INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

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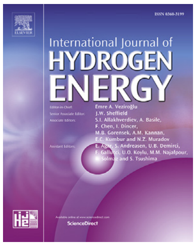

Perovskite $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ materials for chemical looping combustion applications

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A R T I C L E I N F O

Article history:
Received 28 September 2017
Received in revised form
18 January 2018
Accepted 7 April 2018
Available online xxx

Keywords:
Advanced oxide materials
Perovskites
Hydrogen
Chemical looping combustion
CCS
TGA

A B S T R A C T

This paper presents the results of chemical looping combustion (CLC) research. Nowadays, CLC is one of the best prospective combustion technologies, because it enables the production of a concentrated carbon dioxide (CO_2) stream, following water condensation, without any energy penalty for its separation.

The objective of this work was to study chemical looping reaction performance with the application of novel perovskite-type oxygen carriers (OCs). $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ family members were tested for hydrogen combustion for power generation purposes. $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$, which is a perovskite-type oxide, was prepared using the calcination method, where $x = 0$, 0.1 and 0.33. Reactivity tests were performed using a thermogravimetric analyser (TGA, Netzsch STA 409 PG Luxx) under isothermal conditions in multiple reduction–oxidation cycles. Both the temperature (600–800 °C) and number of redox cycles (five cycles) effects on the reaction performance of recently developed OC samples were evaluated in the study. TGA data were used for the assessment of the oxygen transport capacity value, redox reaction rates and stability. $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ showed an excellent stable chemical looping performance. The changing of oxygen content (3.8–4.86 wt%) occurred within approximately 2 min, with the chemical properties of the material maintained during the cycling combustion tests.

In addition, new $SrFeO_{3-\delta}$ OCs, doped with copper (Cu) perovskite-type materials, were analysed using multiple methods: X-ray powder diffraction (XRD); scanning electron microscopy (SEM); surface area by Brunauer–Emmett–Teller (BET) method; and melting behaviour study. In terms of physical properties, the new OCs can resist both high CLC process temperatures and mechanical forces, which are essentially useful. The analysis showed that $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ carriers performed at extremely high melting temperatures (>1280 °C). Results of crushing strength testing showed that developed materials had a pronounced mechanical resistivity with a crushing strength higher than 1 N and will perform well in fluidized beds (4.31–6.23 N).

In this paper, it was demonstrated that known mixed oxygen-ionic and electronic conducting membrane materials such as $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ might also be applied as oxygen carriers. Overall results demonstrated Fe-Cu-based perovskites might be successfully used as OCs in the chemical looping combustion process.

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https://doi.org/10.1016/j.ijhydene.2018.04.046

Please cite this article in press as: Ksepko E, Perovskite $Sr(Fe_{1-x}Cu_x)O_{3-\delta}$ materials for chemical looping combustion applications, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.046

Introduction

In chemical looping combustion (CLC), a carbonaceous fuel is converted into pollutant-free energy carriers such as electricity and hydrogen. In this process, direct contact between combustible air and a fuel is avoided, and the oxygen is delivered using a solid-state oxygen carrier (OC), which is usually a metal oxide (MeO) [1,2]. The oxygen carrier (MeO) transfers oxygen from the air to the fuel in the manner shown in Fig. 1. There are two reactors: a reducing reactor and an oxidizing reactor, also referred to as a fuel and an air reactor, respectively. In the fuel reactor, a carbonaceous fuel (for example, synthesis gas, methane, coal or biomass) reacts with an OC. The fuel is oxidized to carbon dioxide (CO_2) and water (H_2O) while the MeO is reduced to an MeO with a lower oxidation state or to its metallic form [3]. A pure stream of CO_2 is obtained as the water is condensed. In the next step, so-called oxidation of the OC (or regeneration), the reduced MeO is transferred to the air reactor, where the OC is regenerated by the air. By this stage, the OC is ready to react in another loop with the fuel finalizing the redox cycle. The significant advantage of the CLC method compared with other combustion methods is the production of a pure stream of CO_2 without any additional energy penalty for its separation. Furthermore, this method leads to noticeably lower nitrogen oxide (NO_x) emissions into the atmosphere. Finally, the CO_2 stream can be effectively captured without a decrease in combustion efficiency.

Most authors engaged in CLC research historically used predominantly simple solid-state OCs such as nitrogen oxide (NiO), copper oxide (CuO), iron oxide (Fe_2O_3), cobalt oxide (CoO), and manganese oxide (MnO_2) [4]. Later, a significant increase in research related to the potential application of mixed-metal [5–9], and naturally occurring OCs [10] was observed. Nowadays, interest has increased in specific OCs that are of perovskite-type oxides [3,11,12], because they are more attractive for chemical looping applications when compared with other OCs; however, the literature on their potential application is somewhat limited. Perovskite-structured compounds are a group of inorganic compounds with the general formula of ABX_3. In this formula, an A is usually a metal (an alkali-metal or alkaline-earth cation, sometimes a transition-metal cation), while B is a cation with a coordination number equal to six (typically titanium, niobium, tantalum, or manganese), and X is typically an oxide anion, or, rarely, a halide or sulphide ion. The perovskite composition changes through variations in the O_2 partial pressure (pO_2) or in the temperature (T). Changes of the perovskite structure may be reversible (Eqs. (1) and (2)) or non-reversible (Eq. (3)) depending on the decreases in temperature and/or O_2 partial pressure [13]. The resulting general equations describe the possible universal changes in the composition of perovskite-structured oxides:

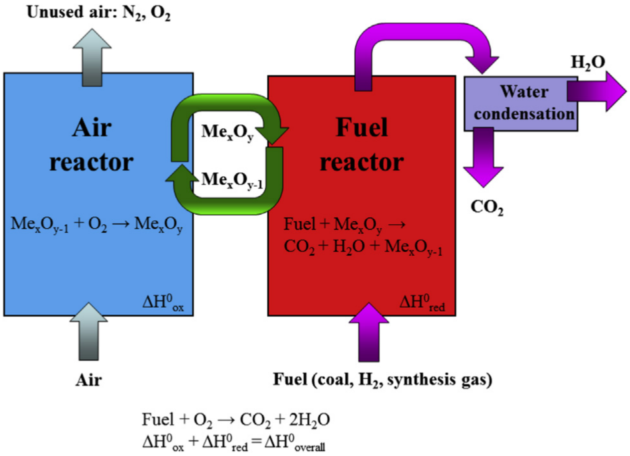

Fig. 1 – Chemical looping combustion (CLC) process concept.

$$ABO_{3-\delta} \leftrightarrow ABO_{3-\delta''} \quad (1)$$

$$ABO_{3-\delta} \leftrightarrow ABO_{3-\delta'} \leftrightarrow (A_nB_nO_{3n-1}) \leftrightarrow A_2B_2O_5 \quad (2)$$

$$(A_nB_nO_{3n-1}) \rightarrow (A_{m+1}B_mO_{3m+1} + BO) \rightarrow AO/A_2O_3 + B \quad (3)$$

The δ, δ', δ'' represent changes of O_2 quantity as a function of p (O_2) and temperature (T). The m is the number of the octahedral layers in the perovskite-like Ruddlesden–Popper phases with the $A_{m+1}B_mO_{3m+1}$ general form, while $n = 2\text{-}\infty$ for the oxygen defected perovskite of the $A_nB_nO_{3n-1}$ series [14]. Eq. (1) shows the redox reactions are reversible with an increase in p (O_2) and temperature. The perovskite reduction reaction might be also reversible when intermediate phases under decreasing O_2 partial pressures are formed [13]. On the other hand, the redox reactions may lead to the non-reversible formation of AO/A_2O_3+B phases. This happens when significant increases in temperature occur. Because a change in oxygen content for perovskite-type materials is reversible under the given reaction conditions, they may have a potential role in CLC processes.

Recently, some perovskites have been intensively investigated for their potential use in CLC applications. It should be emphasized that perovskites can possibly solve numerous problems associated with conventional monometallic OCs. First, the addition of other oxides improves the structural properties of the monometallic OCs by considerably expanding their stability over multiple redox cycles. Secondly, they have been proven to increase both the thermal resistance and the oxygen transport capacity [3,15]. Finally, perovskite-type materials show improved reaction rates [16–18]. Examples of complex oxide materials that are receiving considerably increased attention include $La_{1-x}Sr_xFeO_3$ [17], $Sr(Mn_{1-x}Ni_x)O_3$ [3], $La_{1-x}M_xNiO_4$ (M = Ca or Sr) [19], $La_{1-x}Me_xM_yFe_{1-y}O_3$ (Me = Sr, Ca; M = Ni, Co, Cr, Cu) [20], $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ [13,21]. He et al. [17] showed that $La_{1-x}Sr_xFeO_3$ could be prepared, and pure perovskite-structured phases obtained. It was suggested that the electronic imbalance caused by the partial substitution of lanthanum (La^{3+}) by strontium (Sr^{2+}) was compensated for by the oxidation of a fraction of iron ions Fe^{3+} to Fe^{4+} and/or the generation of oxygen vacancies in the perovskite lattice. Moreover, they also observed the existence of two different oxygen species in the oxides, i.e., surface absorption oxygen and bulk lattice oxygen ions. Certain perovskites have also been shown to exhibit an excellent regeneration ability, such as the $Sr(Mn_{1-x}Ni_x)O_3$ family [3].

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