ELECTRICAL CONDUCTIVITY, SINTERABILITY AND MICROSTRUCTURAL STUDIES ON CALCIUM AND NICKEL DOPED LANTHANUM CHROMITE

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ABSTRACT

The substitution of 10mol% nickel for chromium in calcium doped lanthanum chromites has been shown to promote rapid densification of the compound at low temperatures in air by the formation of a transient liquid phase. Initial stability tests at 900°C in wet forming gas, suggested that the material was stable towards reduction, but in subsequent conductivity measurements at 1000°C, severe microstructural degradation occurred in atmospheres of H₂ and CO₂, liquids were re-generated and samples became embrittled. The processes leading to chemical degradation in the CO₂ containing atmospheres are not fully understood but have been attributed to decomposition of small amounts of residual calcium oxychromites remaining after sintering.

1. INTRODUCTION

The bipolar plate or interconnect material in the SOFC is subjected to high temperatures, chemical environments, current density variations and thermal stresses. The material requirements include chemical and mechanical stability, low volatility, non-reactivity with other cell components, high electronic conductivity but negligible ionic conductivity and thermal expansion characteristics compatible with other cell components. Doped lanthanum chromite is used in the Westinghouse tubular SOFC, and is also considered the most promising candidate material for planar SOFC interconnects. Most of the aforementioned requirements are satisfied by doped lanthanum chromite, but air sinterability and densification has proved to be very difficult owing to the high volatility of Cr. Over the years this problem has been addressed by many authors and has included work on the addition of fluoride mixtures (1), and the addition of SrCO₃ to (La,Sr)CrO₃ (2),(3). More recently cobalt substitutions for chromium have been shown to promote a liquid phase sintering mechanism resulting in dramatic increases in sintered density at low temperatures (4),(5). Sakai et al reported that a 2% chromium deficiency in calcium doped compounds, facilitates densification of the compound at low temperatures in air (6),(7). The authors have recently published work reporting that the calcium doped...
compounds and to a lesser extent strontium doped compounds, densified via cobalt substitutions were not stable under simulated SOFC operating conditions (8). The work concluded that the microstructural degradation was a result of migration of second phase material that facilitated densification of the compounds.

The present paper reports on the sinterability of calcium and nickel doped compounds, and includes electrical conductivity and microstructural studies

2. EXPERIMENTAL

Powders of general composition $\text{La}_x\text{Ca}_{1-x}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (were $x = 0.2, 0.3$ and $0.4$) were prepared by a modified citrate route first developed by Pechini (9). Powders had particle size distributions centred around 2 $\mu$m and surface areas, of 4.5 m$^2$g$^{-1}$. All powders were analysed by XRD and although consisting predominantly of the perovskite, significant traces of CaCrO$_4$ were found for all compositions. 5cm bars were pressed at 150 MPa for electrical conductivity measurements and pellets were pressed at 300 MPa in a 13 mm diameter die for dilatometry, quench and stability tests. All powder compacts were sintered at 1500°C for 2 hours. After sintering, pellets of each composition were polished and re-analysed by XRD. In the sintered material no trace of the CaCrO$_4$ could be found, although very small traces of a second phase were observed which is yet to be identified.

Shrinkage versus temperature data during sintering was collected for a pellet of composition $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$. Samples of composition $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ and $\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ were removed from the furnace at temperatures of 1170°C and 1385°C during the sintering regime and air quenched to room temperature. Fractured cross-sections and edges of the pellets were then examined in SEM in conjunction with EDAX analyses.

Powder and a sintered sample of composition $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ were equilibrated at 900°C in an atmosphere of flowing forming gas (90% N$_2$, 10% H$_2$), for 200 hours. The gas was bubbled through water at a flow rate of 25 ml min$^{-1}$ and the pO$_2$ was measured to be $5 \times 10^{-16}$ atm. Reduced samples were analysed by XRD, fracture surfaces and polished and thermally etched sections of the reduced, sintered sample were examined in SEM in conjunction with EDAX analyses.

Electrical conductivity measurements were made on bar samples (20mm x 5mm x 3mm) by an established DC four probe technique using platinum contact wires, and a constant current of 10 mA. The sample was enclosed inside a quartz tube and the atmosphere adjusted from a bank of gas blenders for air, CO$_2$ and H$_2$. The oxygen partial pressure inside the quartz envelope was measured by an in-situ zirconia probe placed close to the sample. Measurements were made from room temperature up to 1000°C in air followed by measurements under reducing conditions by mixing H$_2$ and CO$_2$. The range of oxygen partial pressures covered by this method was from 0.2 to $10^{-19}$ atm. The change in conductivity was monitored continuously with time and held at the selected pO$_2$ until a steady value was observed. After the final measurement, the sample was allowed to
cool down in the reducing atmosphere with dc current still flowing. Fracture surfaces and polished and thermally etched cross-sections of the bars were then again examined in SEM in conjunction with EDAX analyses.

3. RESULTS

Figure 1 compares shrinkage versus temperature data obtained during the sintering of La$_{0.8}$Ca$_{0.2}$Cr$_{0.9}$Ni$_{0.1}$O$_3$ and La$_{0.8}$Ca$_{0.2}$CrO$_3$. It is quite clear that the substitution of 10 mol% nickel for chromium in the conventional compound results in a dramatic increase in sinterability. The conventional compound shows virtually no shrinkage on heating to 1550°C. Substituting 10 mol% nickel onto the B site in the perovskite structure results in two distinct regions of shrinkage behaviour. The first commences at around 1050°C and continues to 1285°C where there is an inflection in the curve suggesting a change in the sintering mechanism of the compound. Figure 2 is a backscattered SEM micrograph showing the fracture surface close to the edge of a sample of composition La$_{0.6}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_3$. The sample was removed from the furnace at 1170°C during the sintering regime and air quenched to room temperature. Figures 3 and 4 are backscattered micrographs of the actual surface. The micrographs display a phase which was very obviously liquid at 1170°C. EDAX analysis, figure 5, showed this phase to be rich in calcium and chromium. EDAX analysis of liquid in the bulk revealed that impurities such as silicon, potassium and aluminium were generally concentrated in the liquid. The impurities are present in the precursors and can be picked up from the furnace during calcination. The same liquid was also observed in samples containing lower levels of calcium, but to a lesser extent. Although liquid was observed in fracture surfaces in the bulk of the samples, a much higher concentration was observed at the surfaces. Liquid could also be seen in the samples quenched from 1385°C but again to a lesser extent. No evidence of the liquid could be found in fully sintered samples.

Having found that nickel substitutions generate a liquid phase sintering mechanism resulting in a highly sinterable system, stability towards reduction was investigated. Powder and a sintered sample of composition La$_{0.8}$Ca$_{0.2}$Cr$_{0.9}$Ni$_{0.1}$O$_3$ were equilibrated at 900°C in an atmosphere of wet forming gas, as described in the experimental section. XRD analysis of the reduced samples showed no evidence of chemical degradation. The fracture surface of the sintered, reduced sample was examined in backscattered SEM in conjunction with EDAX analysis, the results, which are presented in figures 6 and 7, confirm that the system had remained stable and unaffected by the reduction in wet forming gas.

Electrical conductivity data as a function of oxygen partial pressure at 1000°C is presented in figure 8. The sample of composition La$_{0.8}$Ca$_{0.2}$Cr$_{0.9}$Ni$_{0.1}$O$_3$ had a conductivity of 45 S cm$^{-1}$ in air and followed the classical model for compounds of this type, showing a region of relatively stable conductivity where compensation for the introduction Ca$^{2+}$ ions results in the formation of small polarons as charge carriers, region 1 and then transfers to a region of falling conductivity where the predominant compensation mechanism for the
lower valence cations is changing from electronic to ionic, resulting in the formation of oxygen vacancies, region 2. The sample of composition \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Ni}_{0.7}\text{O}_3 \) had a conductivity of 61 S cm\(^{-1}\) in air, but deviations from the defect model were apparent in the pO\(_2\) range 10\(^{-3}\) to 10\(^{-7}\) atm, where the conductivity was lower than expected. On cooling, the bar sample was found to be cracked and embrittled. The sample of composition \( \text{La}_{0.5}\text{Ca}_{0.4}\text{Cr}_{0.9}\text{Ni}_{0.7}\text{O}_3 \) had a conductivity of 92 S cm\(^{-1}\) in air, during the course of experiment the sample became severely unstable, large deviations from the model were observed, particularly at a pO\(_2\) of 10\(^{-7}\) to 10\(^{-11}\) atm where the conductivity rose to over 200 S cm\(^{-1}\). The test was aborted at a pO\(_2\) of 10\(^{-11}\) atm as the data was becoming too unreliable. As for the previous sample, on cooling the sample was found to be cracked and embrittled.

Figure 9 shows a fracture surface in the bulk of the bar sample of composition \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Ni}_{0.7}\text{O}_3 \) following completion of the electrical conductivity experiment. It is quite clear that the conditions experienced during the course of the experiment forced the system to become unstable and caused severe microstructural degradation. The regular grain structure depicted in figure 6 has been broken down and a quenched liquid can be seen to have spread throughout the structure, wetting the grains. Figure 10 shows the same sample after polishing and thermal etching at 1410°C for 0.5h, the quenched liquid can be seen to contain significant amounts of a brighter, solid phase. EDAX analysis of the liquid, figure 11, shows that it contains a high concentration of impurities and has a composition which is very rich in calcium. Analysis of the brighter, solid phase indicates that it is the original \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Ni}_{0.7}\text{O}_3 \).

### 4. DISCUSSION

The transient liquid phase which facilitates densification of the compound is likely to have been formed by incongruent melting of \( \text{CaCrO}_4 \) present in the powders to a calcium oxychromate liquid of general composition \( \text{Ca}_m(\text{CrO}_4)_n \). Work is underway to determine the exact nature of the liquid, which is likely to change composition with temperature. A change in the composition of the liquid may explain the inflection in the sintering curve. Sakai and co-workers note the formation of a similar liquid during the sintering of chromium deficient lanthanum chromites (8) and report that the Ca/Cr ratio in such calcium oxychromate melts increases with temperature. It is thought that the liquid is soluble in \( \text{La}_x\text{Ca}_{1-x}\text{Cr}_{0.9}\text{Ni}_{0.7}\text{O}_3 \) at high temperatures, leading to grain growth and densification. Less liquid was noted in samples quenched from 1170°C than in those quenched from 1385°C and the solubility of the liquid at high temperatures would explain why the liquid phase appears to be transient.

Microstructural analysis of the samples on completion of the electrical conductivity tests confirm that at a temperature of 1000°C, under atmospheres of CO\(_2\) and forming gas and in combination with a potential difference, liquids are regenerated within the system. The exact nature of the liquid is not yet known and will be reported in a future publication, however EDAX results indicate that it is richer in calcium than the liquid seen in the quench tests. The substantial increase in electrical conductivity in the
sample of composition La_{0.6}Ca_{0.4}Cr_{0.5}Ni_{0.1}O_{3} at a pO_2 of 10^{-7.5} atm suggests that a large amount of liquid was generated in this region of pO_2. It is thought that the liquid seen in the conductivity tests may originate from reaction with the small amount of residual second phase material which was noted during XRD of sintered samples, this residual second phase was not visible in SEM but may be present at grain boundaries.

The fact that the system, even in powder form, remained stable at 900°C under an atmosphere of wet forming gas, suggests that CO_2 is responsible for the chemical degradation. However, we have not yet ruled out the possibility of the electric current exerting an influence. It should also be noted that the initial stability tests were performed at 900°C whereas the conductivity measurements were carried out at 1000°C, but future work will investigate the effect of temperature on degradation.

5. CONCLUSIONS

Nickel substitutions have been shown to promote rapid densification of calcium doped lanthanum chromites by the generation of a liquid phase. However, calcium doped LaCrO_3 based materials which use a liquid phase sintering mechanism to facilitate densification are probably not stable in the presence of CO_2 and the work emphasises the need to evaluate interconnect materials under realistic conditions where chemical degradation by corrosive gases might occur, particularly in SOFC systems run on fuels other than hydrogen.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the U.K. Science and Engineering Research Council, and ICI (Advanced Materials), Runcorn. Mr Geoff Dolman of ICI is acknowledged for providing the dilatometry data.
REFERENCES

(1) B.K. Flandermeyer et al, "Addition of 8-10 wt.% of a (La or Y)-Mg Fluoride mixture as a sintering aid.", Abstracts of the 1986 Fuel Cell Seminar, Washington D.C. (Courtesy Associates Inc.) p.68-71.

(2) D.B. Meadowcroft, "Some properties of Strontium-doped Lanthanum Chromite" Brit. J. Appl. Phys. (J. Phys. D.), 2, ser.(2), p.1225-33.

(3) K.P. Bansal, S. Kumari, B.K. Das and G.C. Jain, "On the Sintering and Dielectric Properties of Ceramic La_{0.96}Sr_{0.04}CrO_3", Trans. J. Br. Ceram. Soc. 80, (1981), 215-19.

(4) R. Koc and H.U. Anderson, "Liquid phase sintering of lanthanum chromite", Journal of the European Ceramic Society, 9, (1992), p.285-292.

(5) M.M. Nasrallah, J.D. Carter, H.U. Anderson and R. Koc, "Low temperature air sinterable LaCrO_3 and YCrO_3, "Proc. of the 2nd International Symposium on SOFC'S", Athens, 2-5 July 1991, p.637-644.

(6) N. Sakai, T Kawada, H. Yokokawa, M. Dokiya and T. Iwata, " Sinterability and electrical conductivity of calcium-doped lanthanum chromites", J. of Materials Science, 25, (1990), p.4531-4534.

(7) N. Sakai, T Kawada, H. Yokokawa, M. Dokiya and T. Iwata, "Thermal expansion of some chromium deficient lanthanum chromites", Solid State Ionics, 40/41, (1990), p.394-397.

(8) N. Sakai, T Kawada, H. Yokokawa and M. Dokiya, "Chemical Stability of (La,Ca)CrO_3 interconnects", Proceedings of Zirconia V, Melbourne, 1992

(9) M. Pechini, Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor" U.S. Patent No. 3,330,697, July 1967
Figure 1: A comparison of linear shrinkage versus temperature during the sintering of La$_{0.8}$Ca$_{0.7}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$, and La$_{0.8}$Ca$_{0.7}$CrO$_{3}$.

![Graph showing linear shrinkage versus temperature for two samples: La$_{0.8}$Ca$_{0.7}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$ and La$_{0.8}$Ca$_{0.7}$CrO$_{3}$, with temperature on the x-axis ranging from 0 to 1750°C and shrinkage on the y-axis ranging from 0 to 2%. The graph indicates a decrease in shrinkage with increasing temperature for both samples.]

Figure 2: Backscattered micrograph close to the surface of La$_{0.6}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$, quenched from 1170°C during sintering, fracture surface, mag. x750.

![Backscattered micrograph showing the surface of La$_{0.6}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$, quenched from 1170°C during sintering. The bar is 100 µm.

Figure 3: Backscattered micrograph of the surface of La$_{0.6}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$, quenched from 1170°C during sintering, mag. x500.

![Backscattered micrograph showing the surface of La$_{0.6}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_{3}$, quenched from 1170°C during sintering. The bar is 100 µm.]

Figure 2 bar = 100 µm  Figure 3 bar = 100 µm
Figure 4: Backscattered micrograph of the surface of La$_{0.4}$Ca$_{0.4}$Cr$_{0.9}$Ni$_{0.1}$O$_3$, quenched from 1170°C during sintering, mag. x75.

Figure 5: EDAX analysis of the liquid in figures 3 and 4.

Figure 6: Microstructure of La$_{0.8}$Ca$_{0.2}$Cr$_{0.9}$Ni$_{0.1}$O$_3$, reduced, wet forming gas 200h, backscattered fracture surface, mag. x1500.
Figure 7: EDAX analysis of the grains in figure 6

Figure 8: Electrical conductivity as a function of oxygen partial pressure for \( \text{La}_{1-x}\text{Ca}_x\text{Cr}_{0.9}\text{Ni}_{1-x} \text{O}_3 \) at 1000°C

Figure 9: Fracture surface of \( \text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.9}\text{Ni}_{1-x} \text{O}_3 \) following completion of the electrical conductivity experiment, mag. x1500.
Figure 10: Polished and thermally etched microstructure of La$_{0.7}$Ca$_{0.3}$Cr$_{0.5}$Ni$_{0.5}$O$_{2}$, following completion of the electrical conductivity experiment, mag. x1500.

![Image of microstructure](image)

bar = 10 μm

Figure 11: EDAX analysis of the quenched liquid in figure 10

![EDAX analysis of liquid](image)

Figure 12: EDAX analysis of the solid phase in figure 10

![EDAX analysis of solid phase](image)