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The impact of sulfur contamination on the performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen transport membranes

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Abstract

An oxygen transport membrane made from $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) has been tested for air separation by oxygen permeation at 900°C with the introduction of sulfur in the form of hydrogen sulfide. 200 ppm of hydrogen sulfide was fed either in the sweep-side (argon-side) or the air-side. The membrane was exposed for hydrogen sulfide for 100 hours. Results show that presence of hydrogen sulfide negatively influenced the oxygen permeation due to formation of strontium sulfate blocking the oxygen permeation pathway. When the hydrogen sulfide was removed from the system, the oxygen permeation was partially restored in case of argon-side contamination, while being fully restored in case of air-side contamination.

Keywords: Perovskite; Oxygen transport membrane; Sulfur contamination; Segregation, Oxygen flux

Introduction

Attention has recently turned to investigating new processes to produce large scale, high purity hydrogen. Currently, the main process is the energy intensive steam reforming of methane (SRM) to produce synthesis gas, a carbon monoxide and hydrogen mixture,

Careful control of the rate of supply of oxygen can facilitate the exothermic partial oxidation of methane (POM) to also produce syngas with the hydrogen to carbon monoxide ratio of two-to-one,

The POM process has advantages over SRM as it does not require heat to initiate the reaction and it overcomes chemical equilibrium limitation. However, the high cost of cryogenic units, to produce high quality oxygen, greatly influence the economics of this process. As an alternative, the emerging oxygen transport membrane (OTM) technology can be integrated in the POM process to offer the following features as they: (i) produce oxygen with 100% purity, (ii) provide a catalytic, active surface area for the reaction and (iii) reduce the oxygen production costs by 35% compared to cryogenic distillation [1-5]. Investigation of OTM materials is currently based on mixed oxygen ion and electron conducting (MIEC) perovskite-type metal oxides of general formula (ABO_3). These materials can be formed into gas-tight membrane structures and possess, theoretically, 100% selectivity to oxygen transport. The oxygen is transported *via* mobile point-defect oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) under an oxygen chemical potential difference across the membrane.

In order for this technology to be transferred from the research environment to industry, the long term durability of OTMs must be tested under simulated, severe operating conditions for prolonged periods of time. The main issues are : (i) segregation of constituent oxides (kinetic demixing) often leading to formation of new phases at the surfaces, (ii) reaction of constituent oxides with traces of acid gases e.g., CO_2 , SO_2 and H_2S present in the hydrocarbon feed (e.g., natural gas) to form carbonates, sulfates and sulfides, and (iii) reaction of products with the OTM [6-11]. These mechanisms can act to reduce the performance of the OTM in the long term and may give rise to failure.

In this contribution we focus on the impact of hydrogen sulfide on the oxygen transport properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) planar membranes introduced on one side of the membrane. Post-operation analyses using SEM-EDS, XRD and XPS on the OTM exposed surface are reported.

Experimental

Membrane reactor and oxygen permeation studies

The gas-tight, LSCF6428 disk membrane (nominally of diameter 1.6 cm and 0.18 cm thickness, geometric area of 2.1 cm²) was fabricated from commercial powder (Praxair). Approximately two grams of the powder were weighed and transferred to a steel die of diameter, 2 cm. The die was then inserted into a mechanical press (Specac, Atlas Power T25) and pressed (3 tonnes) to form the green membrane. The membrane was then sintered at 1250°C using a box furnace (Carbolite, RHF1500) for five hours. The membrane reactor or membrane module was fabricated from Quartz with alumina tubing employed internally. The LSCF6428 active membrane was sealed to the alumina tube using silver paste (Fuel Cell Materials, Ag-I) chosen for the long-term experiments because of its high stability compared to glass and ceramic sealants [12]. Synthetic air (20.5% O₂, 79.5% N₂) was used as the source of oxygen for the air-side while argon (99.999%) was used for the sweep-side (argon-side). Hydrogen sulfide with concentration of 200 ppm in argon was used as the sulfur-containing gas and it was introduced either in the argon-side or the air-side. The gas supply to the membrane was controlled using a bank of mass flow controllers (Brooks, SLA5850). The gas from the argon-side was fed to a gas chromatograph (Varian, CP-3800) equipped with a thermal conductivity detector (TCD) and molecular sieve 5A column. The gas chromatograph was calibrated using a cylinder containing 2% O₂ and 2% N₂ in argon. The membrane was positioned close to the center and in the isothermal zone of a vertical tube furnace (Vecstar, VCTF1). The temperature near the membrane was measured using an internal thermocouple.

Assuming ideal gas behavior, the oxygen flux (J_{O_2}), $\mu\text{mol (STP) cm}^{-2} \text{ s}^{-1}$, is calculated by,

$$J_{O_2} = \frac{\left[y_{O_2} - \frac{0.21}{0.79} y_{N_2} \right]}{24465 \times 60} \times \frac{F}{A} \times 10^6 \quad (3)$$

Where y_{O_2} and y_{N_2} are the mole fractions of oxygen and nitrogen in the argon-side gas measured by the gas chromatograph. F is the flow rate of the inlet gas in ml (STP) min⁻¹ and A is the active membrane cross-sectional area (cm²). The term $\left(\frac{0.21}{0.79} y_{N_2}\right)$ refers to the amount of leaked oxygen from the air-side to the argon-side through the sealant. Leak monitoring was performed by determining the nitrogen in the argon-side. The experiment was considered a failure if more than 5 mol% (1.5 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$) of nitrogen was detected in the argon-side [12]. In the reported experiments the nitrogen mole fraction was less than 2 mol% (0.6 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$). The experiments were performed at atmospheric pressure and the temperature was set to 900°C by ramping at 1°C min⁻¹. For experiments with argon-side contamination by hydrogen sulfide, flowrates of 20 ml (STP) min⁻¹, each, were used for the air and the argon. Hydrogen sulfide was introduced in the argon-side by replacing the pure argon with argon containing 200 ppm of hydrogen sulfide. For experiments with air-side contamination by hydrogen sulfide, air and pure argon, 20 ml (STP) min⁻¹ each, were mixed and fed to the air-side while pure argon was fed to the argon-side using flowrate 20 ml (STP) min⁻¹. The mixing in the air-side results in a lowering of the oxygen partial pressure from 0.21 atm (the reactor was operated at atmospheric pressure) to 0.105 atm and hydrogen sulfide concentration to 100 ppm. In both experiments of argon-side and air-side contamination, the oxygen permeation was measured before, during and after the hydrogen sulfide exposure. The membrane was exposed to hydrogen sulfide for 100 hrs.

Characterization techniques

A Rontec Quantax 1.2 FEI XL30 ESEM-FEG system was used to carry out microstructural characterization by scanning electron microscopy (SEM) and non-quantitative elemental analysis by energy dispersive x-ray spectroscopy (EDS). Crystallinity and phase purity were determined by powder X-ray diffraction (XRD) using a PANalytical X'Pert Pro Multipurpose Diffractometer (PW3040/60) fitted with an X'Celerator and a secondary monochromator. For data acquisition, the Cu anode was supplied with 40 kV and a current of 40 mA to generate Cu K- α radiation ($\lambda = 1.54180 \text{ \AA}$) or Cu K- α_1 ($\lambda = 1.54060 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was employed to determine the elemental composition and the data was collected on a Theta Probe (Thermo Scientific) using a microfocused monochromatic AlK α x-ray source operated at 100W.

Results and Discussion

Oxygen permeation studies with argon-side contamination by hydrogen sulfide

Oxygen permeation was measured at 900°C using feeds of air and argon for 49 hours. Figure 1 shows that the permeation was 0.030 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$ immediately before hydrogen sulfide introduction. The figure also shows that

the permeation increases with time. Such behavior has been reported by many researchers; the time to reach the steady state can be between 25 to 300 hrs [13, 14]. The increase in the permeation rate may be related to the changing degree of reduction of the membrane leading to a change in oxygen vacancy concentration and a decrease in the bulk resistance or a modification of the surface kinetics. After replacing the pure argon with argon containing 200 ppm of hydrogen sulfide, the oxygen permeation instantly dropped (on the timescale of gas sampling of 30 minutes for the GC) to zero (within the measurement uncertainty of the system – a flux of $0.0001 \mu\text{mol cm}^{-2} \text{s}^{-1}$ could be measured). The flux showed some sign of recovery when the hydrogen sulfide was replaced with argon and 42% ($0.012 \mu\text{mol cm}^{-2} \text{s}^{-1}$) of the permeation was restored and remained approximately constant for a further 193 h.

SEM was used to characterize the membrane surface after the exposure to hydrogen sulfide and secondary phases were apparent. EDS indicated that these phases have high amounts of sulfur and strontium. XPS was employed to determine the form of sulfur and it was assigned to metal sulfate with a binding energy of 169.1 and 170.2 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively (Fig. 3). No metal sulfide or elemental sulfur was detected at 161 eV. XRD also identified this metal sulfate as strontium sulfate (Fig. 4). Strontium sulfate can be formed by the following reaction, thermodynamic data as taken from [15],

The rate of oxygen release into the argon side should not be confused with the rate of oxygen permeation through the membrane. Oxygen permeation coupled with complete conversion of this oxygen through reaction (4) may result in no oxygen release into the argon side. To investigate this statement, an oxygen mass balance was performed and there should be $0.019 \mu\text{mol cm}^{-2} \text{s}^{-1}$ of oxygen in excess after the consumption in reaction (4). However, the rate of oxygen permeation was undetectable in the argon-side and this could be due to the formation of strontium sulfate on the surface blocking the surface and preventing sufficient release of oxygen. After removal of hydrogen sulfide from the argon-side, a fraction of the initial oxygen permeation (42% or $0.012 \mu\text{mol cm}^{-2} \text{s}^{-1}$) was recovered. This value of oxygen permeation is the same as that required to fully oxidize the hydrogen sulfide in reaction (4). Therefore, restoration of the oxygen permeation may have been due to the absence of hydrogen sulfide rather than any reverse of the poisoning mechanism.

Oxygen permeation studies with air-side contamination by hydrogen sulfide

Oxygen permeation was measured at 900°C over 98 hours before hydrogen sulfide introduction to the air side. Immediately before hydrogen sulfide introduction the permeation rate was $0.095 \mu\text{mol cm}^{-2} \text{s}^{-1}$ (Fig. 2). The permeation rate decreased to 44% of its initial value ($0.042 \mu\text{mol cm}^{-2} \text{s}^{-1}$) during the exposure but was fully restored after the removal of hydrogen sulfide from the air-side. SEM and EDS showed a secondary phase enriched with strontium and sulfur on the surface exposed to hydrogen sulfide. XRD confirmed that the phase is strontium sulfate (Fig. 3). Interestingly, XPS analysis (Fig. 4) indicated that the amount of strontium sulfate on the surface in the air-side experiment is higher than the argon-side experiment. This could be as a result of strontium segregation to the air-side surface increasing the formation of strontium sulfate [16]. It is difficult to draw definite conclusions about the different deactivation mechanisms that may be occurring in the presence of the argon-side and air-side contamination. However we must recall that the environments of the two surfaces are quite different. First, the membrane surface under air-side contamination will have a higher oxygen chemical potential than the argon-side contamination. Second, the oxygen in the air-side could react with hydrogen sulfide to form sulfur dioxide before interacting with the membrane surface thus; the environment is also different from that of the case of argon-side contamination.

Conclusions

In this study, membranes made of LSCF6428 were investigated for oxygen permeation using air under the presence of hydrogen sulfide introduced with the sweep argon or the air feeds. Results show that presence of hydrogen sulfide instantly decreases oxygen permeation. Characterization of the membrane surface indicated formation of strontium sulfate and this blocking layer could be the reason for the reduction in oxygen permeation. After removing the hydrogen sulfide from the feed, the membrane performance was partially restored in case of argon-side contamination, while being fully restored in case of air-side contamination. This partial restoration of permeation in the case of argon-side contamination could be due to the fact that oxygen is no longer being consumed by strontium sulfate formation as well as reversal of the poisoning of the membrane surface. The fact that oxygen permeation could be fully restored in the air-side contamination experiment could be related to the higher oxygen chemical potential of that surface (resulting in a resistance to poisoning) or the different gaseous

environment as hydrogen sulfide could be converted to sulfur dioxide before interacting with the membrane in this case.

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Fig. 1. Oxygen permeation of LSCF6428 membrane after introduction of hydrogen sulfide (200 ppm in argon) in the argon-side at 900°C. The permeation was partially restored after removal of hydrogen sulfide feed.

Fig. 2. Oxygen permeation of LSCF6428 membrane after exposure to hydrogen sulfide (200 ppm in argon) fed to the air-side at 900°C.

Fig. 3. XPS analysis of the surface exposed to hydrogen sulfide (200 ppm in argon) for the two experiments of argon-side and air-side contamination.

Fig. 4. XRD data of the surface exposed to hydrogen sulfide (200 ppm in argon) in the argon-side and air-side experiments.