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Lanthanum chromite based perovskites for oxygen transport membrane

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ABSTRACT

Judicious selection of mixed ionic–electronic conducting (MIEC) perovskite oxide as oxygen transport membrane (OTM) offers the potential to enhance overall process economics and systems performance for a wide variety of industrial applications ranging from clean and efficient energy conversion (oxy-combustion) to selective gas separation (high purity oxygen production) and value added chemicals (syngas and liquid fuel) production with near-zero greenhouse gas emissions. Doped lanthanum chromite perovskites have been considered as promising material of choice for oxygen transport membrane (OTM) due to their superior thermo-chemical stability in aggressive environment (800–1000 °C, 0.21–10^{-20} P_{O_2}) than the other mixed ionic–electronic conducting (MIEC) perovskites such as ferrites and cobaltite's. Thermo-physical properties of the lanthanum chromite, required for optimum oxygen transport can be tuned by modifying the crystal structure, chemical bonding, and ionic and electronic transport properties through selection of dopant's type and level. A perspective on the development of lanthanum chromite-based oxygen transport membranes is presented with an insight based on the pertinent literature and data analysis. The role of various A- and B-site dopants on the crystal structure, densification, thermal expansion, electrical transport, oxygen permeation, mechanical properties, and thermochemical stability of lanthanum chromite is discussed to enlighten 'composition–structure–property' correlations. It has been found that: the preferred dopants are strontium at A-site and manganese, nickel, iron, and titanium at B-site to obtain the desired thermo–chemo–electro–mechano properties. Challenges for long term performance and structural stability of doped lanthanum chromite as an oxygen transport membrane are outlined for the applications under 'real system' exposure conditions.

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1. Introduction

Oxygen transport membrane offers potential for applications in a wide variety of industrial processes ranging from high purity oxygen separation from air to oxy-combustion of carbonaceous and hydrocarbon fuels as well as production of syngas for subsequent conversion to liquid fuels and hydrogen. Efficient and clean oxy-combustion of fossil fuels enable reduction of greenhouse gas emissions responsible for global climate change [1,2]. In the oxy-fuel combustion process, oxygen is separated from air and exclusively used for the fuel combustion unlike conventional combustion process where air is used as an oxidant. Use of oxygen results in significant increase in the process efficiency resulting in decrease in fuel consumption, heat loss, reduction in the size of the flue gas and NO_x emissions treatment. The replacement of air to oxygen in the natural-gas fired furnaces, for example, reduced the fuel consumption and NO_x emissions from 15% to 50% and from 50% to 90% respectively [1]. The flue gas after oxy-combustion predominantly consists of CO_2 and steam. After condensation of steam through cooling, the available CO_2 gas is easily captured, stored, and/or used for chemical production by well-established industrial technologies. Higher flame stability, better heat transfer characteristics, reduced gas volume and lower particulate emissions are other advantages of the oxy-fuel combustion process [2].

For oxy-combustion, it is to be noted that high purity oxygen makes a difference not only by reducing the harmful gas emissions (e.g. NO_x and SO_x) but also, it is important for CO_2 capture from the flue gas [3,4]. This is because, the CO_2 purity level in the flue gas decreases with decrease in O_2 purity level. Lower purity oxygen containing impurities (e.g. nitrogen) are amenable to forming NO_x as a combustion product, and be present with others (SO_x, Ar, N_2 etc.) in the flue gas. Lower purity oxygen used in oxy-combustion process is also considered detrimental to compression and liquefaction processes commonly used for the transportation of CO_2. Large scale conventional transportation process for transporting CO_2 includes the use of gas pipelines, ships and vessels. For such processes, it is required to compress CO_2 to supercritical state (~80–150 bar) for pipeline transport. On the other hand, CO_2 needs to be liquefied (~6.5 bar and −51 °C) for ship transport [4]. It is often found difficult to compress as well as liquefy the CO_2 gas stream if the impurities level is high (approximately greater than 4%) [4]. The impurities present in the post combustion CO_2 gas stream as well as compressed gas stream can also cause corrosion when introduced into the pipeline [3,4]. The presence of inerts constituents (e.g. N_2, Ar, He etc.) in the gas stream is also required to be removed and controlled as it can also increase the critical pressure of CO_2 in the pipeline [3]. Gas conditioning (a sub-system to remove impurities from CO_2 gas stream) step is conventionally incorporated to purify CO_2 along with CO_2 compression and drying. The specific energy requirement for gas conditioning is 100–200 kWh/ton (t) captured CO_2 (~360–720 kJ/kgCO_2). However, for approximately pure CO_2 stream, the energy requirement for compression is significantly reduced to 90 kWh/t captured CO_2 (~324 kJ/kgCO_2) [4].

An oxygen transport membrane (OTM) is required to separate high-purity oxygen from air for oxy-combustion of fuel [2,5–12]. The high-purity oxygen also finds application in metallurgical (iron and steel plants), chemical, petrochemical, medical and paper industries, welding and cutting [13]. Fig. 1 shows a simplified process flow diagram depicting the use of an oxygen transport membrane (air separation unit) in an integrated gasification combined cycle (IGCC) [14].

In the IGCC process, oxygen separated from air (air separation unit) reacts with coal particles or slurry to produce syngas at high temperature and pressure (~1000 °C and ~394.8 atm) [15]. The

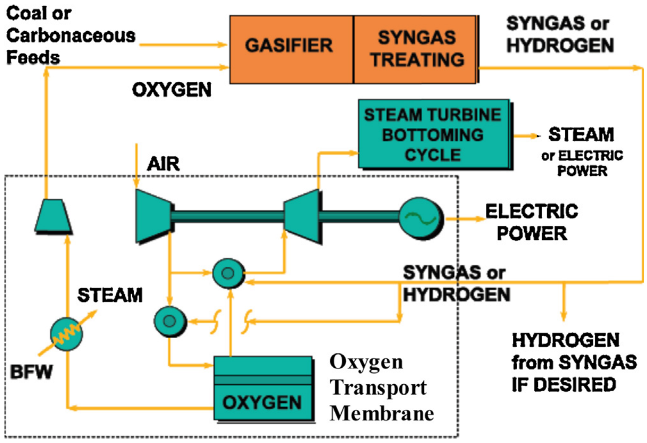

Fig. 1. Simplified process flow diagram of an oxygen transport membrane integrated in IGCC (BFW: Boiler Feed Water) [14].