CONF-921114--4

PNL-SA--21446

DE93 004837

EFFECTS OF COMPOSITION ON SINTERING OF CURRENT INTERCONNECTS IN SOFC

L. A. Chick
J. L. Bates

November 1992

Presented at the
1992 Fuel Cell Seminar
November 29 - December 2, 1992
Tucson, Arizona

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

EFFECTS OF COMPOSITION ON SINTERING OF CURRENT INTERCONNECTS IN SOFC

Larry A. Chick and J. Lambert Bates
Pacific Northwest Laboratory*
Richland, WA 99352

Introduction. PNL is investigating the sintering behavior of alkaline-earth-substituted lanthanum and yttrium chromites, which are candidates for the current interconnect in solid oxide fuel cells (SOFC). Extensive commercialization of SOFC technology may involve co-sintering as a method to reduce production costs. Co-sintering will require that the interconnect material reaches high density (closed porosity) under conditions in which the air-electrode material, a manganite, maintains substantial porosity and remains stable. Therefore, ideal chromite compositions are those that attain greater than 94% of theoretical density in high Po_2 atmosphere at temperatures near or below 1400°C.

Experimental. Chromite powders were synthesized by the glycine/nitrate process using a "stoichiometric" molar ratio of glycine-to-nitrate ($g/n \approx 0.55$)[1,2]. The powder was calcined at 650°C for 0.5 hr, uniaxially pressed (no binder) at 35 MPa and then isostatically pressed at 140 MPa into appx. 21 mm diameter by 3 mm thick samples. The pellets were set on edge in alumina racks and sintered in an electrical resistance-heated furnace in air. Sintered densities were measured by immersion weighing in ethyl alcohol; theoretical densities were based on lattice parameters by X-ray diffraction. Sintering shrinkage curves were determined on dry-pressed pellets (appx. 5 mm right cylinders) in a vertical push-rod dilatometer by heating at 2°C/min.

Results and Discussion. Chromites have the ABO_3 perovskite structure, in which the number of "A-site" cations (La or Y plus Ca or Sr) is nominally equal to the number of "B-site" cations (Cr). However, it has been demonstrated that slight enrichment or depletion of the A-site cations in relation to the B-site cations can substantially alter sintering behavior of the chromites[3-5]. This effect is shown in Figure 1, a plot of percent of theoretical density achieved versus calcium content when pellets of $La_{0.7}Ca_xCrO_3$ were heated at 100°C/hr to 1400°C and then quenched. Samples that were slightly enriched in calcium relative to the stoichiometric level ($x>0.30$) sintered nearly to theoretical density, while those that were slightly depleted ($x<0.30$) remained highly porous. Similar density changes have also been observed near $A/B=1.0$ in $La(Sr)CrO_3$ and $Y(Ca)CrO_3$ systems[3].

Operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830.

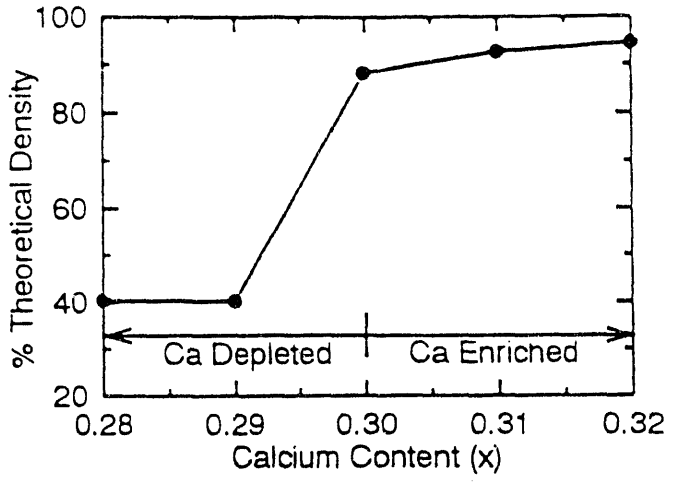

Figure 1. Percent of theoretical density attained by $La_{0.7}Ca_xCrO_3$ samples as a function of the calcium content, x. Samples were heated at 100°C/hr to 1400°C and quenched.

Due to the difficulty of determining the absolute composition of these chromites, it cannot yet be stated with certainty whether the steep increase in sintered density occurs as the A-site content is increased *up to* the stoichiometric amount from below, as indicated by Figure 1, or as the A-site content is increased to levels *above* the stoichiometric amount.

The characteristic differences in sintering shrinkage curves between A-site depleted and A-site enriched chromites are illustrated for two calcium-substituted systems in Figures 2 and 3. All four of the curves in these plots exhibit rapid-shrinkage events indicative of liquid-phase sintering[3]. However, for both chromite systems, the A-site enriched material has *two* rapid-shrinkage episodes, while the A-site depleted composition shows only *a single* such event. Also, notice that the *onset* of the first event occurs at a lower temperature in the A-site enriched samples (≈950°C) than in the A-site depleted samples (≈1000°C).

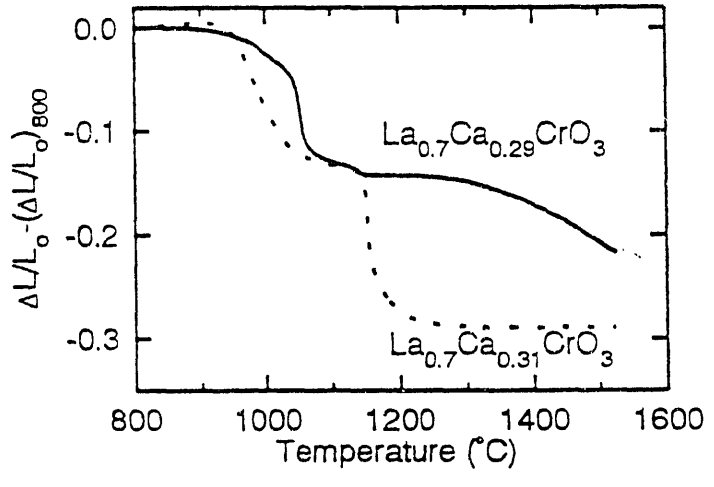

Figure 2. Sintering shrinkage curves for $La_{0.7}Ca_{0.29}CrO_3$ and $La_{0.7}Ca_{0.31}CrO_3$. Samples were heated in a vertical dilatometer at 2°C/min. Data normalized to zero at 800°C.

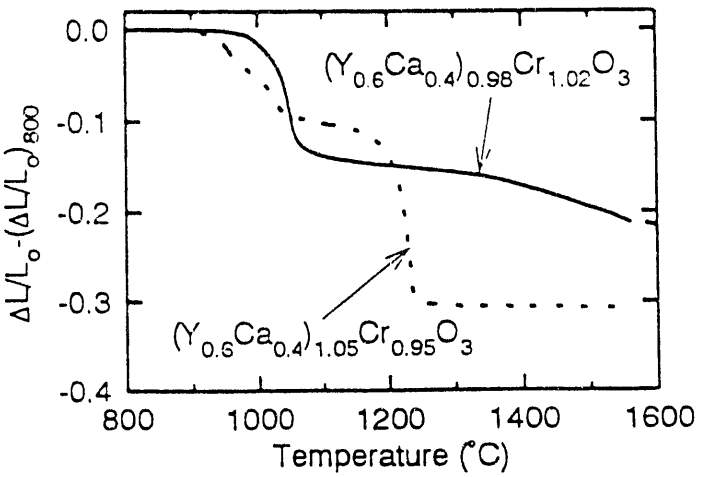

Figure 3. Sintering curves for $(Y_{0.6}Ca_{0.4})_{0.98}Cr_{1.02}O_3$ and $(Y_{0.6}Ca_{0.4})_{1.05}Cr_{0.95}O_3$. Samples were heated in a vertical dilatometer at 2°C/min. Data normalized to zero at 800°C.

The rapid shrinkage events in all of these samples are associated with the exsolution, decomposition and melting of calcium chromate, $CaCrO_4$, as discussed elsewhere[3]. However, although the characteristic changes caused by A-site enrichment (the lower onset and the second event) are reproducible and occur in both $La(Ca)CrO_3$ and $Y(Ca)CrO_3$ systems, the mechanistic reasons for the changes are not yet understood.

Another approach to increasing the shrinkage rates of chromites is to add various elemental substitutions for chromium on the B-site. The sintering curve for a sample with 10% cobalt substitution is compared to that of the corresponding material with slight A-site enrichment in Figure 4. The cobalt-containing sample does not reach high density until 1400°C or above.

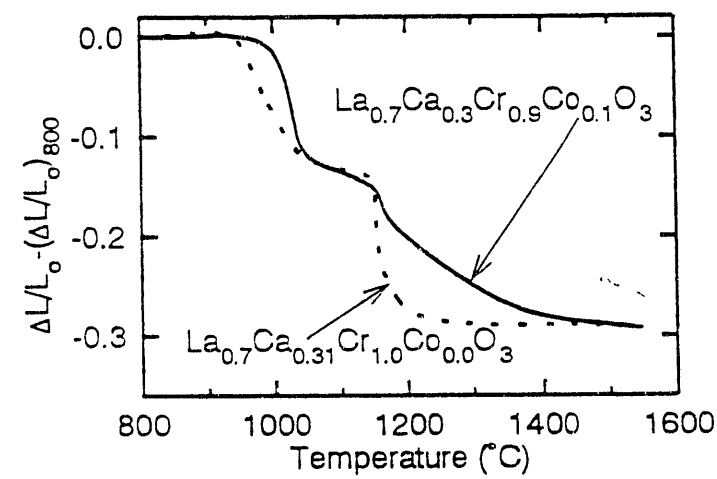

Figure 4. Sintering curves for $La_{0.7}Ca_{0.30}Cr_{0.9}Co_{0.1}O_3$ (cobalt-substituted) and $La_{0.7}Ca_{0.31}Cr_{1.0}Co_{0.0}O_3$ (A-site enriched, no cobalt). Samples were heated in a vertical dilatometer at 2°C/min. Data normalized to zero at 800°C.

Figure 5 compares sintering curves of the A-site depleted chromite, $(Y_{0.6}Ca_{0.4})_{1.05}Cr_{0.95}O_3$, with that of a candidate air electrode material, $Y_{0.4}Ca_{0.6}MnO_3$. As required for co-sintering, the chromite reaches high density by about 1250°C in air, at which point the manganite still retains significant open porosity.

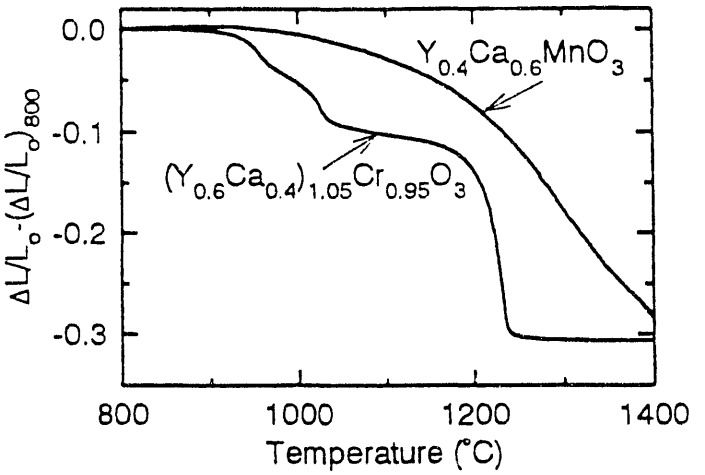

Figure 5. Sintering shrinkage curves for $(Y_{0.6}Ca_{0.4})_{1.05}Cr_{0.95}O_3$ and $Y_{0.4}Ca_{0.6}MnO_3$. Samples were heated in a vertical push-rod dilatometer at 2°C/min. Shrinkages are normalized to zero at 800°C.

Conclusion. Successful co-sintering will require management of relative green densities to control stresses induced by the different sintering rates as well as control of possible liquid-phase wicking. Nevertheless, this work demonstrates that chromite A/B ratio can be manipulated to indicate possible co-sintering with an appropriate manganite.

References.

1. LA Chick, LR Pederson, GD Maupin, JL Bates, LE Thomas, and GJ Exarhos, Mater. Lett. 10 (1990) 6.

2. LA Chick, LR Pederson, GD Maupin and JL Bates. "Ultra-Fine Powders Using Glycine-Nitrate Combustion Synthesis", in Proceedings of the Fifth Annual Conference on Fossil Energy Materials. CONF-9105184 and ORNL/FMP-91/1 Oak Ridge National Laboratory, Oak Ridge, TN (1991) 117.

3. LA Chick, JL Bates and GD Maupin. "Air-Sintering Mechanisms of Chromites", in Proceedings Second International Symposium on Solid Oxide Fuel Cells. F. Grosz, P. Zegers, S.C. Singhal and O. Yamamoto, Eds. EUR 13564. Athens Greece. Commission of the European Communities, Luxembourg (1991) 621.

4. N Sakai, T Kawada, H Yokokawa, and M Dokiya. Solid State Ionics 40/41 (1990) 394.

5. M Mori, N Sakai, T Kawada, H Yokokawa, and M Dokiya. Denki Kagaku 59(4) (1991), 314.

END

DATE FILMED

4/20/93