Oxygen permeability and surface kinetics of composite oxygen transport membranes based on stabilized δ-Bi₂O₃

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Abstract

Composite ceramic membranes based on the ionic conducting Tm-stabilized δ-Bi₂O₃ (BTM) and the electronic conducting (La₀.₈Sr₀.₂)₀.₉₉MnO₃₋δ (LSM) exhibit among the highest oxygen flux values reported for Bi₂O₃-based membranes. Here, we use pulse-response isotope exchange (PIE) and oxygen flux measurements to elaborate on limiting factors for the oxygen permeation in BTM - 40–70 vol% LSM composites. Once both phases percolate, between 30 and 50 vol% BTM, the flux is essentially independent of the BTM/LSM volume ratio. The oxygen permeability is under mixed diffusion- and surface control, gradually becoming more bulk-limited with increasing temperature. The oxygen exchange coefficients of BTM-LSM are significantly higher than its constituent phases, revealing that a cooperative surface exchange mechanism enhances the kinetics. Some of the Tm was substituted with Pr to introduce electronic conductivity in BTM. (Bi₀.₈Tm₀.₁₅Fe₀.₆₅)₂O₃₋δ (BTP) exhibits higher surface exchange coefficients compared to BTM, but the oxygen flux remains one order of magnitude lower than that of percolating BTM-LSM composites.

1. Introduction

Dense, ceramic oxygen transport membranes (OTMs) combining high oxygen flux with chemical and mechanical stability find applications such as in oxy-fuel combustion and reactors for partial oxidation of methane. A few single-phase materials have shown the required transport properties, but suffer from reactivity towards acidic gases [1], while technologically implementation [3]. Oxygen transport in dual-phase membranes is commonly limited by the oxide ion conductivity.

In its narrow stability range from approximately 825 to 730 °C, cubic bismuth oxide (δ-Bi₂O₃) exhibits the highest reported oxide ion conductivity among binary oxides [4,5]. In order to prevent phase transition to the poorly conducting α-phase, the δ-phase is stabilized to lower temperatures by substitution with rare-earth cations of similar radii and the same valence as Bi [6–11]. Since the electronic conductivity of Bi₂O₃ is inherently low, Bi₂O₃-based phases need to be combined with an electronic conductor to reach appreciable oxygen fluxes [12]. There are several reports in the literature on composites between stabilized δ-Bi₂O₃ and a metallic phase (cermet) consisting of either Ag or Au. The highest flux has been achieved with 40 vol% Ag, where the oxygen flux increases by 1–2 orders of magnitude compared to single-phase Bi₂O₃, mainly attributed to improved electronic conductivity [12–15]. Effects of the metallic phase on the surface exchange kinetics are elusive with conflicting literature results [12–14,16–18].

Ceramic mixed conducting composites comprising oxide ion and electronic conducting phases are alternatives to cermet and single-phase mixed oxide ion-electron conductors [19,20]. Oxide ion conductors such as Gd-doped ceria and Y-stabilized zirconia combined with an electronically conducting oxide have been tested as OTMs, yielding only moderate oxygen fluxes [21–26]. We have recently reported a composite membrane of 60 vol% (Bi₀.₈Tm₀.₂)₂O₃₋δ (BTM) and 40 vol% (La₀.₈Sr₀.₂)₀.₉₉MnO₃₋δ (LSM) that shows high oxygen fluxes - comparable to that of e.g., (Bi₀.₈Tm₀.₁₅Fe₀.₆₅)₂O₃₋δ (BSCF) [27].

The present contribution addresses the surface and bulk properties of the BTM-LSM system to determine the limiting factors for the oxygen permeation. We seek to optimize the performance by improving the microstructure and varying the BTM/LSM volume ratio. To examine the potential of stabilized δ-Bi₂O₃ as a single-phase OTM, we introduce...
mixed conductivity in BTM by substituting some of the Tm with Pr, yielding \((\text{Bi}_0.8\text{Tm}_{0.2})_2\text{O}_3\) (BTP). Flux measurements were performed as a function of temperature and oxygen partial pressure gradient, and oxygen exchange coefficients were measured as a function of temperature by means of pulse-response isotope exchange (PIE).

2. Experimental

Powders of \((\text{Bi}_{0.8}\text{Tm}_{0.2})_2\text{O}_3\) (BTM) and \((\text{Bi}_{0.8}\text{Tm}_{0.15}\text{Pr}_{0.05})_2\text{O}_3\) (BTP) were synthesized by solid-state reactions. \((\text{La}_{0.8}\text{Sr}_{0.2})_2\text{O}_{3-\delta}\) (LSM) powder synthesized by spray pyrolysis was purchased from Cerapotech AS. The BTM-LSM composites were made by mixing defined volume ratios of the constituent phases, pressing pellets and finally sintering at 1000 °C for 10 h. Table 1 presents the compositions investigated in this work. For more details, see S-2.2 in the Supporting Information.

The sintered membranes were sealed to the alumina support tube of a ProboStat™ measurement cell using a gold ring. Mass flow controllers defined the supply of \(\text{O}_2\), \(\text{He}\) and \(\text{N}_2\) feed gas mixtures and \(\text{Ar}\) sweep gas. The composition of the sweep gas was measured at the outlet with a gas chromatograph (GC). Oxygen flux measurements were performed in the temperature range 600–900 °C (S-2.2 for details).

Oxygen exchange kinetics of BTM, BTP, BTM-LSM 60/40, BTM-LSM 50/50 and BTM-LSM 30/70 were investigated by means of PIE [28]. Powders of 90–125 μm dense particles were studied in the temperature range 600–900 °C at a \(p_{\text{O}_2}\) of 0.21 atm. \(\text{Ar}\) was used as carrier gas. The \(\text{O}_2/\text{Ar}\) pulse response was analyzed at the exit of the reactor using a quadrupole mass spectrometer (MS) (S-2.3 for details).

3. Results

Fig. 1 presents the temperature dependence of the oxygen flux for single-phase BTP and samples with different volume ratios of BTM and LSM. The oxygen flux of BTM-LSM 30/70 is more than one order of magnitude higher than that of BTM, due to the volume ratio of BTM and LSM having only a minor influence on the electrical conductivity [10]. We address three different limiting cases; pure electrical conductivity [10]. We address three different limiting cases; pure electrical conductivity, mixed electrical conductivity and a combination of both. The nonlinear behaviors in Fig. 1 indicate that more than one process affects the overall oxygen permeation. The transport properties of BTM and LSM render high ambipolar oxide ion-electron conductivity which may result in effects of surface kinetics on the oxygen permeation, even for millimeter thick membranes. Aiming to further rationalize the data, the oxygen exchange kinetics was investigated. Fig. 4 shows an Arrhenius representation of the oxygen exchange coefficient, \(k\), for BTP, BTM, BTM-LSM 60/40, 50/50 and 30/70 composites and, moreover, literature data for LSM [29]. The composites exhibit significantly higher oxygen exchange coefficients than their constituent phases; one order of magnitude higher than BTM and two orders of magnitude higher than LSM. The volume ratio of BTM and LSM has only a minor influence on the value and temperature dependence of \(k\). BTP exhibits higher oxygen exchange coefficients than the other two single-phase materials.

Disregarding that \(k\) does not strictly follow Arrhenius behavior, the BTM-LSM composites exhibit apparent activation energies for oxygen exchange in the same range as single-phase BTM and LSM [29], varying between 110 and 140 kJ/mol.

4. Discussion

To rationalize the oxygen flux characteristics, we use the temperature and oxygen pressure dependence of the flux data and the surface kinetics measurements in combination with literature data on the electrical conductivity [10]. We address three different limiting cases; pure diffusion control, and surface kinetics control with linear and non-linear relations between the oxygen chemical potential gradient and the oxygen flux. Details on the models, the assumptions and data analyses are presented in the Supporting Information, S-1 to S-3.

The relation between the flux and the oxygen chemical potential gradient is linear for surface-controlled oxygen flux as long as the gradient across the permeate side is relatively small. For large \(p_{\text{O}_2}\) gradients, however, nonlinear relations are prone to affect interpretation of oxygen flux data. As for the present dataset, we have applied a Butler-Volmer based formalism to assess effects of large chemical potential gradients across the permeate side solid-gas interface (S-3.1 and S-3.2, Fig. S-2 a and b) [30–32]. Moreover, the oxygen flux assuming bulk control was estimated using literature data on the electrical conductivity.

Table 1: Sample abbreviations, phase compositions and volumetric ratios for the samples investigated in this work.

<table>
<thead>
<tr>
<th>Sample abbreviation</th>
<th>Phase A</th>
<th>Phase B</th>
<th>Volumetric ratio A and B</th>
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<tbody>
<tr>
<td>BTM</td>
<td>((\text{Bi}<em>0.8\text{Tm}</em>{0.2})_2\text{O}_3)</td>
<td>-</td>
<td>100 %</td>
</tr>
<tr>
<td>BTM-LSM 30/70</td>
<td>((\text{Bi}<em>0.8\text{Tm}</em>{0.2})_2\text{O}_3)</td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})<em>2\text{O}</em>{3-\delta})</td>
<td>30 % and 70 %</td>
</tr>
<tr>
<td>BTM-LSM 50/50</td>
<td>((\text{Bi}<em>0.8\text{Tm}</em>{0.2})_2\text{O}_3)</td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})<em>2\text{O}</em>{3-\delta})</td>
<td>50 % and 50 %</td>
</tr>
<tr>
<td>BTM-LSM 60/40</td>
<td>((\text{Bi}<em>0.8\text{Tm}</em>{0.2})_2\text{O}_3)</td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})<em>2\text{O}</em>{3-\delta})</td>
<td>60 % and 40 %</td>
</tr>
<tr>
<td>BTP</td>
<td>((\text{Bi}<em>{0.8}\text{Tm}</em>{0.15}\text{Pr}_{0.05})_2\text{O}_3)</td>
<td>-</td>
<td>100 %</td>
</tr>
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Fig. 1. Oxygen flux as a function of inverse temperature for BTM-LSM composite membranes with different phase ratios. The data for BTM-LSM 60/40 is taken from Ref. [27]. The thickness of BTM-LSM 60/40 is 1.35 mm, while both BTM-LSM 50/50 and BTM-LSM 30/70 are 1.5 mm thick. The thickness of BTP is 1.3 mm.
of BTM. Fig. 5 shows that the BTM-LSM 60/40 flux data fall between the estimated surface- and diffusion controlled flux. The oxygen flux in-creases due to the large interfacial chemical potential gradient when surface kinetics is limiting (see also Fig. S-2). With increasing temper-ature, both the measured flux values and the apparent activation energy gradually approach the estimated diffusion-controlled flux. One should recognize that the effect of the nonlinear relation between the flux and the potential gradient depends on the parameter \( \beta \) (see S-3).

The relative influence of surface and bulk processes on the overall oxygen flux can be expressed by the ratio between the surface exchange kinetics and the ambipolar diffusion. Here we will adhere to the Biot number, as defined in S-Eq.12 [33–35] (S-3.4, Fig. S-4) and presented in Fig. 6 for the BTM-LSM 60/40 membrane. The Biot number increases with increasing temperature, but the values remain essentially within the range representing mixed rate control [32]. One should recognize that the Biot numbers determined using the measured surface kinetics data (cf. Fig. 4) are lower than those estimated from modelling of the flux data.

Alternatively, following the procedure by Chen et al. [14], flux data and ambipolar conductivity can be applied to derive resistances in series for surface and bulk kinetics in a simplified equivalent circuit. The resistances of the two processes are equal at approximately 830 \( ^\circ \)C (cf. Fig S-1, S-3.1 for derivation). Above this temperature, the resistance related to ambipolar conductivity is higher than that for oxygen exchange. This is in reasonably good agreement with the Biot numbers in Fig. 6.

As encountered in Fig. 3, the oxygen pressure dependence on the oxygen flux was not directly proportional to the chemical potential gradient. Analyses in S-3.3 (Fig. S-4) show that the oxygen flux is rather close to being proportional to \( (p_{O_2}^{(I)} - p_{O_2}^{(II)}) \). Ten Elsof et al. [12] reported virtually the same characteristics for a BE25-40Ag cermet - both the actual values of the oxygen flux and their functional dependences on the measurement conditions.

The significant increase in the oxygen flux for \( \text{Bi}_2\text{O}_3 \)-based materials with addition of an electronic conductor could principally originate only from the high electronic conductivity of the second phase. However, there is potentially an additional gain from enhancement of the surface exchange kinetics. This is encountered by the increase in the oxygen flux with the more catalytically active Ag compared with Au as the metallic phase of BE25 based cerments [14]. Although single-phase \( \text{Bi}_2\text{O}_3 \)-based materials have shown remarkably high oxygen surface exchange, far better than for LSM [11,29,36], the superior oxygen fluxes of BTM-LSM show that LSM contributes more than by promoting the electronic
of electron holes in Bi
unarguably showing that LSM plays a role in the surface exchange coefficient when merging LSM with BTM (cf. Fig. 4), conductivity. This is in line with the significant increase in the oxygen ambipolar conductivities (S-Eq. 4). The fluxes under surface limitation are derived based on the surface exchange coefficients in Fig. 4 for linear (S-Eq. 5) and nonlinear (S-Eq. 7) relations to the oxygen chemical potentials, with β = 0.35. In all three cases it is assumed that the entire oxygen potential gradient is across the respective region, i.e., bulk and permeate side solid-gas interface.

Concentration polarization (gas-phase double-layers) may affect oxygen flux measurements, particularly for materials with high oxygen fluxes. Evaluation of the present dataset, however, reveals only a minor effect (S-3.5, Fig. S-5). This is in line with the hypothesis of ten Elsof et al. [12]. There are controversial reports in the literature as to whether triple-phase-boundaries (TPBs) contribute or not to the generally higher oxygen fluxes for composites compared to single-phase materials [35, 48] [47]. Since the phases in the BTM-LSM composites are not that well dispersed, optimization of the fabrication giving less agglomeration should yield better oxygen flux performance if the TPB is important to the surface kinetic. However, as evident from S-5 we did not come to any conclusive results.

Concentration polarization (gas-phase double-layers) may affect oxygen flux measurements, particularly for materials with high oxygen fluxes. Evaluation of the present dataset, however, reveals only a minor effect (S-3.5, Fig. S-5). This is in line with the hypothesis of surface diffusion controlled oxygen exchange kinetics, since double layers are expected to be less prominent for mechanisms with surface diffusion as the rds. In this respect, it should be recognized that, analyses based on the Butler-Volmer relations become less adequate if surface diffusion represents the rds. However, surface diffusion of charged species across space charge layers at the composite phase boundaries may introduce potential differences introducing polarization that has been described by Butler-Volmer type formalisms [37].