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Air separation using a catalytically modified mixed conducting ceramic hollow fibre membrane module

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Abstract

A membrane reactor module consisting of four gas-tight hollow fibre membranes made of the mixed ionic-electronic conducting perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ has been tested for oxygen permeation in the temperature range of 650–1000 °C with air on one side and helium on the other. The module was operated under gradientless gas-phase conditions and in the absence of mass transfer limitations at lower temperatures. Also at lower temperature the rate-determining step for oxygen permeation was found to be oxygen reduction with the oxygen permeation performance of the module being significantly enhanced by deposition of a porous platinum catalyst film onto the air-side of the membranes. A stable but mass transfer limited flux of 0.56 μmol cm^{-2} s^{-1} (0.73 ml STP cm^{-2} min^{-1}) was achieved after a period of 4 days of operation at 1000 °C and continued at this rate for a further 4 days. A non-mass transfer limited flux of *ca* 0.14 μmol cm^{-2} s^{-1} was obtained at 800 °C. The membrane module was operated for 500 h before the onset of significant leakage. Post operation qualitative analysis indicated localised changes in the stoichiometry of the membranes with no discernable trend, quantitative analysis on the other hand revealed that the perovskite had retained its starting composition.

Post-operation analysis of the membranes revealed the presence of sulfur in the form of sulfates of strontium, cobalt and calcium and a change of surface microstructure for both the air- and lumen-side membrane surfaces. Possible sources of this sulfur contamination are: the glass-ceramic sealing material employed, the helium sweep gas and atmospheric sulfur dioxide. This contamination may contribute to the decrease in the long-term oxygen permeation rates. The metal cation stoichiometry of the perovskite showed changes in localised areas of the membranes following oxygen permeation studies.

Keywords: Perovskite; $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$; Hollow fibre; Porous platinum catalyst film; Oxygen permeation

1. Introduction

The rich magnetic, optical, redox and catalytic properties of metal oxides can be utilised for many applications [1]. Amongst the most studied family of metal oxides is the highly versatile cubic perovskite phase [2–4]. These ABO_3 solid oxides are formed from combining lanthanide or group II element cations (A-site cation) and typically, thought not exclusively, first row transition metal cations (B-site cation) into the cubic close packed structure. They possess rich defect chemistry created by doping of suitable cations into the structure and evidenced by the creation of oxygen vacancies within the oxygen sublattice, $V_O^{\bullet\bullet}$, (represented in Kröger–Vink notation) and electronic n- and p-type conductivity at high temperature under appropriate gas atmosphere compositions. Thus the material is imparted with mixed ionic-electronic conducting (MIEC) properties.

When formed into dense membranes and subjected to high temperatures and oxygen chemical potential differences, these membranes can transport pure oxygen through the combination of mobile oxygen vacancies and electronic defects while simultaneously excluding the transport of other gas-phase species. Interest has grown in applying MIEC membranes to industrial processes such as air separation, oxidative coupling of methane and synthesis gas production in catalytic membrane reactors (CMR) as they offer product separation and oxygen supply in one unit [5]. Commercial advantage can also be gained if freely available atmospheric oxygen is used. Their inherent electronic conductivity removes the necessity of external circuitry to pump the oxygen from one side to the other, simplifying the reactor and also removing electrode-membrane contact resistances, an inherent problem with pure ionic conductors.

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The mechanism of oxygen transport through MIECs involves oxygen disassociation and reduction on the membrane surface followed by incorporation into the perovskite lattice as oxygen anions, O_O^x (in Kröger–Vink notation), that can migrate through the crystal lattice via oxygen vacancy defect sites. This process is activated and can be hindered by slow surface kinetics at the membrane surface and long solid-state diffusional path length i.e., large membrane thicknesses. The impact of these two factors can be reduced by employing membranes of high surface area and small wall thickness. This can be achieved with membranes in the form of hollow fibres. The hollow fibres provide a high membrane surface area per unit volume of reactor compared to the conventional disc and tubular forms typically used. The hollow fibres have diameters typically *ca* 1–2 mm with wall thicknesses in the range 0.2–0.3 mm; disk and tube membranes typically have thicknesses of *ca* 1–2 mm. Interest in hollow fibres is growing, and a number of groups have begun work in fabricating and characterising the structure and oxygen permeation performance of a number of perovskite based hollow fibre membranes [6–17]. One of the most studied perovskite membrane materials is $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{33-\delta}$ (abbreviated to LSCF6428) because of its stability. Stability of the crystal structure is crucial if commercial exploitation is to be realised as degradation over time caused by kinetic demixing of the constituent cations under a thermodynamic gradient may lead to membrane failure [18–20]. Catalytic modification of the membrane surface can increase the rate of surface processes and therefore the oxygen permeation performance when such processes are limiting. This approach has been tried, and proved successful, using photolithography to deposit regularly spaced platinum disks onto a disk membrane of $SrCo_{0.5}FeO_x$ MIEC [21]. The oxygen permeation achieved was up to double that of an unmodified test sample of the same material in the temperature range 600–800 °C.

In our previous work a hollow fibre membrane reactor of the shell and tube type (with the tube replaced with a bundle of hollow fibres) was tested for oxygen permeation and methane oxidation using catalytically unmodified membranes [22]. The reactor was operated under conditions under which there was an axial oxygen chemical potential gradient on both sides of the membrane giving rise to a gradient in oxygen permeation rate. In contrast to this, a gradientless reactor would allow oxygen permeation rates to be accurately determined as a function of operating conditions.

In this contribution we report on the performance of a catalytically unmodified and catalytically modified MIEC LSCF6428 gradient-less hollow fibre reactor module with respect to oxygen permeation over the temperature range of 650–1000 °C and also present information on post-operation characterisation.

2. Experimental

2.1. Characterisation

Commercial LSCF6428 (Praxair) was used to produce the dense hollow fibre membranes by the phase inversion technique. This method and the membrane gas-tightness testing apparatus are described elsewhere [13,14]. Crystallinity and phase purity was ascertained by powder X-ray diffraction (XRD) using a PANalytical X'Pert Pro diffractometer fitted with a X'Celerator and employing Cu Kα radiation, $\lambda = 1.54180$, or Cu Kα1, $\lambda = 1.54059$. A nominal step size of 0.033 degrees two-theta with a step time of 100 s in continuous mode was routinely used. Diffractograms were recorded on ground membrane samples and whole hollow fibre samples. A Röntec Quantax 1.2 FEI 30XL ESEM FEG system was used to perform scanning electron microscopy (SEM) for microstructure characterisation and for standard-less qualitative elemental analysis by energy dispersive X-ray analysis (EDS). Elemental mapping was performed after EDS to ascertain possible segregation of elements. Quantitative analysis of the bulk composition of the used hollow fibre membranes was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Unicam 701 ICP-OES. Calibration for the elements of interest over the range 0–100 ppm was done using certified single element standards. The sample was introduced at a rate of 1 ml min^{-1} and the plasma was operated at a power of 1 kW with a coolant flow of 13 L min^{-1} and an auxiliary flow of 0.5 L min^{-1}.

2.2. Catalytic surface modification

A module was made comprising of four hollow fibres whose outer air-side surfaces were coated with a layer of platinum. A platinum resinate (M603B supplied by Metalor, UK) containing 14 wt% platinum was crudely applied onto the outer surface of the central 5 cm of each hollow fibre using a small fine brush. The membranes were then fired using a programmed temperature ramp of 10 °C min^{-1} to 400 °C, held for 1 h, then 10 °C min^{-1} to 900 °C, held for 1 h, and then 10 °C min^{-1} to 25 °C to remove the organic resin and sinter the platinum metal onto the membrane surface. The average surface loading of the catalytically modified hollow fibres was *ca* 3 mg cm^{-2}. Hollow fibre membranes coated with platinum will be referred to hereafter as Pt-HF and uncoated as HF. A diagram of the hollow fibre reactor module is given in Fig. 1 with an expanded schematic of a single hollow fibre indicating the central 5 cm exposed to the atmosphere.

2.3. Oxygen permeation experiments

The membrane performance apparatus employed consisted of gas supply and gas flow control, the hollow fibre reactor module with furnace and online gas chromatography for analysis of the gas stream. All experiments were performed at a total pressure of one atmosphere on both sides of the membrane. The gas supply to the lumen-side of the reactor module was controlled by an Aalborg mass flow controller calibrated for 100% helium and ranged from 0 to 200 ml min^{-1}. All gas flows are quoted at standard temperature and pressure (STP). The upstream and downstream gas flow rates through the lumen were independently monitored using a digital flow meter (Varian). The apparatus has been described elsewhere [22] and will not be repeated here, the only difference being the reactor modules used in this work have no shell. A heating or cooling rate of 1 °C min^{-1} was used when required throughout this investiga-