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Electrical conductivity and oxygen transfer in gadolinia-doped ceria (CGO)–$Co_3O_{4-\delta}$ composites

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Abstract

Dense, mixed-conducting ceramic membranes can be used for separation of oxygen from air. Dual-phase composites are an interesting way to obtain mixed conductivity because it is easy to tailor the electrical and transport properties by varying the fractions of the ionic and electronic components. In this study, mixed-conducting $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO)–$Co_3O_{4-\delta}$ composites were fabricated with density about 95% theoretical values. The solubility of $Co_3O_{4-\delta}$ in CGO was found to be lower than 1 mol% (or 1.6 vol.%). The total conductivity of the CGO–$Co_3O_{4-\delta}$ composites increased with increasing $Co_3O_{4-\delta}$ content. A microstructure with two interconnected phases was obtained for a $Co_3O_{4-\delta}$ content above 10 mol% (or 15 vol.%). Isotopic exchange depth profiling (IEPD)/secondary ion mass spectrometry (SIMS) method was used to investigate the oxygen diffusion and surface exchange reaction in the composites. The diffusivities of the composites were almost constant within the experimental error with significantly enhanced surface exchange kinetics by adding $Co_3O_{4-\delta}$ to CGO.

Keywords: CeO_2; Composites; Diffusion; Electrical conductivity; Tracer diffusion; Surface exchange; Co_3O_4

1. Introduction

In recent years there has been a great interest in developing mixed conductors, which have both high ionic and electronic conductivity, for a wide range of applications, such as solid oxide fuel cells (SOFCs) and oxygen separation membranes, etc.[1–3] It has been found that using a mixed conductor as a cathode material for SOFCs significantly improved performance as it promoted a high oxygen permeation flux and a fast surface exchange rate.[4,5]

Both single-phase ceramics and dual-phase composites can be used to produce such a mixed conductor. The single-phase pervoskite oxides, such as $La_{1-x}Sr_xT_MO_3$ (T_M = Co, Mn, Fe, Cr, etc.) system, have been studied the most and their transport properties are well documented. However, it is difficult to fulfil all the potential requirements with a single-phase material. An alternative is to produce a composite having one component with oxide ionic conductivity and a metal oxide with high electronic conductivity, mixed in such proportions to give an interconnected pathway for each component. There have been investigations on such dual-phase mixed-conducting materials, such as ZrO_2–Mn_2O_3,[6] ZrO_2–NiO,[7] ZrO_2–In_2O_3,[8] and ZrO_2–TiO_2,[9] as the properties can be easily tailored for a composite. However, a high concentration of such metal oxide (above 30 mol% for ZrO_2–Mn_2O_3 composite) is required in order to produce a three-dimensionally interconnected microstructure. These may compromise the oxygen ion conductivity of the composite, as the electronically conducting phase will act as a block to oxygen transport.

In this study, the electronic conductor $Co_3O_{4-\delta}$ was added to CGO to produce a mixed-conducting material for an oxygen separation membrane application. CGO (gadolinia doped ceria) is one of the most promising materials used in solid electrochemical devices. The solubility of Co in CGO has been reported to be as low as 0.5cat%.[10] Also, for practical applications it is important to evaluate the transport properties, particularly its surface oxygen exchange, in order to extend the understanding of mechanisms at solid/gas interface. There have been many investigations on the electrical conductivity of CGO, however,

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data on the oxygen diffusivity, especially data on metallic oxide doped CGO, are sparse.[11,12] Therefore, the oxygen diffusion property of the CGO–$Co_3O_{4-\delta}$ composites were investigated by an isotopic exchange depth profiling (IEPD)/secondary ion mass spectrometry (SIMS) methods in this study.

2. Experimental

Gadolinia doped ceria ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) (Rhône Poulenc) and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) (Aldrich, purity: 99.999%) powders were used as starting materials. CGO powder and cobalt nitrate with the desired amount of $Co_3O_{4-\delta}$ in the final product were mixed in ethanol for 24 h with ZrO_2 milling media. The powder mixtures were then oven dried at 70 °C and subsequently reground. Following calcination at 650 °C for 1 h, the powder blends were milled in ethanol again. After drying, they were sieved through a 53 μm sieve. The powders were uniaxially pressed into pellets (13 mm diameter) at a pressure 75 MPa, then followed by isostatic pressing at 300 MPa. The green bodies were then sintered in air at different temperatures.

The density of the composite was determined by the Archimedes' method. Phase identification was performed using X-ray diffractometry (XRD) on a Philips PW1710 X-ray diffractometer. A Cu Kα target with a monochromator was used with a voltage of 40 kV and a current of 40 mA. A least squares refinement method was used to determine the lattice parameters of the composites. Using a four-probe dc technique, the electrical conductivity of dense ceramic bar samples was measured as a function of temperature in air.

The diffusion of oxygen ions in this study was investigated by introducing ^{18}O tracer isotope of oxygen followed by SIMS depth profiling. Prior to the annealing experiment the samples were all ground flat and polished with successive diamond paste down to 0.25 μm. They were then annealed in research grade oxygen (99.996% pure O_2) at 800 °C for a long enough time to ensure thermodynamic equilibrium. After cooling down to room temperature, the specimens were annealed in an ^{18}O isotope enriched gas for the required time. The exchanged samples were then cut perpendicular to the diffusion surface and the cross-sections were mechanically polished to 0.25 μm finish. The isotope concentration was measured by secondary ion mass spectrometer (ATOMIKA 6500) using an 8 keV $^{132}Xe^+$ beam. In all cases, the primary ion beam was at normal incidence to the sample. To prevent electrical charging on pure CGO sample during analysis, it was co-bombarded with a 2 keV electron beam.

A non-linear least squares regression based upon the solution of the diffusion equation for isotope tracer diffusion in a semi-infinite medium[13] was used to fit the oxygen diffusion coefficient, D_T, and surface exchange coefficient, k.

Table 1
Properties of the $(1-x)$CGO–$x$$Co_3O_{4-\delta}$ composites

x (mol%)	x (vol.%)	Sintering temperature (°C)	Sintering time (h)	Density (% TD)
0	0	1400	4	98.8
0.05	0.08	1000	2	96.7
0.1	0.15	1200	2	96.2
0.2	0.29	1200	2	94.5

3. Results and discussion

3.1. Densification behaviour

The dense $(1-x)$CGO–$(x)$$Co_3O_{4-\delta}$ composites with x in the range of 0–20 mol% were fabricated. The compositions of samples studied, together with densities, are listed in Table 1. The pure CGO sample achieved 98.8% theoretical density by sintering at 1400 °C. Composites with density above 95% could be achieved at lower sintering temperatures by adding certain amount of cobalt to CGO.

XRD study shows that the CGO is a single-phase material of cubic fluorite-type structure and that all the CGO–$Co_3O_{4-\delta}$ composites with $Co_3O_{4-\delta}$ content from 1 to 20% are dual-phase materials. Fig. 1 shows the lattice parameter of CGO and CGO–1, 2 and 5 mol% $Co_3O_{4-\delta}$ composites. It is seen that the solubility of $Co_3O_{4-\delta}$ in CGO is lower than 1%. This low solubility would promote $Co_3O_{4-\delta}$ segregation as a separate phase in the samples fabricated.

3.2. Electrical conductivity

The conductivities of CGO and the $(1-x)$CGO–$(x)$$Co_3O_{4-\delta}$ composites ($x = 0.05$, 0.1, 0.2 and 1, respectively) were measured by a four-probe dc technique. An Arrhenius plot of the total conductivity as a function of reciprocal temperature is shown in Fig. 2. Measurements were conducted below the phase transformation temperature from $Co_3O_{4-\delta}$ to $CoO_{1.07}$ (900–950 °C[14]). The conductivity of CGO–5% $Co_3O_{4-\delta}$ specimen is similar to that of pure CGO. The

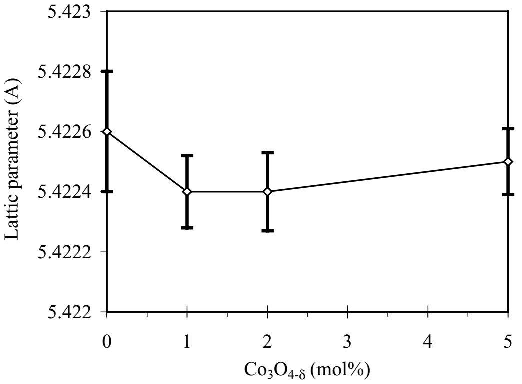

Fig. 1. Lattice parameter of the CGO–$Co_3O_{4-\delta}$ composites as a function of the $Co_3O_{4-\delta}$ content.

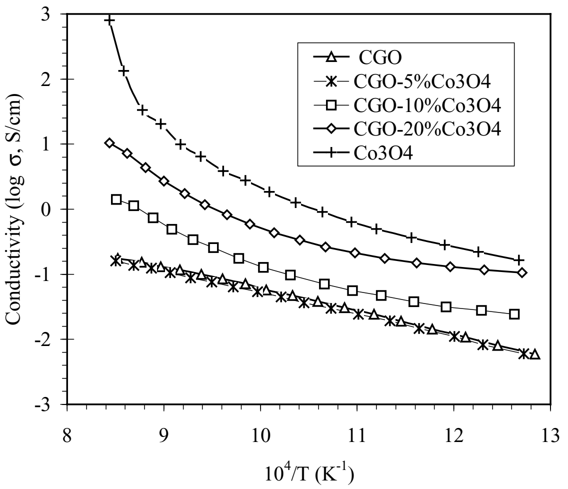

Fig. 2. Arrhenius plot of electrical conductivity in air of the CGO–$Co_3O_{4-\delta}$ composites.

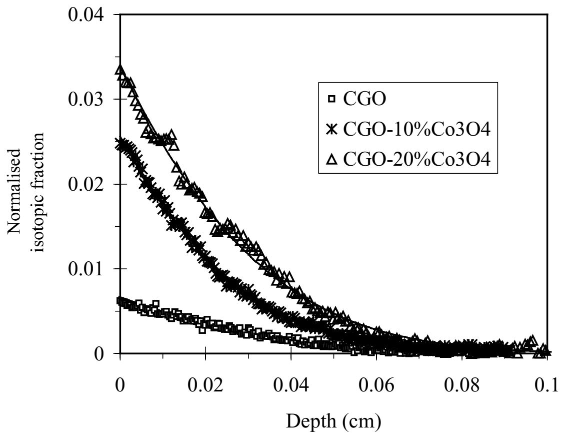

Fig. 3. ^{18}O diffusion profiles for the CGO–$Co_3O_{4-\delta}$ composites exchanged at 800 °C.

conductivity of the CGO–$Co_3O_{4-\delta}$ composites increases with increasing $Co_3O_{4-\delta}$ when the $Co_3O_{4-\delta}$ content is higher than 5% in the final product.

The conductivity of CGO and CGO–5% $Co_3O_{4-\delta}$ follows an Arrhenius behaviour, i.e., the data obey the equation

$$\sigma T = A \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

Therefore, the activation energy E_a was calculated using the slopes of the lines and was 75 and 73 kJ/mol, respectively, for CGO and CGO–5% $Co_3O_{4-\delta}$ ceramic. Adding up to 5% $Co_3O_{4-\delta}$ to CGO does not seem to change the electrical properties of the matrix. However, curvature is apparent for pure $Co_3O_{4-\delta}$ and CGO–$Co_3O_{4-\delta}$ composites with $Co_3O_{4-\delta}$ content more than 10%. The conductivity of composites increases greatly when adding 10% $Co_3O_{4-\delta}$ to CGO. The highest conductivity was achieved by CGO–20% $Co_3O_{4-\delta}$ ceramic among the composites studied.

When 5% $Co_3O_{4-\delta}$ phase is present in the ion-conducting CGO matrix, the $Co_3O_{4-\delta}$ phase exists as discrete particles without three-dimensional percolation, which would block ionic transport and thus behave as an insulator for the conduction of oxygen ions. Therefore, a decrease in the conductivity is expected. A greatly increased conductivity was observed at 10% $Co_3O_{4-\delta}$ addition to the CGO and the conductivity increased further with increasing $Co_3O_{4-\delta}$ content. This suggests the interconnection of the $Co_3O_{4-\delta}$ phase and that the conductivity is mostly determined by the electronic conducting phase of $Co_3O_{4-\delta}$.

Oxygen diffusion and surface exchange on pure CGO, CGO–10 and 20 mol% $Co_3O_{4-\delta}$ composites with two interconnected phases were investigated by the IEPD/SIMS method. Fig. 3 shows typical ^{18}O depth profiles measured for CGO and CGO–$Co_3O_{4-\delta}$ composites exchanged at 800 °C for approximately 5400 s at 100 mbar. The diffusion profiles are in general accurately described by the non-linear regression. The irregularities seen in the CGO–20% $Co_3O_{4-\delta}$ composite could be indicative of porosity or inhomogeneity in the sample. It is in agreement with the slightly lower density of this sample. For CGO the ^{18}O surface concentration is lower than the two CGO–$Co_3O_{4-\delta}$ composites. This suggests a low oxygen surface exchange rate at the CGO surface and improved values for the composites. The tracer diffusion coefficient (D_T) and surface exchange coefficient (k) of composites are plotted in Fig. 4. The tracer diffusion coefficients of CGO–$Co_3O_{4-\delta}$ composites were comparable to the CGO within experimental error. Adding $Co_3O_{4-\delta}$ to the CGO, however, increased the surface exchange coefficient significantly. Data on the pure CGO are in agreement with the literature,[12] however, there are no such data available on CGO matrix composites. This is the first set of such data on CGO–$Co_3O_{4-\delta}$ composites.

It is known that the diffusion of oxygen ions through fluorite structure is via a vacancy mechanism. Therefore, the

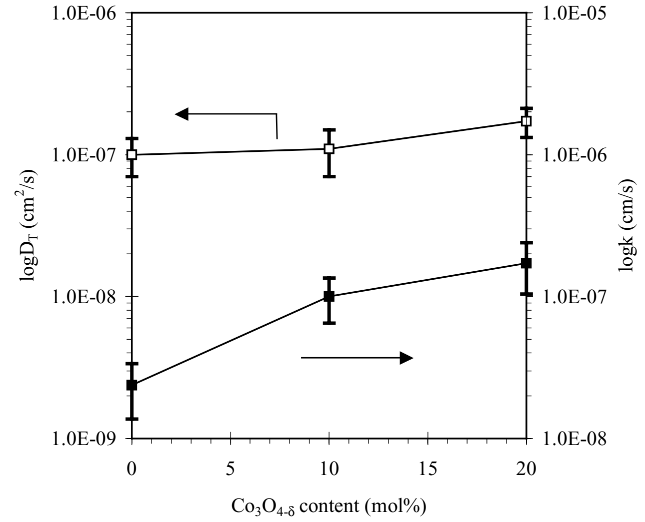

Fig. 4. Trace diffusion and surface exchange coefficient of the CGO–$Co_3O_{4-\delta}$ as a function of the $Co_3O_{4-\delta}$ content.

concentration of vacancies plays an important role in the diffusivity of oxygen. CGO is a good oxygen ionic conductor in normal temperature and oxygen partial pressure range. $Co_3O_{4-\delta}$ is an electronic conductor. The connectivity of the two phases is crucial to produce a mixed-conducting composite. It is shown that the interconnection started to form when 10 mol% $Co_3O_{4-\delta}$ is added to CGO. Below that point $Co_3O_{4-\delta}$ particles would block the conduction of oxygen ions. Thus, the oxygen transport properties were only investigated on the composites with an interpenetration network. It is seen from Fig. 4 adding $Co_3O_{4-\delta}$ to the CGO produced similar diffusivities as that of the pure CGO. It suggests that the oxygen diffusivity of the composite materials may be determined by the volume fraction and connectivity of the CGO phase.

The surface exchange reaction is generally described as

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \rightarrow O_O^X \qquad (2)$$

The oxygen exchange process from the gas phase into the oxide bulk may be divided into a number of possible reaction steps, including adsorption, dissociation and reduction, of oxygen molecules and incorporation of oxygen ions into the oxide bulk. Each of these reactions determines the overall rate of oxygen surface exchange, *k*, and may be rate-limiting. Manning et al.[15] investigated the oxygen surface exchange behaviour of CGO and suggested the surface exchange reaction could be simplified into two steps, a molecular dissociation step and the incorporation of the oxygen into the bulk. It was found that at high temperatures (>700 °C) the dissociation of oxygen is slow in relation to the bulk incorporation and is rate-limiting. Lane and Kilner[12] also suggested that the oxygen exchange reaction on CGO surface is limited by the availability of free electronic species for charge transfer. Therefore, the concentration of electrons limits the kinetics of the exchange process. In this case, the surface exchange rate of the pure CGO was effectively improved by adding $Co3O_{4-\delta}$ phase without a significant effect on the oxygen diffusion coefficient. The CGO–$Co_3O_{4-\delta}$ phase boundaries on the surface of the composite may be highly active for the exchange of oxygen by providing electrons in the vicinity of the surface oxygen vacancies. It suggests that availability of electrons may be the rate-limiting step for surface oxygen exchange at high temperature in the fluorite structured CGO phase.

4. Conclusions

$Ce_{0.8}Gd_{0.2}O_{1.9}$–$Co_3O_{4-\delta}$ composites with different $Co_3O_{4-\delta}$ contents have been fabricated. Adding certain amount of $Co_3O_{4-\delta}$ to CGO significantly decreased the sintering temperature resulting in composites with densities of 95%. XRD results confirmed that the solubility of $Co_3O_{4-\delta}$ in CGO is lower than 1 mol% which promotes the $Co_3O_{4-\delta}$ as a separate phase. The conductivity of the CGO–$Co_3O_{4-\delta}$ composites increases with increasing $Co_3O_{4-\delta}$ content when more than 5 mol% $Co_3O_{4-\delta}$ is present. A three-dimensional interconnection is formed when the $Co_3O_{4-\delta}$ is greater than 10 mol% which was confirmed by conductivity measurement. The oxygen diffusion behaviour of the composites was measured by isotope exchange/SIMS. Adding $Co_3O_{4-\delta}$ to CGO increased the surface exchange coefficient effectively which indicates that the availability of electrons is rate-limiting reaction for surface exchange in the CGO materials.

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References

1. Steel, B. C. H., Hori, K. M. and Uchino, S., Kinetic parameters influencing the performance of IT-SOFC composite electrode. *Solid State Ionics* 2000, **135**, 445–450.
2. Huijsmans, J. P. P., van Berkel, F. P. F. and Christie, G. M., Intermediate temperature SOFC—a promise for the 21st century. *J. Power Sour.* 1998, **71**, 107–110.
3. Dyer, P. N., Richards, R. E., Russck, S. L. and Taylor, D. M., Ion transport membrane technology for oxygen separation and syngas production. *Solid State Ionics* 2000, **134**, 21–33.
4. Huang, K., Schroeder, M. and Goodenough, J. B., Oxygen permeation through composite oxide-ion and electronic conductors. *Electrochem. Solid State Lett.* 1999, **2**, 375–378.
5. Adler, S. B., Lane, J. A. and Steele, B. C. H., Electrode kinetics of porous mixed-conducting oxygen electrodes. *J. Electrochem. Soc.* 1996, **143**, 3554–3564.
6. Kim, J. H. and Choi, G. M., Mixed ionic and electronic conductivity of $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{1-y}\cdot(MnO_{1.5})_y$. *Solid State Ionics* 2000, **130**, 157–168.
7. Park, Y. M. and Choi, G. M., Mixed ionic and electronic conduction in YSZ–NiO composite. *J. Electrochem. Soc.* 1999, **146**, 838–889.
8. Gauckler, L. J. and Sasaki, K., Ionic and electronic conductivities of homogeneous and heterogeneous materials in the system ZrO_2–In_2O_3. *Solid State Ionics* 1995, **75**, 203–210.
9. Duran, P., Capel, F., Moure, C., Gonzalez-Elipe, A. R., Caballero, A. and Banares, M. A., Mixed (oxygen ion and n-type) conductivity and structural characterization of titania-doped stabilized tetragonal zirconia. *J. Electrochem. Soc.* 1999, **146**, 2425–2434.
10. Lewis, G. S., Aktinson, A., Steele, B. C. H. and Drennan, J., *Solid State Ionics* 2002, **152**, 567–573.
11. Ruiz-Trejo, E., Sirman, J. D., Baikov, U. M. and Kilner, J. A., Oxygen ion diffusivity, surface exchange and ionic conductivity in single crystal gadolinia doped ceria. *Solid State Ionics* 1998, **113–115**, 565–569.
12. Lane, J. A. and Kilner, J. A., Oxygen surface exchange on gadolinia doped ceria. *Solid State Ionics* 2000, **136/137**, 927–932.
13. Crank, J., *The Mathematics of Diffusion*. Oxford University Press, 1975, p. 28.
14. *Handbook of Chemistry (The Chemical Society of Japan)*. Maruzen, Tokyo, Japan, 1984, p. 128.
15. Manning, P. S., Sirman, J. D. and Kilner, J. A., Oxygen self-diffusion and surface exchange studies of oxide electrolytes having the fluorite structure. *Solid State Ionics* 1997, **93**, 125–132.