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High oxygen permeability in fluorite-type $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ via the use of sintering aids

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Abstract

Minor (2 mol%) additions of cobalt oxide are highly effective as a sintering additive for the fluorite material $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ allowing dense materials to be formed at 1000 °C with sub-micron grain size. The addition gives slightly enhanced total conductivity due to an enhanced electronic conductivity of around two to three times, whilst the level and nature of ionic conductivity is unaffected. This produces a decrease in ionic transference number, an increase in the ambipolar conductivity and importantly a decrease in oxygen surface exchange limitations. The combination of these effects boosts the level of oxygen permeability offered by this fluorite material to levels that can compete with some of the best perovskite oxygen permeation membranes at intermediate temperatures, (<850 °C), in a material that offers good redox stability. As such, the material $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ containing minor (2 mol%) additions of cobalt oxide offers one of the highest levels of oxygen permeability reported to date for a single component, mixed conducting, fluorite material.

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1. Introduction

Materials with mixed oxide ion and electronic conductivity (MIEC) have been suggested for many solid-state electrochemical applications, including fuel cells, sensors, electrocatalysts, etc. One of the most important practical applications is their use in electrochemical ceramic membranes for oxygen separation and partial oxidation of light hydrocarbons [1–5]. Typically, the materials considered as most promising for membrane reactors are those based on phases with perovskite-related structures, such as $SrCoO_{3-\delta}$ or $SrFeO_{3-\delta}$, which offer high ambipolar conductivities and subsequent high oxygen permeabilities at high temperatures [1–6]. Significant drawbacks to the widespread adoption of ceramic membranes derived from both these parent perovskite compositions have been their poor redox stabilities at high temperature leading to decomposition, degradation of ion transport parameters, and/or mechanical failure due to elevated thermal and chemical expansion [1–4]. Moreover, these common perovskite-related materials are in general unsuitable for use in intermediate temperature devices due to considerable activation energies which lead to poor levels of oxygen permeability at lower temperatures, due to extensive vacancy-ordering processes [5–7].

Materials with the fluorite structure have on the whole shown less promise as oxygen separation membranes due to lower levels of ambipolar conductivity. As such, focus continues to rely heavily on the development of perovskite related materials for this application. In this work, we show how minor (2 mol%) additions of cobalt oxide as a sintering aid can significantly boost the level of oxygen permeability in a fluorite material to a level that can compete with the more common perovskite-type membrane materials, providing promising oxygen permeabilities at intermediate temperatures in a material that also offers superior redox stability. This is important not just due to the positive behaviour noted for the current material but also as a possible technique to boost permeability in other ceramic oxide materials including the perovskites. To the authors best knowledge we also document the highest oxygen permeability reported to date for a stable, single component, mixed conducting, fluorite material.

Of the fluorite materials, bismuth oxide based MIECs are usually quoted as offering the highest levels of oxygen permeability, although the disordered fluorite phases based on

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δ-Bi_2O_3 are thermodynamically unstable below 700 °C under oxidizing conditions where phase transformation leads to a dramatic decrease in ionic transport, and are completely decomposed in even moderately reducing atmospheres [2]. Materials from the fluorite solid solution $Ce_{1-y}Pr_yO_{2-\delta}$ have traditionally been suggested for use as possible gas sensors, catalyst supports and/or oxygen storage materials in automotive catalysis [8–14] due to their ability to accommodate extensive deviations from stoichiometry with high rates of oxygen exchange and diffusion, whilst offering good stability in repeated redox cycles. Recent interest, however, has focused on these materials as possible oxygen separation membranes. The material $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ was previously shown to offer a non-competitive level of oxygen permeability that was limited by both the level of electronic conductivity and oxygen surface exchange limitations [15–18]. We now show that the minor addition of 2 mol% cobalt oxide as a sintering aid to this material can enhance electronic conductivity and can eradicate the detrimental oxygen surface exchange limitations, successfully boosting the level of oxygen permeability to competitive levels. The idea behind this work follows from the observation of a significant enhancement of electronic conductivity in the material $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) by minor (2 mol%) additions of sintering aids [19,20] and the observation that this enhancement of electronic conductivity dramatically improved oxygen reduction kinetics [21].

2. Experimental

Stoichiometric amounts of high-purity Pr_6O_{11}, and $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in an aqueous solution of hot nitric acid. After drying, the nitrate mixture was decomposed at 700 °C for 5 h. The resultant powder was ball-milled in a nylon mill with zirconia balls. Addition of the cobalt oxide sintering aid was in the form of an aqueous solution of the nitrate to the $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ powder followed by drying and further light milling in an agate pestle and mortar. Pellets of the Co-doped and Co-free material were uniaxially dry pressed at a pressure of 30 MPa followed by isostatic pressing at 200 MPa. Sintering behaviour was studied on a Linseis dilatometer on rectangular green compacts approximately (2 mm × 3 mm × 8 mm) with a constant heating rate of 5 °C/min. Further samples were prepared for microstructural and electrical characterisation. Co-free compositions were sintered at 1600 °C for 10 h followed by cooling at 2 °C/min. while Co-doped compositions were sintered at 1000 °C for 5 h with the same slow cooling rate. Overall phase composition was determined by X-ray diffraction (XRD) using a Rigaku Geigerflex diffractometer (Cu Kα radiation), (5–80°, step 0.02, 6 s/step). Microstructural characterisation was performed by scanning electron microscopy (SEM) for the Co-free samples, polished and then thermally etched for 60 min at temperatures 100 K below that of the sintering temperature, Co-doped samples were analysed by atomic force microscopy (AFM) in tapping mode. Average grain sizes were calculated using an image-processing program based on the intercept method [22].

Total conductivity in air was performed on dense bars, approximately 3 mm × 4 mm × 14 mm using the ac impedance method. Steady state oxygen permeability was performed in a ceramic cell based on closed chambers with the material under study functioning as a permeating wall. The establishment of an oxygen potential gradient between the inner and outer surfaces of the chamber walls was by means of an electrochemical pump, as described elsewhere [23,24]. Active membrane diameter was approximately 8 mm. The absence of leaks was confirmed by monitoring the temperature dependence of permeability and the transient recovery of the cell from reducing to oxidizing conditions after current interruption, as described elsewhere [25]. All data on the oxygen permeability presented in this paper correspond to the membrane feed-side oxygen partial pressure (p_2) equal to 0.21 atm, atmospheric air. The permeation processes are discussed using the quantities of oxygen flux density, j, and specific oxygen permeability, $J(O_2)$, which are interrelated as

$$J(O_2) = jd\left[\ln\frac{p2}{p1}\right]^{-1} \tag{1}$$

where $p1$ is the oxygen partial pressure at the membrane permeate side ($p1 < p2$). The quantity $J(O_2)$ is useful to identify surface exchange rate-limiting effects on oxygen permeation by analyzing the dependence of the permeation flux on membrane thickness [23]. As this quantity is proportional to *jxd by definition*, the values of $J(O_2)$ should be thickness independent when surface limitations are negligible. In this situation, $J(O_2)$ is proportional to the ambipolar conductivity (σ_{amb}), averaged for a given oxygen partial pressure range ($\overline{\sigma_{\mathrm{amb}}}$) where t_o is the oxygen ion transference number, and σ, σ_o, and σ_e represent the total, oxygen ionic, and electronic conductivities, respectively.

$$J(O_2) = \frac{RT}{16F^2}.\overline{\sigma_{\mathrm{amb}}} = \frac{RT}{16F^2}\overline{\frac{\sigma_o\sigma_e}{\sigma_o+\sigma_e}} = \frac{RT}{16F^2}\overline{\sigma t_o(1-t_o)} \tag{2}$$

When oxygen surface exchange limitations are considerable the values of $J(O_2)$ should increase with membrane thickness due to a decreasing role of the surface exchange, for a given oxygen chemical potential gradient.

Minor electron–hole conductivity was separated from total electrical conductivity using the modified e.m.f. method first proposed by Gorelov [26]. This modification of the classical e.m.f. technique, based on determination of the open-circuit voltage of oxygen concentration cells, increases measurement sensitivity and eliminates possible errors in the determination of ion transference numbers arising due to electrode polarization, errors that are shown to be non-negligible for electrolyte-type materials which possess relatively minor electronic conductivity [27]. The experimental set-up, measurement procedure and also comparison of this technique with the traditional approach are well documented in the literature [27]. The activation energy (E_a) for the partial ionic conductivities, Table 1, was calculated by the standard Arrhenius equation

$$\sigma_o = \frac{A_o}{T}\exp\left[-\frac{E_a}{RT}\right] \tag{3}$$

where A_o is the pre-exponential factor.

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