

Chemical Compatibility of Chromium-based Interconnect Related Materials with Doped Cerium Oxide Electrolyte

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Abstract

X-ray diffraction and scanning electron microscopy were used to study the chemical compatibility of (La, Sr)CrO₃, SrCrO₄, CaCrO₄ and Cr₂O₃ (materials associated with the interconnect of a solid oxide fuel cell) with gadolinia-doped cerium oxide electrolyte (CGO). Powder mixtures and multilayer pellets of the interconnect related materials were annealed with CGO in air at temperatures ranging from 650 to 1600°C for durations of up to 400 h. No reaction was observed between (La,Sr)CrO₃ and Ce_{0.8}Gd_{0.2}O_{1.9} after annealing at 1600°C for 10 h. However, SrCrO₄, CaCrO₄ and Cr₂O₃ reacted with CGO, forming an unidentified phase. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

The single-cell solid oxide fuel cell (SOFC) consists of an anode and cathode (porous electrodes), separated by a solid electrolyte (typically yttria stabilised zirconia), which conducts ions between the two electrodes. For practical applications, the single cells are connected in series to form a stack. This connection is achieved by utilisation of an interconnect which electrically interconnects the single cells such that repeat units of anode, electrolyte, cathode and interconnect are stacked on top of each other. These stacks can then be placed into series to increase the voltage, or in parallel to increase the total power output.¹

Alkaline earth-doped lanthanum chromites and chromia forming alloys (alloys that form a protective and conductive Cr₂O₃ coating) are commonly used as interconnects in SOFCs.¹ The use of chromia forming alloys has led to reduced cell performance as chromium has been shown to evaporate from the surface of the metal interconnect into the cathode. This evaporation can be reduced by the surface treatment of the alloy separator.^{2,3} In addition, the metal interconnect can be coated with a perovskite (typically doped LaCrO₃ or LaCoO₃), which has been shown to decrease contact resistance and improve the stability of cell performance over time.^{3–6}

To improve the sinterability and electrical conductivity of these protective/conductive coatings, dopants are added to the lanthanum chromites such as Sr and Ca (A-site) and Co (B-site).¹ (La,Ca)CrO₃, for example, can be sintered in air at 1300°C via the assistance of a transitory liquid phase that belongs to the CaO–Cr₂O₃ phase system. Under certain conditions, CaCrO₄ emanates as a secondary phase from (La,Ca)CrO₃. At 1022°C, this secondary phase melts incongruently to form a liquid and solid mixture. By addition of excess Ca into (La,Ca)CrO₃ improved sintering can be achieved as the addition of Ca enhances the sintering characteristics of the liquid phase.⁷ The improved sinterability of LaCrO₃, doped with Sr, was assumed to be due to a SrCrO₄ melt.¹ The SrCrO₄ phase melts in air incongruently at 1251°C forming Cr₂O₃, liquid, and O₂.⁸

There have been a number of investigations that report on the reactivity of the SOFC components with each other.^{7,9,10} Few, however, report on the reaction of the interconnect with the electrolyte material. Mori *et al.*¹⁰ have studied the reactions between alkaline earth doped lanthanum chromite and yttria stabilised zirconia. The authors found

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that $\text{Sr}_4\text{Zr}_3\text{O}_{10}$ formed when a mixture of 7.5 mol% yttria stabilised zirconia (YSZ) was reacted with $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ at 1500°C for 24 h, while $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ($x = 0.1$ and 0.2) showed no reaction product with YSZ at 1500°C for 168 h. Furthermore, all the elements of the perovskite diffused into the YSZ at 1500°C. Carter *et al.*⁷ showed the difficulty of co-sintering (La,Ca)CrO₃ with YSZ. The Ca migrates from (La,Ca)CrO₃, via a Ca–Cr–O liquid phase, to react with YSZ to form an intermediate layer of CaZrO₃, where-by the depth of the CaZrO₃ layer deposited was shown to increase with increasing Ca content in the exsolved Ca–Cr–O liquid phase.

(La,Sr)CrO₃ and (La,Ca)CrO₃ coated chromia-forming alloys may react with electrolytes such as gadolinia-doped ceria (CGO) during co-sintering. For example, in a similar fashion to that of CaCrO₄ which was shown to react with YSZ,⁷ it is plausible that SrCrO₄, detected at the alloy interconnect/(La,Sr)CrO₃ interface,³ and CaCrO₄, present in Ca doped-lanthanum chromites, may react with CGO. Similarly, Cr₂O₃ formed on the surface of the chromia forming alloys may also react with CGO.

This study, therefore, focuses on the compatibility of (La,Sr)CrO₃, SrCrO₄, CaCrO₄ and Cr₂O₃ with CGO.

2 Experimental Procedure

2.1 Sample Preparation

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ was synthesised using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Arcos and Aldrich respectively, $\geq 99.9\%$ pure) by using the reverse strike co-precipitation method.¹¹ A 0.5 M aqueous oxalic acid solution was prepared and the pH adjusted to between 6.7 and 6.9 using a dilute ammonia solution. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water and then added drop-wise to the oxalic acid solution. Ammonia was added at the same time to maintain a pH of

between 5.0 and 6.0. The precipitate was filtered, then washed using distilled water and ethanol respectively. After drying, the powder was calcined at 700°C for 1 h, pressed, then sintered at 1600°C for a further 10 h. $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ (where $x = 0.0$ – 0.4) was prepared by employing the glycine nitrate process (GNP).¹² Stoichiometric mixtures of aqueous nitrate solutions containing $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Rectapur, Univar and Acros, respectively, $\geq 99.9\%$ purity) with glycine, were heated in a beaker until ignition. The resulting powders were calcined in air at 900°C for 12 h, pressed then sintered at 1650°C for 10 h.

SrCrO₄ was synthesised by placing the appropriate stoichiometric quantities of SrCO₃ and Cr₂O₃ (BDH) into a Retsch centrifugal ball mill with ethanol and partially stabilised zirconia grinding media (PSZ), and milling for 24 h. The as-synthesised powders were then calcined at 800°C for 2 h.

Using the GNP, Ca and Cr nitrates with glycine were combusted to produce CaCrO₄, the resulting powder was then calcined in air at 800°C for 2 h.

2.2 Pressing

The ceramic powders were mixed in a pestle and mortar with 2 wt% polyvinyl butyral (Aldrich). Enough acetone was then added to form a highly viscous mixture, which was then placed in an oven at 50°C until dry. The powder was ground, placed in a 15 mm diameter die, compacted with an uniaxial press using 30 MPa pressure, followed by pressing in an isostatic press at 200 MPa (Stansted Fluid Power Ltd. FPG2347). The binder was then burnt out by placing the samples in a furnace, ramped at 0.5 K/min to 500°C, held for 1 h, then cooled at 10 K/min to room temperature.

2.3 Powder mixtures

Powder mixtures, as detailed in Table 1, were prepared by mixing the powders together in a pestle and mortar then pressing them into pellet form. Powder mixtures of 1:1 molar ratios of $\text{La}_{1-x}\text{Sr}_x$

Table 1. Composition, molar ratio, reaction conditions and phase analysis of mixed powders (all powders were mixed with CGO in the ratios described)

Composition	Molar ratio	Reaction conditions	Phase analysis
$\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ($x = 0$ – 0.4)	1:1	1300°C/400 h	LSC and CGO
		1420°C/10 h	LSC and CGO
		1600°C/10 h	LSC and CGO
SrCrO ₄	1.36:1	750°C/67 h	SrCrO ₄ and CGO
SrCrO ₄	1.36:1	1300°C/24 h	SrCrO ₄ , SCC and CGO
CaCrO ₄	1.36:1	1300°C/24 h	CaCrO ₄ , CGO, Ca–Ce–Gd–Cr–O
Cr ₂ O ₃	1:1	650°C	Cr ₂ O ₃ and CGO
		1300°C/400 h	Cr ₂ O ₃ and CGO
		1400°C/10 h	Cr ₂ O ₃ and CGO
		1600°C/10 h	Cr ₂ O ₃ , CGO, Cr–Gd–O

Note: LSC = $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, CGO = $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, SCC = $\text{Sr}_{2.67}\text{O}_{0.33}(\text{CrO}_4)_{1.33}(\text{CrO}_4)_{0.67}$.

CrO_3 (where $x = 0.0, 0.1, 0.2, 0.3, 0.4$) and CGO, or of Cr_2O_3 and CGO were pressed into pellets. Similarly, CGO was mixed with either SrCrO_4 or CaCrO_4 in a 1:1.36 ratio. As described in the paper by Carter *et al.*,⁷ the amount of Ca for reaction with the YSZ electrolyte in $(\text{La,Ca})\text{CrO}_3$ was restricted, therefore mixtures of CaCrO_4 and thus SrCrO_4 were reacted with CGO in the molar ratio of 1.36:1. CaCrO_4 was considered to be of a similar composition to the transient liquid phase in $(\text{La,Ca})\text{CrO}_3$, therefore any reaction products associated with the $\text{CaCrO}_4/\text{CGO}$ mixture could be related to those of the transient liquid phase. SrCrO_4 was considered in a similar context.

All pellets were then annealed in air at various times and temperatures as described in Table 1. The pellets were then ground and analysed using X-ray powder diffraction (XRD) (Philips PW 1700 series automated powder diffractometer), equipped with a graphite monochromator. The characterisation was performed using Co-K_α radiation of weighted mean wavelength $\lambda = 1.79026 \text{ \AA}$ with generator settings of 45 kV and 35 mA.

2.4 Reaction couples

To study the interfacial compatibility of CGO with the related interconnect materials, interfacial reaction couples, given in Table 2, were prepared in the following manner. Cr_2O_3 and CGO pellets were pressed separately and the binders burnt out as described above. The Cr_2O_3 pellet was then fired at 1200°C for 2 h while CGO was fired at 1600°C for 10 h. After firing, the pellets were then polished down to a $1 \mu\text{m}$ diamond paste. The polished faces of Cr_2O_3 and CGO were then placed together with a 10 g weight on top inside a furnace. The reaction couple was then annealed for the various times and at the temperatures described in Table 2. The reaction couple of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ (pellet sintered at 1650°C), and CGO were prepared and reacted in a similar fashion.

In order to access the interfacial reactivity of SrCrO_4 and CaCrO_4 with CGO, SrCrO_4 and CaCrO_4 pellets were placed onto the polished faces of CGO sintered plates. As detailed in Table 2, $\text{SrCrO}_4/\text{CGO}$ reaction couples were then annealed at 1300°C for 24 h. Similarly, the $\text{CaCrO}_4/\text{CGO}$

reaction couple was prepared in the same fashion and annealed in air at 1300°C for 24 h.

All reaction couples were embedded in resin, sliced perpendicular to the interface and polished using $1 \mu\text{m}$ diamond paste. Scanning electron microscopy (SEM) (Cambridge Stereoscan MkII), equipped with energy dispersive X-ray analysis (Oxford-Link) was used to examine the lateral distribution of the elements across the reaction interface of the pellets.

3 Results and Discussion

3.1 Powder mixtures

Powder mixtures were fired at various temperatures and times in order to identify any reaction products between CGO and related interconnect materials; Table 1 shows these results. No reaction was observed, between $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ($x = 0.0-0.4$) at $1300, 1420$ or 1600°C . Similarly, as again described in Table 1, no reaction between SrCrO_4 and CGO was detected at 750°C for 67 h. However, as described in Fig. 1, $\text{Sr}_{2.67}\text{O}_{0.33}(\text{CrO}_4)_{1.33}(\text{CrO}_4)_{0.67}$ (SCC)⁸ was shown to form in the powder mixture reacted at 1300°C for 24 h. The CaCrO_4 1.36:1 CGO molar ratio fired at 1300°C over 24 h revealed that an unidentified phase was formed; the XRD trace is shown in Fig. 2. This unidentified phase was considered to be a perovskite, possibly orthorhombic in nature, as it was shown to closely match the ICDD* powder diffraction file number of InRhO_3 (21-409) and also match, to a lesser extent, those of LaCrO_3 (33-701), GdCrO_3 (25-1056) and CaCrO_3 (21-137), although, as described later, this is somewhat inconclusive. Based on this evidence the cell dimensions were determined to be approximately, $a = 5.3, b = 5.4, c = 7.6 \text{ \AA}$. When the Cr_2O_3 1:1 CGO molar ratio was fired over a range of temperatures, 650 to 1600°C , the only reaction product detected was for the sample fired at 1600°C . The reaction product, as observed in Fig. 3, was thought to be $\text{Ce}_{1-x}\text{Gd}_x\text{CrO}_3$ perovskite, as the XRD peaks are similar to those in the ICDD powder diffraction data base for LaCrO_3 and GdCrO_3 .

3.2 Interfacial studies of Cr_2O_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ on sintered CGO

The polished faces of the Cr_2O_3 and CGO pellets showed no visual signs of reaction after annealing at 1300°C for 400 h. EDX and SEM analysis were performed on the reaction faces and revealed no detectable migration of elements between the

Table 2. Reaction of associated interconnect materials on CGO sintered plates

Compound	Reaction conditions	Observations
Cr_2O_3	$1300^\circ\text{C}/400 \text{ h}$	No reaction
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$	$1300^\circ\text{C}/400 \text{ h}$	No reaction
SrCrO_4	$1300^\circ\text{C}/24 \text{ h}$	Enveloped and melted through pellet
CaCrO_4	$1300^\circ\text{C}/24 \text{ h}$	Enveloped and melted through pellet

*ICDD, International Centre on Diffraction Data, Newtown Square, PA.

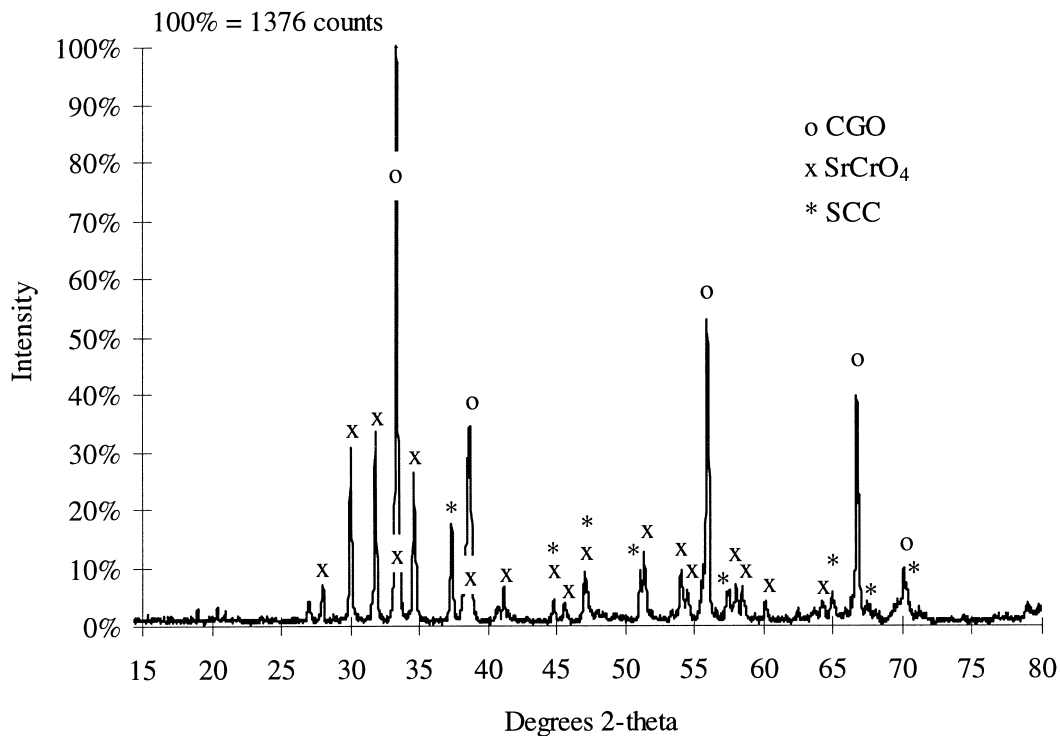


Fig. 1. XRD trace of a 1:36:1 molar ratio of SrCrO₄ and CGO powders fired at 1300°C over 24 h.

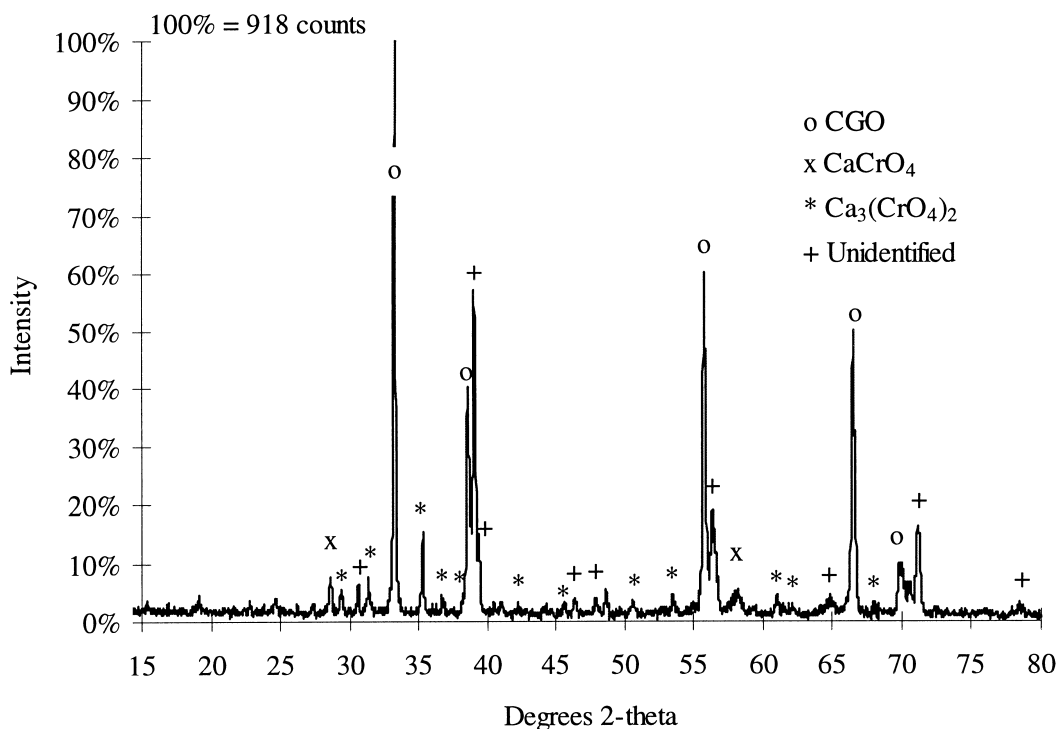


Fig. 2. XRD trace of a 1:36:1 molar ratio of CaCrO₄ and CGO powders fired at 1300°C over 24 h.

reaction couple. No reaction, as shown in Table 2, was detected for the La_{0.8}Sr_{0.2}CrO₃ and CGO reaction couple.

3.3 Interfacial studies of SrCrO₄ on sintered CGO

After annealing the SrCrO₄/CGO pellet couple in air at 1300°C for 24 h, visual examination showed the SrCrO₄ had partially melted and enveloped the entire surface of the CGO pellet. The SrCrO₄ pellet

had changed colour from yellow to a dark black-green with inclusions of crystals. The couple was mounted in resin and polished. A dark green discolouration was observed where the SrCrO₄ had migrated into the CGO. SEM and EDX analysis were then performed to understand the nature of the interaction at the SrCrO₄/CGO interface.

A backscatter image (Fig. 4), shows the reaction regions; position A shows a grain at the interface,

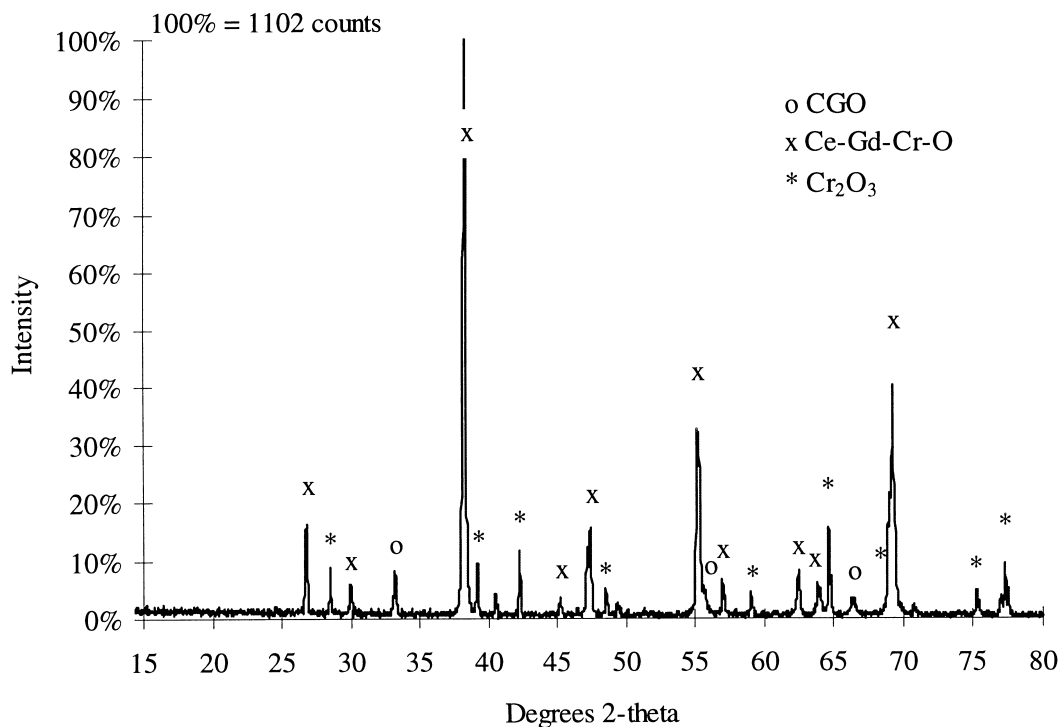


Fig. 3. XRD trace of a 1:1 molar ratio of Cr_2O_3 and CGO powders fired at 1600°C over 10 h.

position B shows a banded region on the edge of the CGO saturated with pores, position C shows that there is no reaction within the bulk of the CGO, and position D shows dark contrasted grain boundaries in the CGO.

As described in Table 3, using EDX point analysis at position A, a grain on the $\text{CGO}/\text{SrCrO}_4$ interface was shown to contain higher concentrations of Cr and Gd than Sr or Ce. As shown in the EDX map (Fig. 5) the grains present at the $\text{CGO}/\text{SrCrO}_4$ interface contain higher concentrations of Gd and Cr than Sr and Ce. In addition, EDAX line analysis confirmed Gd had diffused, forming a larger component of the grain than Ce, leaving behind the Ce in higher concentrations in the banded region, Fig. 4 position B of the CGO. Position

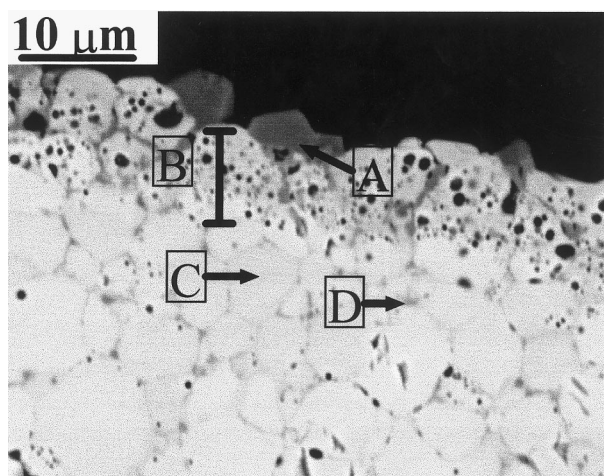


Fig. 4. SEM backscattered image of the $\text{SrCrO}_4/\text{CGO}$ reaction couple interface annealed at 1300°C for 24 h.

B, the reacted band on the CGO edge, was composed of a mixture of Sr and Cr at very low concentrations, and Ce and Gd in greater concentrations. Ce, relative to Gd, was seen to contain a proportionally higher concentration than in the bulk, position C, of the CGO sample due to the diffusion of the Gd into grains at the interface and grain boundaries D. The darker spots in the band were identified as pores.

Below the band on the edge of the CGO, EDX results indicated that bulk diffusion of Sr and Cr into CGO did not occur, as shown at position C. However, Cr was shown in position D to be present at the grain boundaries. It was considered that the phase formed in the grain boundaries was the same as that formed at the interface at position A. In addition, it was evident that Gd was in higher concentrations in the grain boundary relative to Ce than in the bulk grains of the CGO.

3.4 Interfacial studies of CaCrO_4 on sintered CGO

After annealing at 1300°C for 24 h, the CaCrO_4 pellet had melted and enveloped the CGO pellet.

Table 3. EDX point analysis of the $\text{SrCrO}_4/\text{CGO}$ reaction couple interface annealed at 1300°C for 24 h

Element	Position A (element wt%)	Position B (element wt%)	Position C (element wt%)	Position D (element wt%)
Sr	9	1	—	1
Cr	24	7	—	5
Ce	15	27	69	56
Gd	31	12	17	23

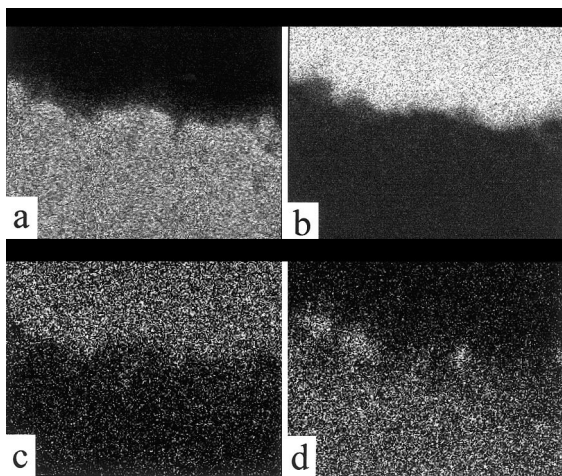


Fig. 5. X-ray backscattered map of the SrCrO₄/CGO reaction couple interface annealed at 1300°C for 24 h: (a) Ce; (b) Sr; (c) Cr; (d) Gd.

The CaCrO₄ had turned black and had appeared, upon visual examination, to have melted through the CGO. Analysis of the backscattered SEM micrograph [Fig. 6 (position A)], indicated that the lighter contrasted CGO grains were reacting with Ca–Cr–O transient liquid phase and being digested as the Ca–Cr–O migrated along grain boundaries, and the free surface, to form unidentified darker contrasted grains in very high concentration, position B. Pores present in CGO grains were shown to exist only after annealing, thus their formation was attributed to the reaction of CGO with CaCrO₄.

Table 4 shows the results of the EDX point analysis performed on the CaCrO₄/CGO reaction couple. Analysis of an unreacted CGO grain, position A (Table 4, Fig. 6), shows there to be only Ce and Gd present. The unidentified dark grain, position B (Table 4, Fig. 6), was shown to contain Ce, Gd, Cr, and Ca, where-by these dark grains contain relatively high concentrations of Cr and Gd compared to Ca and Ce. It was the high concentration of these dark grains that was attributed to the unidentified XRD pattern shown in Fig. 2,

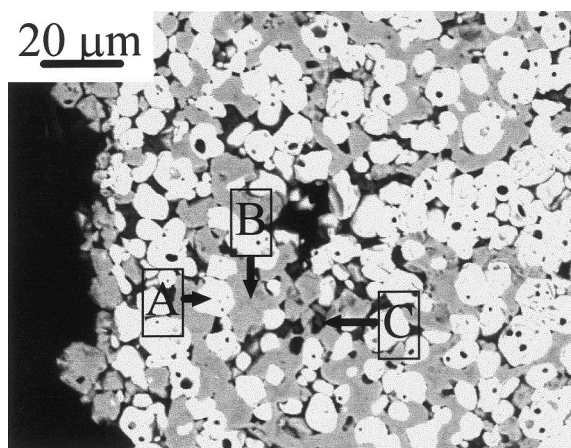


Fig. 6. SEM backscattered image of the CaCrO₄/CGO reaction couple interface annealed at 1300°C for 24 h.

Table 4. EDX point analysis of the CaCrO₄/CGO reaction couple interface annealed at 1300°C for 1 h

Element	Position A (element wt%)	Position B (element wt%)	Position C (element wt%)
Ca	2	11	32
Cr	2	26	23
Ce	67	12	2
Gd	10	28	6
O	15	23	25

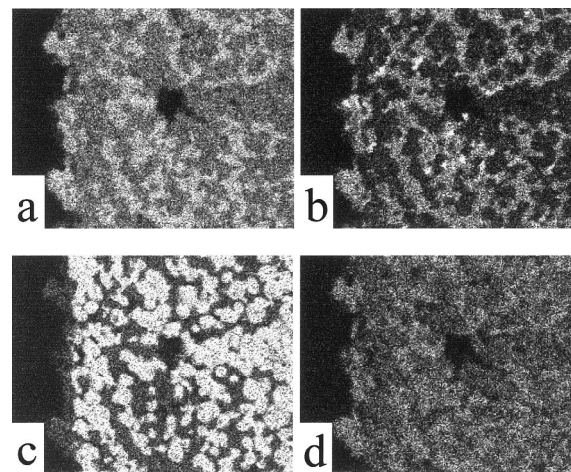


Fig. 7. X-ray backscattered map of the CaCrO₄/CGO reaction couple interface annealed at 1300°C for 24 h: (a) Cr; (b) Ca; (c) Ce; (d) Gd.

obtained from the previous powder mixture experiments involving the annealing of a CaCrO₄ 1:36:1 CGO molar ratio reacted at 1300°C (Table 1). However, although the XRD analysis suggested the structure of the unidentified phase was a perovskite, EDX analysis did not show this. Therefore, no conclusions as to the structure of the unidentified phase could be drawn.

A third phase, position C (Table 4, Fig. 6), was present in very low concentrations and shown to contain higher amounts of Ca and Cr than Ce or Gd; again Gd was shown to be in higher concentration than Ce. The EDX map shown in Fig. 7 clearly identifies the distribution of the two phases present. It appeared that the SrCrO₄/CGO and CaCrO₄/CGO reaction couples, position A (Table 3, Fig. 4) and position B (Table 4, Fig. 6), had similar EDX elemental wt% for Ce, Gd and Cr. This indicated that the phase at the interface for SrCrO₄/CGO couple may have been the same as the unidentified phase observed in the XRD trace of the CaCrO₄/CGO powder mixture in Fig. 2.

4 Conclusions

SrCrO₄ was shown to react by way of a Sr–Cr–O liquid phase with CGO. An unknown phase

formed at the SrCrO₄/CGO interface and grain boundaries, consisting of Ce, Gd, Sr, and Cr. Similarly, CaCrO₄ reacted with CGO via a transient Ca–Cr–O phase, digesting CGO grains, forming an unknown phase similar to that observed above. Phase pure (LaSr)CrO₃ did not react with CGO even at temperatures well above co-sintering temperatures, while Cr₂O₃ was shown to be compatible with the electrolyte and only reacted at temperatures well above the operational and co-sintering temperatures.

This study shows the detrimental effect the presence of SrCrO₄ and CaCrO₄ in doped lanthanum chromites can have on the chemical stability of CGO at the temperatures required for co-sintering, and illustrates how chemical compatibility can be achieved by use of single phase (LaSr)CrO₃ material.

References

1. Dokiya, M., Horita, T., Saki, N., Kawada, H., Yokokawa, van Hassel, B. A. and Montross, C. S., Interconnector chemistry. In *Proceedings of the 14th Risø International Symposium on Materials Science 1993*, ed. F. W. Poulsen, J. J. Bentzen, T. Jacobsen, E. Skou and M. J. L. Østergård. Risø National Laboratory, Roskilde, Denmark, 1993, pp. 33–41.
2. Akiyama, Y., Taniguchi, S., Yasuo, T., Kadowaki, M. and Saitoh, T., Surface treatment of alloy separator in a planar-type solid oxide fuel cell. *J. Power Sources*, 1992, **50**, 361–368.
3. Schmidt, H., Bruckner, B. and Fischer, F., Interfacial functional layers between the metallic bipolar plate and the ceramic electrodes in the high temperature solid oxide fuel cell. In *Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells (SOFC-IV)*, ed. M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal. The Electrochemical Society, Yokohama, Japan, 1995, pp. 869–878.
4. Kimura, T., Namikawa, T. and Yamazaki, Y., Metal-wire current collectors for SOFC cathode. *Denki Kagaku*, 1993, **6**, 1115.
5. Kadowaki, T., Shiomitsu, T., Matsuda, E., Nakagawa, H., Tsuneyumi, H. and Maruyama, T., Applicability of heat resisting alloys to the separator of planar type solid oxide fuel-cell. *Solid State Ionics*, 1993, **67**, 65–69.
6. Shiomitsu, T., Kadowaki, T., Ogawa, T. and Maruyama, T., The influence of (LaSr)CoO₃ coatings on the electrical resistance of Ni–20Cr alloys in high temperature oxidising atmosphere. In *Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells (SOFC-IV)*, ed. M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal. The Electrochemical Society, Yokohama, Japan, 1995, pp. 850–857.
7. Carter, J. D., Appel, C. C. and Mogensen, M., Reactions at the calcium-doped lanthanum chromite–yttria stabilized zirconia interface. *Journal of Solid State Chemistry*, 1996, **122**, 407–415.
8. Negas, T. and Roth, R. S., The system SrO–chromium oxide in air and oxygen. *J. Res. Nat. Bur. Stand.*, 1996, **73A**(4), 431–442.
9. Kawada, T., Sakai, N., Yokokawa, H., Dokiya, M. and Anzai, I., Reaction between solid oxide fuel-cell materials. *Solid State Ionics*, 1992, **50**, 189–196.
10. Mori, M., Itoh, H., Mori, N., Abe, T., Yamamoto, O., Takeda, Y. and Imanishi, N., Reaction between alkaline earth metal doped lanthanum chromite and yttria stabilized zirconia. In *Science and Technology of Zirconia*, Vol. V, ed. S. P. S. Badwal, M. J. Bannister, and R. H. J. Hannink. Technomic, Lancaster, PA, 1993, pp. 776–785.
11. Herle, J. V., Horita, T., Kawada, T., Sakai, N., Yokokawa, H. and Dokiya, M., Preparation of doped ceria powder. In *Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells (SOFC-IV)*, ed. M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal. The Electrochemical Society, Yokohama, Japan, 1995, pp. 1082–1091.
12. Chick, L. A., Pederson, L. R., Maupin, G. D., Bates, J. L. and Exharhos, J. G., Glycine–nitrate combustion synthesis of oxide ceramic powders. *Mater. Lett.*, 1990, **10**, 1–26.