of the membrane.
4. To combine the best membrane that can withstand (2) and (3) in a multiple membrane reactor for a simultaneous methane reforming and water splitting processes.

### **1.4 Thesis Outline**

This thesis is divided into six chapters. The first chapter discusses on the problem statement, the background of the research and scope of the research. Chapter 2 reviews on the use of alternative methods in hydrogen production starting from the early days of hydrogen being produced until the advancement in these methods. State of the art research for the design of the membrane reactor involving an oxygen transport membrane will also be discussed in detail. Further description on the theory and the advancement this study will contribute to the body of knowledge in the membrane reactor field will also be looked at in detail.

Chapter 3 deals with the preliminary results run for individual membrane for (i) oxygen permeation without reducing gas on the shell side (ii) oxygen permeation with methane reforming reactions on the shell side and (iii) oxygen permeation performance having methane reforming reactions on the shell side and water splitting processes on the lumen side. These three types of experiments were run on two different membrane materials namely  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF6428) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF5582). Thorough explanations are made on the experimental techniques, membrane characterisation, reactor setup, leak tests and gas analysis in this chapter. The calculation techniques and error propagation applied in the calculations will also be discussed.

Chapter 4 will discuss the preliminary experiment of an autothermal process. In this chapter only one type of selected hollow fibre was used; the LSCF6428 membrane. The membrane was used to perform (i) oxygen permeation from oxygen feed stream and (ii) water splitting processes in the both the different lumens. The shell was fed with methane to assist the oxygen permeation and simultaneously perform methane reforming processes. Further analysis from the results obtained from this chapter revealed that the amount of oxygen permeated into the shell increased the oxygen partial pressure in the shell side and halted the water splitting in the lumen of the second LSCF6428 membrane. Determining the cause led to several modifications aiming to increase the oxygen utilisation in the shell side. Only one of them showed good results.

In Chapter 5 the processes conducted in and discussed previously in Chapter 4 were separated into three reactors namely Reactor 1 (R1), Reactor 2 (R2) and Reactor 3 (R3). Three reactors were used to separate the processes; R1 is specifically aimed for full combustion and partial oxidation of methane reactions in the shell side and

oxygen permeation in the lumen side. R2 is used to further improve the selectivity of CO over CO<sub>2</sub> in the product stream of the shell side from R1 and R3 is for methane reforming in the shell side and water splitting processes in the lumen side of the membrane. Results are discussed in terms of the total oxygen permeation rates throughout the whole system, selectivity of CO in R2 and hydrogen production rates from the water splitting process in R3.

The summary and conclusions achieved in the experiments conducted in this study are presented in Chapter 6.