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A novel dual phase composite oxygen membrane (Al$_{0.02}$Ga$_{0.02}$Zn$_{0.96}$O$_{2}$ – Gd$_{0.1}$(Ce$_{0.9}$O$_{1.95}$)$_{0.1}$) was successfully prepared and tested. The membrane shows chemical stability against CO$_2$ and SO$_2$, and a stable oxygen permeation over 300 hours in CO$_2$ was demonstrated. ZnO is cheap and non-toxic and is therefore highly advantageous compared to other common materials used for the purpose.

Dense ceramic oxygen transport membranes (OTMs) can selectively separate oxygen from air at temperatures above 600 °C. The energy consumption of oxygen produced by OTMs can be significantly lower compared to conventional technologies such as cryogenic distillation or vacuum pressure swing adsorption, especially if the OTMs are thermally and/or chemically integrated with a high temperature process. Main applications considered for OTMs include small scale manufacturing process. The development of a CO$_2$-, SO$_2$- tolerant membrane without expensive and toxic transition metals is therefore necessary for commercialization of OTMs.

Here we report on the use of doped ZnO with Gd$_{0.1}$(Ce$_{0.9}$O$_{1.95}$)$_{0.1}$(GCO10) for high temperature oxygen transport membranes. ZnO offers the following advantages for the use in OTM: i) The electronic conductivity of ZnO is susceptible to tailoring via extrinsic doping. Doping of a slight amount of trivalent elements e.g. Al, Ga and In can drastically enhance the electronic conductivity of ZnO, rendering it a good electronic conductor. ii) ZnO is chemically stable in both CO$_2$ and SO$_2$ containing atmospheres. According to thermal dynamic calculation, decomposition of ZnCO$_3$ into ZnO and CO$_2$ occurs above 200 °C in air. A phase diagram (Fig. S3 ESI†) shows that the reaction between ZnO and SO$_2$ will only occur under high oxygen and sulfur dioxide partial pressures at low temperature. Typical conditions in an oxy-fuel power plant or cement plant would include SO$_2$ levels up to 100 ppm on the permeate side of the membrane. The chemical stability of ZnO should thereby meet the requirements for the membranes under the aforementioned conditions. iii) Furthermore, a ZnO dopant can enhance the electronic conductivity of the ceria itself over a wide range of temperature and oxygen partial pressure. It is found that this enhancement may occur without a sacrifice of ionic conductivity. The grain boundary conductivity of GCO10 can even be enhanced by doping 1 mol % ZnO at low temperatures (< 500 °C). Schmale et al. reported that the electronic conductivity of Zn-doped ceria exhibits a striking jump when the concentration of ZnO is above 30 mol% due to the formation of a ZnO-rich percolation network along the grain boundary. iv) The thermal expansion coefficient (TEC) difference between ZnO (8×10$^{-6}$ K$^{-1}$ at 300 K) and GCO10 (12×10$^{-6}$ at 300 K-273 K) is moderate and therefore cracks between the micro grains of the two different phases can be avoided for suitable composite microstructures. v) Finally, zinc oxide is
non-toxic, abundant and inexpensive. ZnO based dual phase OTMs thus has numerous merits for the use in the commercialization of the technology. The composite membrane investigated in the present study consists of 50 vol.% Al,Ga co-doped ZnO (Al_{0.25}Ga_{0.75}Zn_{0.95}O_{1.02}) and 50 vol.% Gd_{0.5}Ce_{0.5}O_{1.95} (GCO10) (the composite is abbreviated AGZO-GCO55). Al_{0.25}Ga_{0.75}Zn_{0.95}O_{1.02} and Gd_{0.5}Ce_{0.5}O_{1.95} serve as electronic and oxide ion conducting phase, respectively. According to Han et al.\textsuperscript{19}, doping small amount of Al and Ga into ZnO will not change the grain structure. From the XRD patterns, it can be seen that the dual phase system merely consists of cubic fluorite structured GCO10 (space group 225; Fm3m) and hexagonal wurtzite structured AGZO (space group 186; P63mc). No secondary phases resulting from reactions could be detected within the resolution limit of the XRD, indicating sufficient mutual stability between GCO10 and AGZO. The crystal structure of the composite remains unaltered in the temperature range from 25 to 900 °C in air (Fig. S9 ESI\textsuperscript{†}), XRD patterns of AGZO-GCO55 powders annealed in 100% CO\textsubscript{2} remains unaltered in the temperature range from 25 to 900 °C in air (Fig. S9 ESI\textsuperscript{†}). XRD patterns of AGZO-GCO55 powders annealed at 1200 °C for 5 hours, sintered membrane annealed in 100% CO\textsubscript{2} for 120 hours at 850 °C, shows that AGZO-GCO55 is chemically stable in CO\textsubscript{2} at high temperature. Also, identical XRD patterns for the powder before and after annealing in a SO\textsubscript{2} rich atmosphere indicate no formation of sulphate, whereas formation of SrSO\textsubscript{4}, (Fig. S8 ESI\textsuperscript{†}) is observed from a reference sample (La_{0.5}Sr_{0.5}FeO_{3+δ}-Gd_{0.5}Ce_{0.5}O_{1.95}). This implies that AGZO-GCO55 with respect to SO\textsubscript{2} tolerability is superior to the Sr-containing perovskite. The results are also in good agreement with thermodynamic predictions (Fig. S3 ESI\textsuperscript{†}).

By HRTEM imaging of the grain boundary between a GCO10 and a AGZO grain (Fig. 2e), the characteristic (111) GCO10 and (100) ZnO planes were identified on each side of the grain boundary. The presence of new phases could not be detected along the grain boundary.

Fig. 1 Normalized XRD patterns of dual phase AGZO-GCO55 membrane sintered at 1200 °C for 5 hours, sintered membrane annealed in 100% CO\textsubscript{2} for 120 hours and membrane annealed in SO\textsubscript{2} for 2 hours at 850°C. Diffraction patterns for single phase Al_{0.25}Ga_{0.75}Zn_{0.95}O_{1.02} and Gd_{0.5}Ce_{0.5}O_{1.95} are also shown.

Fig. 2 displays the scanning transmission electron microscopy (STEM) (See Fig.2a), EDX elemental mapping (Figs. 2b and 2c), EDX spectrum (Fig. 2d) and high resolution TEM (HR-TEM) image (Fig. 2e) of the crushed powder of the AGZO-GCO155 membrane. According to the Ce and Zn maps, GCO10 and AGZO grains are homogeneously distributed without any agglomeration of one phase and no obvious correlation of the Ce and Zn distribution could be observed, indicating no significant reaction between the grains or the formation of grain boundary layers.

Fig. 3 shows Arrhenius type plots of the oxygen permeation fluxes of a 1.1 mm thick GCO10 pellet coated with La_{0.5}Sr_{0.5}CoO_{3-δ} (LSC) layer and AGZO-GCO55 membranes with and without LSC coating measured with pure N\textsubscript{2} and CO\textsubscript{2} as sweep gas under a fixed oxygen partial pressure (ln(pO\textsubscript{2}/pO\textsubscript{2}'')=5 and 8) in the temperature range between 600 °C and 1000 °C. LSC catalytic layers were used to ensure that the surface exchange reaction does not limit the flux. The flux data is also plotted for a fixed outlet flow (flow fixed over the temperature variation rather than fixing the driving force). Also, a calculated maximum flux for an ideal short circuited GCO10 and a pure GCO10 membrane (calculated based on the ionic conductivity and electronic conductivity from Ref. \textsuperscript{20, 21}) under the same driving force is plotted for comparison. The uncertainty of the measured flux mainly originates from the uncertainty on the area of the membrane being tested and small leaks at the sealing (ESI\textsuperscript{†} Table S1). Based on two nominally identical tests, the obtained results are clearly reproducible (Fig. S5 ESI\textsuperscript{†}). Oxygen permeation fluxes for both sweep gases (N\textsubscript{2} and CO\textsubscript{2}) show thermally activated feature with apparent activation energies (E\textsubscript{a}) of 74.5±2 kJmol\textsuperscript{-1} and 75.4±2 kJmol\textsuperscript{-1}, respectively. The almost equivalent oxygen flux observed under the same driving force conditions suggests that the prevailing rate limiting process is identical when using N\textsubscript{2} or CO\textsubscript{2} as sweep gas. In addition, the oxygen permeation flux measured using CO\textsubscript{2} as the sweep gas is slightly lower than that measured in N\textsubscript{2}, “A slight suppression of the oxygen permeation flux in CO\textsubscript{2}”, when compared to N\textsubscript{2} has also been found in other studies of OTMs.\textsuperscript{25-26} The phenomenon is suggested to be a consequence of suppressed oxygen surface exchange rate due to the chemisorption of CO\textsubscript{2} on the surface of the activation layer with the occupation of oxygen vacancies by the oxide ions of CO\textsubscript{2}.\textsuperscript{24} On the other hand, the existence of a stagnant gas layer in the vicinity of the permeate side of OTMs has also been reported\textsuperscript{27}. Such a stagnant gas layer can give rise to diffusion limitations at low oxygen partial pressures. The binary diffusion coefficient of oxygen in nitrogen (D_{O2-N2}=0.75 cm\textsuperscript{2}s\textsuperscript{-1}) is slightly higher than that in carbon dioxide (D_{O2-CO2}=0.70 cm\textsuperscript{2}s\textsuperscript{-1}) at 900 °C. The different binary diffusion coefficients can therefore lead to different local oxygen partial pressures on the surface.
of the permeate side and as consequence lead to slightly different oxygen fluxes even though the $p_O$, of the effluent gas is identical.

The oxygen permeation flux of AGZO-GCO55 is ca. half of the calculated flux of short circuited GCO50 and two orders of magnitude higher than that measured for single phase GCO50. The enhanced oxygen flux of AGZO-GCO55 relative to GCO50 is due to the contribution of the $n$-type electronic conductivity originating from the percolating doped ZnO, as evidenced by the flux increase and the larger electrical conductivity (ESI† Fig.S6). The depressed flux of AGZO-GCO55 relative to short circuited GCO50 is ascribed to the partial blocking of the oxide ion paths by the AGZO and the more tortuous path for oxide ions, which is a general phenomenon observed in dual phase OTMs. The membrane behaves as expected from the reported absence of chemical inter-reaction between the two phases simply as an ideal composite where naturally the addition of the electronic conductor takes up a volume otherwise available to ionic transport thus reducing the flux relative to ideally achievable in a pure ceria membrane. It is noted that the apparent activation energy of AGZO-GCO55 (74.5 ± 2 kJ mol$^{-1}$) is slightly higher than that expected from the conductivity of GCO50 (66.1 kJ mol$^{-1}$). The larger apparent activation energy may originate from: i) a not insignificant contribution from the surface activation since the typical activation energy for a LSC electrode is 106 kJ mol$^{-1}$; ii) For the bulk diffusion, oxide ions will jump in the crystal structure of GCO50. The presence of ZnO surrounding GCO50 may result in strain effects or grain boundary effects that can possibly increase the energy barrier for oxide ion movement. Noticeably, the flux and larger activation energy must be attributed to poor catalytic activity towards oxygen exchange of the composite AGZO-GCO55, which is consistent with the work on the use of ZnO as a SOFC electrode material. It should be pointed out that the activation energy of the flux for a fixed flow of the effluent is 62 kJ mol$^{-1}$, and thus lower than that measured under a fixed driving force. The lower activation energy is due to a continuous change of the driving force, as the oxygen permeating through the membrane reduces this with increasing temperature.

The tested AGZO-GCO55 shows an oxygen permeation flux comparable to numerous ceria based dual phase membranes (ESI† Table S2). However, compared to most other systems studied in literature, the use of ZnO as the electronic conductor is advantageous due to its low cost and non-toxicity as previously stated. It is clear that future commercial membrane applications require significantly higher oxygen fluxes than reported here for 1.1 mm thick disks. A higher flux can be achieved by using a thin film membrane on a porous support structure. An additional advantage of the use of composites of GCO and ZnO is the possibility to tailor a thermal expansion coefficient of the composite to match that of cheap high toughness ceramics such as $Y_{0.25}Zr_{0.65}O_{1.95}$ (3YSZ) or mixtures of magnesium and alumina.

As shown in Fig. 4, the membrane flux was tracked for close to one month with $N_2/CO_2$ as the sweep gas at 860 °C followed by a measurement at 940 °C. The measurement was voluntarily terminated. A stable flux of 0.22 (STP) ml cm$^{-2}$ min$^{-1}$ with $N_2$ as the sweep gas in the first 30 hours was observed. After switching the sweep gas to 100% CO$_2$, the flux decreases to 0.19 (STP) ml cm$^{-2}$ min$^{-1}$ and levels off at 0.18 (STP) ml cm$^{-2}$ min$^{-1}$ after 100 hours. After the sweep gas was switched back to 100% $N_2$, the flux effectively recovered to the initial level. The XRD patterns (Fig. S10 ESI†) of the feed and permeate side with the LSC activation layers before and after the measurement show no formation of new phases. No changes in the microstructure of the membrane layer itself compared to a fresh membrane could be observed after the 500 hour test (ESI† Fig.S11b). Also no microstructural changes of the feed side activation layer of LSC could be detected after test. The permeate side activation layer, however, showed a densified region (extending approximately 10 µm adjacent to the membrane) after test. EDS analysis (Fig.S12b ESI†) revealed the formation of a strontium rich layer along the interface between the activation layer and the membrane, which is ascribed to a reaction between $La_{0.6}Sr_{0.4}CoO_3$ and CO$_2$. Over the 350 hours of test in CO$_2$, the flux through the coated membrane reduced by 7% with a tendency of a decreasing rate (Fig.S13 ESI†). Over a similar period (500 hours), the flux through an uncoated membrane (though much smaller) showed a clear increase (300%). This, together with the post-test microstructural findings, clearly shows that the dense membrane layer itself is chemically stable in CO$_2$ and that the decreasing flux observed for the coated membrane must be ascribed to
the catalyst layer on the permeate side. For most common membrane materials based on perovskite or similar structures, such as Ba$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF), the oxygen flux usually dramatically drops once CO$_2$ is introduced$^{3}$. The dual phase AGZO-GCo$_{55}$ membrane material studied here shows in contrast a relatively stable flux in CO$_2$. Further improved CO$_2$ stability can be expected if a more CO$_2$ stable electrocatalysts is used instead of LSC.

Conclusions

A novel CO$_2$ and SO$_2$ tolerant dual phase composite membrane material, consisting of 50 vol.% Al$_{0.02}$Ga$_{0.98}$Zn$_{0.8}$O$_{1.95-δ}$ and 50 vol.% Gd$_{0.02}$Ce$_{0.98}$O$_{1.96}$ (AGZO-GCo$_{55}$) was synthesized and tested as oxygen transport membrane. The total conductivity of the composite is mainly $n$-type electronic and originates from the percolating Al$_{0.02}$Ga$_{0.98}$Zn$_{0.8}$O$_{1.95-δ}$ network. Fairly stable oxygen permeation in CO$_2$ could be proven in a 1.1 mm thick membrane for more than 500 hours at 860 °C and 940 °C. The AGZO-GCo$_{55}$ composite material showed also sufficient stability in SO$_2$, making it a very good candidate for integration schemes of oxygen transport membrane into industrial applications that require direct contact with CO$_2$ and SO$_2$ containing environments.

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Notes and references