

# The use of strontium ferrite in chemical looping systems

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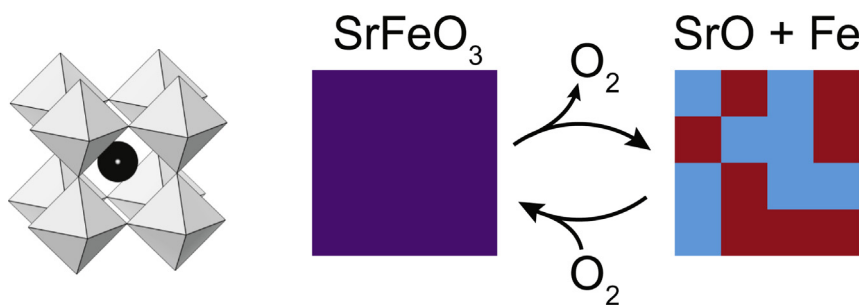
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## HIGHLIGHTS

- Stable performance (conversion, particle durability) in fluidized bed tests over 30 redox cycles.
- Easily reduces below  $\delta = 0.5$ ; the final products of  $\text{SrFeO}_{3-\delta}$  reduction are Fe and SrO.
- Attractive for CO or  $\text{H}_2$  production; the reduced material regenerates in mild oxidizers ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ).
- Catalytically assists with combustion of lean  $\text{CH}_4$  (2.5%) in fluidized bed tests at  $T > 550^\circ\text{C}$ .

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

This work reports a detailed chemical looping investigation of strontium ferrite ( $\text{SrFeO}_{3-\delta}$ ), a material with the perovskite structure type able to donate oxygen and stay in a nonstoichiometric form over a broad range of oxygen partial pressures, starting at temperatures as low as  $250^\circ\text{C}$  (reduction in CO, measured in TGA).  $\text{SrFeO}_{3-\delta}$  is an economically attractive, simple, but remarkably stable material that can withstand repeated phase transitions during redox cycling. Mechanical mixing and calcination of iron oxide and strontium carbonate was evaluated as an effective way to obtain pure  $\text{SrFeO}_{3-\delta}$ . In-situ XRD was performed to analyse structure transformations during reduction and reoxidation. Our work reports that much deeper reduction, from  $\text{SrFeO}_{3-\delta}$  to SrO and Fe, is reversible and results in oxygen release at a chemical potential suitable for hydrogen production. Thermogravimetric experiments with different gas compositions were applied to characterize the material and evaluate its available oxygen capacity. In both TGA and in-situ XRD experiments the material was reduced below  $\delta = 0.5$  followed by reoxidation either with  $\text{CO}_2$  or air, to study phase segregation and reversibility of crystal structure transitions. As revealed by in-situ XRD, even deeply reduced material regenerates at  $900^\circ\text{C}$  to  $\text{SrFeO}_{3-\delta}$  with a cubic structure. To investigate the catalytic behaviour of  $\text{SrFeO}_{3-\delta}$  in methane combustion, experiments were performed in a fluidized bed rig. These showed  $\text{SrFeO}_{3-\delta}$  donates  $\text{O}_2$  into the gas phase but also assists with  $\text{CH}_4$  combustion by supplying lattice oxygen. To test the material for combustion and hydrogen production, long cycling experiments in a fluidized bed rig were also performed.  $\text{SrFeO}_{3-\delta}$  showed stability over 30 redox cycles, both in experiments with a 2-step oxidation performed in  $\text{CO}_2$  followed by air, as well as a single step oxidation in  $\text{CO}_2$  alone. Finally, the influence of  $\text{CO}/\text{CO}_2$  mixtures on material performance was tested; a fast and deep

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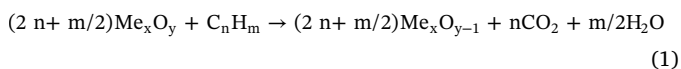
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reduction in elevated  $p_{\text{CO}_2}$  makes the material susceptible to carbonation, but the process can be reversed by increasing the temperature or lowering  $p_{\text{CO}_2}$ .

## 1. Introduction

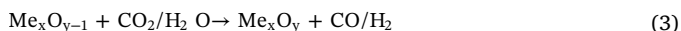
The concept of chemical looping (CL) utilises the reversible reduction and oxidation of suitable materials in many interesting processes. It was demonstrated that the reduction of metal oxides ( $\text{Me}_x\text{O}_y$ ) can be employed in air-less combustion, where the oxygen needed for fuel conversion comes from the solid material instead of air:



The reduced oxide can be then regenerated in a separate process, e.g. in air, closing the chemical loop:

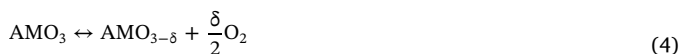


Besides combustion, the chemical looping concept was also proposed for hydrogen production. It has been shown that for some reduced oxides even very mild oxidizers such as  $\text{H}_2\text{O}$  or  $\text{CO}_2$  might be used [1], and a combustible gaseous product is generated: hydrogen or carbon monoxide respectively, i.e.



Over the last 20 years, extensive research has been carried out to firstly investigate, then design materials that can work as oxygen carriers (OC), providing oxygen for the combustion application. Most of them involved oxides of transition metals, which in the suitable temperature range (500–800°C) exist as solid compounds in various oxidation states. Fe, Ti, Mn, Cu, Ni oxides as mono-metallic carriers and their mixtures as bi-metallic carriers were investigated extensively, in laboratory scale as well as pilot scale combustion experiments [2–5]. To improve the oxygen carrier's stability during the redox cycling, an addition of supporting component that is nominally inert ( $\text{Al}_2\text{O}_3$  [6],  $\text{ZrO}_2$  [7]) or active ( $\text{CeO}_2$  [8]) is usually employed. Comprehensive reviews on metal oxides used for combustion are given by Imtiaz et al. [9] and Luo et al. [10], and for hydrogen production by Thursfield et al. [11] and Voitic and Hacker [12].

Ternary oxides with a perovskite structure  $\text{AMO}_3$  (where A is commonly some alkaline earth or rare earth metal and M some transition metal), are also frequently considered for chemical looping applications. At elevated temperature and/or in reducing conditions some perovskites have been shown to maintain their crystal structure while gradually losing oxygen [13]:



The resulting  $\text{AMO}_{3-\delta}$  structure is stable, containing M-cations with mixed valency and significant oxygen nonstoichiometry. Moreover, depending on the oxygen partial pressure,  $p_{\text{O}_2}$ , and temperature, T, the cubic perovskite structure  $\text{AMO}_{3-\delta}$  may completely or partially convert to brownmillerite, an orthorhombic phase  $\text{AMO}_{2.5+\delta}$  with some surplus oxygen. As a result either one of the nonstoichiometric structures or both may be detected during reduction [14,15].

Previous studies indicate that the kinetics of oxygen release from the perovskite structure (reaction (4)) are very fast under typical process conditions. Thus, when the oxygen release occurs, it often becomes limited by  $\text{O}_2$  fugacity [16]. However, a partial substitution of A and/or M-site cations by metallic dopants with similar ionic size can alter the thermodynamic behaviour of the material in reaction (4) [17,18]. Perovskites have been proposed for use in many processes, such as carrier materials for oxygen production and storage applications [14,19,20], oxygen carriers in combustion and hydrogen production [17,21–23]; electrodes in solid oxide fuel cells [24,25]; as well as

materials for selective ionic membranes in  $\text{H}_2$  production [17,26] or  $\text{CO}_2$  separation [27,28].

Potential materials with perovskite structures tested in chemical looping applications include  $\text{CaMnO}_{3-\delta}$ ,  $\text{SrFeO}_{3-\delta}$ ,  $\text{LaFeO}_{3-\delta}$ ,  $\text{SrCoO}_{3-\delta}$  [4,16,29,30] and multi-component materials with mixed metals for A or M cation sites, or for both sites, such as:  $\text{SrFe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ ,  $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$  and  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  [14,20,31]. Similar materials, usually perovskites of Fe or Mn, were also investigated for hydrogen production:  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ,  $\text{LaFeO}_{3-\delta}$ ,  $\text{LaFe}_x\text{Co}_y\text{O}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  [17,32–36].

For chemical looping applications the main incentive in solid carrier selection will be its cost, inseparably linked to material's stability and abundance. One of the perovskite type compounds that may fulfil these requirements is  $\text{SrFeO}_{3-\delta}$  as it does not contain expensive elements, such as rare (lanthanum) or toxic (cobalt) metals. Thus far, the strontium ferrite perovskite has been primarily considered for oxygen storage and air separation processes due to the low temperature at which the material starts losing oxygen, even at high  $p_{\text{O}_2}$  (around 400°C in air) [14,29].

This study shows that  $\text{SrFeO}_{3-\delta}$  is also attractive for two additional processes: hydrogen production and catalytic  $\text{CH}_4$  combustion. Experiments in fluidized bed setup reveals that lean  $\text{CH}_4$  (2.5%) combusts on  $\text{SrFeO}_{3-\delta}$  at moderate temperatures > 550°C. The investigation also explores  $\text{SrFeO}_{3-\delta}$  characteristics during high temperature reduction carried out in highly reducing atmospheres. The reversibility has also been studied here by oxidation either with air or with a mild oxidizer. This work reports that the reduction from  $\text{SrFeO}_{3-\delta}$  to SrO and metallic Fe is remarkably reversible and results in oxygen release at a chemical potential suitable for hydrogen production, despite the severe changes in structure during the phase transition. The subsequent reoxidation, either in  $\text{CO}_2$  or air, quickly regenerates the material from SrO and Fe back to a perovskite structure:  $\text{SrFeO}_{2.5}$  in  $\text{CO}_2$ , or  $\text{SrFeO}_{3-\delta}$  in air. Owing to reversibility of the reconstructive phase transition, the useful oxygen capacity is much higher than would be expected considering the maximum available by exploiting the  $\text{SrFeO}_{3-\delta}$  phase alone.

## 2. Experimental

### 2.1. Materials preparation

Preliminary investigation used solid state synthesis by manual mixing of stoichiometric amount of  $\text{Fe}_2\text{O}_3$  with either SrO or  $\text{SrCO}_3$  (all > 98 wt%, Sigma Aldrich), using a mortar and a pestle until a mixture with homogenous appearance was obtained. The mixture was then calcined in a muffle furnace at 1000°C, for 3 h in air. Characterization of this material showed that the precursor  $\text{SrCO}_3$  was much more effective in producing the desired  $\text{SrFeO}_{3-\delta}$  phase.

In order to scale up the production of the perovskite for experiments in the fluidized bed rig, a planetary ball mill (MTI, model MSK-SFM-1) was used for powder mixing. Stoichiometric amounts of  $\text{SrCO}_3$  (0.72 mol) and  $\text{Fe}_2\text{O}_3$  (0.36 mol) were mixed in the ball mill for 3 h at 25 Hz. Ethanol (50 mL, 99.8%, Fisher Scientific) was added as a binder to improve mixing. The mixture was dried for 24 h at 50°C, and sieved to < 50  $\mu\text{m}$ , 50–180  $\mu\text{m}$  and 180–355  $\mu\text{m}$  fractions. Then the particles were calcined in 1 to 4 stages, with each stage consisting of calcination at 1000°C for 3 h, followed by cooling to room temperature. As a result, four batches of material were prepared, differing in the total duration of calcination (between 3 and 12 h). All materials were sieved again after

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