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# Oxygen permeability and Faradaic efficiency of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$–$La_{0.7}Sr_{0.3}MnO_{3-\delta}$ composites

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## Abstract

Composite $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO, solid electrolyte) and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM, electronic conductor) ceramics were tested as dual-phase membranes for oxygen separation. Oxygen permeation through CGO–LSM composite ceramics containing similar percentages of both phases is limited by bulk ionic transport. In contrast to electronic transport, oxygen ion transport in these composites depends strongly on processing conditions, decreasing with interdiffusion of components. Oxygen ions are blocked by low ionic conductivity layers formed by diffusion of cations of LSM to the contacts between CGO grains. Testing of CGO–LSM membranes at high oxygen pressures (1–50 atm) showed that the composite ceramics are stable in these conditions and exhibit Wagner-type permeation fluxes. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* $CeO_2$; Ionic conductivity; Membranes; Oxygen permeation; Perovskites

## 1. Introduction

Mixed-conducting ceramic membranes have promising technological applications namely in the production of high-purity oxygen and partial oxidation of hydrocarbons.[1] However, well-known mixed conductors possess specific disadvantages limiting their use as oxygen membranes. For perovskite-type oxides with dominant electronic conductivity and high oxygen permeability, these disadvantages include thermodynamic and dimensional instability under large oxygen chemical potential gradients, reactivity with gas species such as $CO_2$, and relatively high thermal expansion coefficients.[1,2] Mixed conductors based on solid electrolytes with a fluorite-type structure show poor electronic conductivity and low oxygen permeability.

The present work describes an attempt to combine in dual-phase composites some of the best properties of single phase materials with high electronic and high ionic conductivities. Perovskite-type lanthanum-strontium manganite, $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM), and one of the best oxide solid electrolytes, gadolinia-doped ceria $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO), with a fluorite-type structure, were selected for this purpose. Previous dilatometric studies of the individual ceramic phases demonstrated good compatibility between LSM and CGO. The difference in average thermal expansion coefficients (TECs) of the membrane components in air is as low as 2%.[3] Thus, the negligible difference in TECs suggests an acceptable stability of CGO–LSM composite membranes under thermal cycling conditions. Based on previous evidence on the role of processing conditions on the performance of these composite membranes,[3] the present work exploited the role of different firing schedules on the structural characteristics of individual components and transport properties of composite membranes.

## 2. Experimental procedure

Dense LSM–CGO composites were prepared from commercial powders of LSM and CGO (PSC, Seattle, WA). The preparation route included mixing in the 50:50 wt.% proportion, ball-milling, pressing into disk-shaped

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pellets and sintering in air. Details on the preparation procedure and results of LSM and CGO characterization were published elsewhere.[3] Sintering took place at 1520°C for different periods of time, with heating/cooling rates of 5°C/min. Composite ceramics sintered for 4 h at 1520°C, deserving special attention in this work, will be designated by CGO/LSM-1. Sample characterization was carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The transport properties were evaluated from measurements of total electrical conductivity (four-probe DC technique), steady oxygen permeation fluxes and Faradaic efficiency. Details on the experimental procedure and equipment used for the characterization can be found elsewhere.[2–5]

## 3. Results and discussion

XRD analysis of the composite ceramics confirmed the co-existence of two phases. The fluorite lattice parameter is larger in the composites than in pure CGO (Fig. 1), whilst the unit-cell parameters of LSM remained nearly unchanged. The expansion of CGO unit cell is likely to be caused by incorporation of lanthanum and strontium cations into the CGO lattice due to diffusion of these cations to the fluorite phase.[6] In fact, changes in CGO composition due to loss of cerium or gadolinium ions are unlikely. $Ce^{4+}$ ions cannot dissolve in the manganite phase and the thermodynamic stability of gadolinium manganite is lower than that of lanthanum manganite. Only formation of strontium cerate might be expected.[7] Therefore, diffusion of cations from CGO to LSM is less probable than diffusion of $La^{3+}$ and $Sr^{2+}$ from LSM to CGO. On the other hand, the introduction of manganese into CGO leads to decreasing unit cell,[5] which is not supported by experimental evidence. The assumed $La^{3+}$ and $Sr^{2+}$ diffusion to CGO is also confirmed by an increase in the fluorite unit cell parameter with sintering time (Fig. 1).

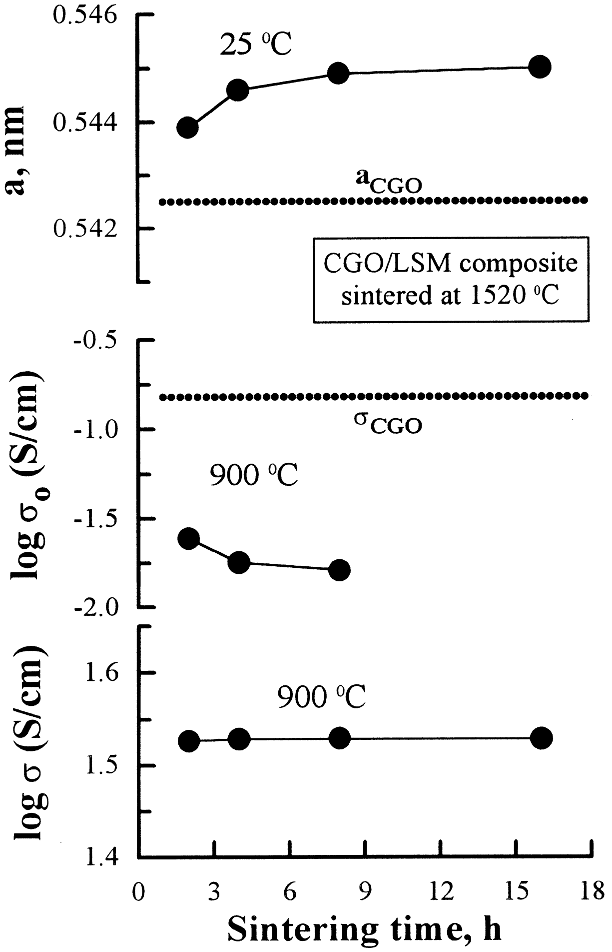

Fig. 1. Dependence of the unit cell parameter of the fluorite-type ceria-based phase (room temperature) and ionic and total conductivities of CGO/LSM composites (900°C) on time of sintering.

Volume fractions of both phases in CGO–LSM ceramics determined from the theoretical densities of the individual phases (determined from XRD) and batch composition (weight dosage) showed that the volume ratio between LSM and CGO is approximately 52:48. A similar estimate was obtained from the relations between powder densities determined by a standard picnometric technique. This ratio should ensure percolation of both phases, with the overall conductivity of the composite determined by the most conductive phase (LSM), predominantly electronic.

Within the exploited range of membrane dimensions, the oxygen permeation flux dependence on membrane thickness showed that oxygen transport through these composite ceramics was limited by bulk ionic conductivity.[3] This conclusion was supported by Faradaic efficiency measurements. The oxygen ion transference numbers estimated by these different techniques for freshly prepared membranes were sufficiently close to each other, in the order of $10^{-3}$ at 950°C. These data confirmed the dominant electronic conductivity in these composite membranes, but thermal treatments introduced serious changes in the composites performance. This will be the subject of the following paragraphs.

The ionic conductivity ($\sigma_0$) of CGO–LSM membranes decreases with sintering time at constant sintering temperature, being about one order of magnitude lower than the ionic conductivity of pure CGO. The effect is most pronounced for sintering periods up to about 10 h (Fig. 1). The most probable reason for this behavior is the formation of ionically-resistive layers between CGO–CGO grain contacts, due to diffusion of La, Sr and Mn from LSM to these interfaces. As the diffusion process occurs mostly during high temperature sintering, the blocking effect due to transport of foreign cations to these interfaces increases with the duration of thermal treatment. Also, for high dopant contents, increasing concentration of either tri- or divalent dopants in the fluorite lattice is responsible for a drop in oxygen conductivity and higher activation energy due to formation of defect associates between oxygen vacancies and dopant cations.[6] Both processes (formation of blocking interfaces and abatement in bulk conductivity) are believed to be effective in this case. However, the former should prevail over the latter considering the global mass transport required to change considerably the dopant concentration and bulk ionic conductivity of the base electrolyte. Lastly, changes in the fluorite unit cell parameter and ionic conductivity are insignificant with further increase in sintering time (Fig. 1), in agreement with a parabolic-type time dependence typical for solid-state diffusion processes.

Diffusion of $La^{3+}$ and $Sr^{2+}$ into CGO should lead to A-site substoichiometry in the LSM phase unless free manganese oxide is also formed. However, free manganese oxide was not detected in the composites either by XRD or by SEM combined with microanalysis. In fact, this means that this phase could be present in minor quantities but below the detection limits of these analytical techniques. Overall concentrations in the order of 1–2% of free manganese oxide spread along the grain boundaries would be hardly detected by such techniques. Diffusion of minor quantities of manganese oxide to CGO–CGO interfaces or even into CGO, and formation of thin layers of A-site deficient LSM at the CGO–LSM boundaries could also explain the negligible changes found in the unit cell parameter of the perovskite phase. Lastly, the conductivity of manganites is not significantly dependent on A-site deficiency,[7] which explains why the total conductivity of these composites is approximately independent of sintering time (Fig. 1), while the ionic conductivity shows such a significant change.

Long-term stability tests of the permeation flux densities ($j$) through CGO–LSM membranes demonstrated their degradation after annealing at 950°C for 70–100 h (Fig. 2). However, XRD studies of these ceramic membranes after prolonged annealing exhibited no detectable phase changes. Besides the previously assumed formation of blocking layers of A-site deficient LSM and/or manganese oxide rich layers, formation of thin layers of phases such as $Sr(Ce,Ln)O_{3-\delta}$ (Ln = Gd, La) along the boundaries of CGO grains is also thermodynamically acceptable.[7] Strontium cerate is a mixed oxygen-ionic and p-type electronic conductor in air with ionic conduction considerably lower than that of CGO.[7] Although formation of strontium cerate layers along the grain boundaries can also block the ionic transport leading to degradation of oxygen transport properties, structural and microstructural evidence is scarce to hold this hypothesis.

Following the same trend already observed while studying the role of the sintering time on transport properties, the electronic conductivity is not affected by segregation of secondary phases along the CGO grain boundaries and remains about constant even after aging for hundreds of hours (Fig. 2). This result is again coherent with the preservation of the perovskite network within the composite, with only small deviations in composition and properties.

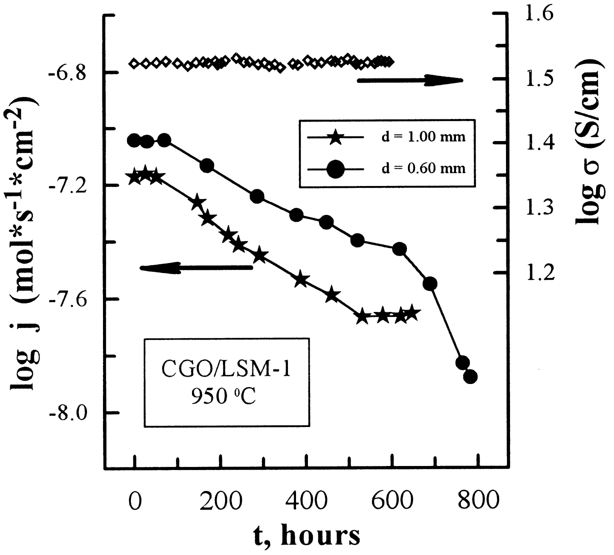

Fig. 2. Time dependence of the oxygen permeability and total electrical conductivity of CGO-LSM composite membranes at 950°C.

One potential high-temperature application of oxygen membranes is in combination with gas turbines. This requires an elevated gas pressure at the oxygen generator output.[8] Permeation tests at high oxygen pressures were thus performed. Dense CGO membranes tested at high oxygen pressure with short-circuited platinum electrodes showed serious instability of the Pt-layers in contact with the electrolyte. For example, at 807°C under an oxygen pressure gradient of 50 atm/1 atm, the permeation flux decreased from $1.8\times10^{-8}$ to $7.2\times10^{-9}$ mol $s^{-1}$ $cm^{-2}$ after 20 h of operation (Fig. 3). Subsequent analysis of the cell showed that most platinum disappeared from the surface, probably due to oxidation and volatilization of the electrode material. Similar results were obtained in the course of high-pressure tests of short-circuited CGO cells with electrodes of other materials, presumably for different reasons. In fact, in the case of ceramic electrodes, dimensional changes with oxygen activity are believed to be the major reason for electrode degradation. In contrast, dual-phase membranes of CGO–LSM composites showed sufficient stability under these conditions. No degradation in permeation flux was observed during about 100 h at 750°C.

Fig. 4 shows the oxygen fluxes through one LSM/CGO-1 membrane with feed-side oxygen pressures between 18 and 50 atm. The dependence of log $j$ vs. log $(p_2/p_1)$ is logarithmic, corresponding to the linear increase in the permeation flux with increasing oxygen chemical potential gradient, in agreement with the classical Wagner model developed for common single-phase

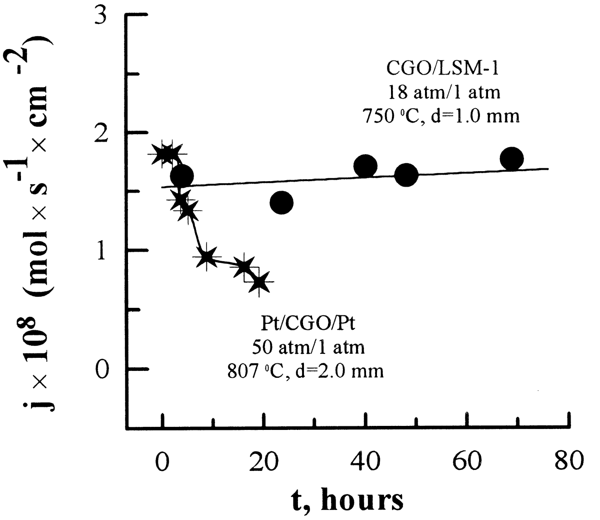

Fig. 3. Time dependence of the oxygen permeation flux through one CGO/LSM-1 composite membrane and through one short-circuited CGO-based electrochemical cell with Pt electrodes, at high feed-side oxygen pressures.

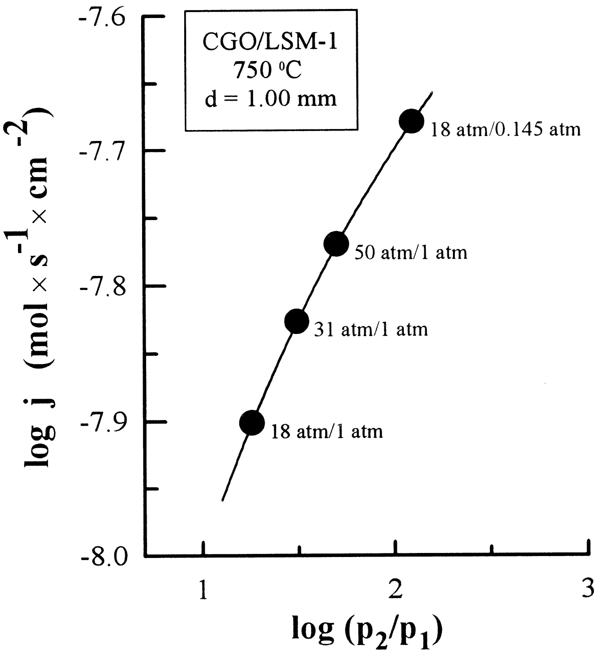

Fig. 4. Dependence of oxygen permeation flux through one CGO/LSM-1 composite membrane on the feed-side oxygen pressure at 750°C. The solid line corresponds to a logarithmic dependence, according to Wagner's prediction for common mixed conductors.

mixed conductors. According to a simple prediction for a short-circuited cell based on a common solid electrolyte, the permeability should be proportional to the oxygen chemical potential gradient.[9] This suggests that the global transport properties (ionic and electronic) of these composites are governed by the local transport characteristics through the thin layers formed during sintering and annealing.

As a summary, the observed interaction between lanthanum-strontium manganites and gadolinia-doped ceria in the course of fabrication of several electrochemical cells, including oxygen separation membranes and solid oxide fuel cells (SOFCs), may lead to a dramatic decrease in ionic conduction and should thus be prevented by an appropriate choice of fabrication conditions.

## 4. Conclusions

CGO–LSM composites can be processed as dense ceramic membranes with potential application in the field of oxygen technology. However, long term operation and sintering at high temperature easily promote the formation of blocking layers between CGO grains, due to diffusion of several constituents from the perovskite. Irrespective of the high volume fraction of the solid electrolyte, corresponding to concentrations well above the percolation limit, the ionic conductivity of the composite is quite poor when compared to the pure electrolyte. On the contrary, both percolation of the perovskite phase and electronic transport properties are preserved due to tolerance to slight deficit in the perovskite A-site occupancy without degradation of performance.

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