A Novel Approach to Develop Dense Lanthanum Calcium Chromite Sintered Ceramics with Very High Conductivity

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Solid oxide fuel cells (SOFCs), wherein chemical energy of a gaseous fuel is converted to electrical energy through solid state electrochemical reactions, have great potential as power-generating devices for both mobile and stationary applications. SOFC is a solid-state device consisting of two porous electrodes (anode and cathode) separated by a dense solid ion-conducting electrolyte. Since individual cells generate relatively low voltage, a number of cells need to be connected in both series and parallel to have a realistic power source, and for this purpose an interconnect is used as an integral part of the stack. The primary function of the SOFC interconnect is to connect the anode of one cell to the cathode of the adjacent cell, in addition to separating fuel from the oxidant and providing mechanical support to the planar SOFC stack.[1−3]

Acceptor substituted lanthanum chromite perovskite oxides are currently considered to be the most promising interconnect materials.[3−5] However, the poor sinterability of these compounds in air due to high chromium evaporation imposes a major constraint to their fabrication and utility. To improve the sinterability of doped (Mg, Ca, Sr) lanthanum chromite powders several attempts have been made such as addition of sintering aids,[6−8] substitution of chromium and lanthanum by other elements,[3,5−9] sintering in reducing atmosphere,[10] using chromium deficient nonstoichiometric composition[11,12] and using sinteractive precursor powder.[13−16] It was found that the presence of low-melting Ca-rich secondary phases such as $CaCrO_4$ or $Ca_n(CrO_3)_m$ helps in the sintering of $La(Ca)CrO_3$ by a liquid-phase-assisted sintering mechanism.[4,17,18] Consequently, it was established that for successful air sintering of the chromite based perovskites, the presence of $CaCrO_4$ was essential and the sintering occurred mainly by liquid-phase-assisted sintering mechanism. Nevertheless, it is worth noting that the liquid-phase-assisted sintered products of $La_{1-x}Ca_xCrO_3$ ceramics in general lead to compositional inhomogenity, thus making the ceramic unsuitable for long-term applications.[3,5] In general, liquid-phase sintering was achieved in $LaCrO_3$ based oxides by using composite starting powders consisting of a mixture of low melting $CaCrO_4$ phase and partially reacted $La_{1-x}Ca_xCrO_3$ phases.[17,18] To the best of our knowledge, no reports are available up to now where dense $La_{1-x}Ca_xCrO_3$ ceramics with high conductivity have been developed using homogeneously reacted single-phase starting powders. A novel approach to develop highly dense $La_{0.7}Ca_{0.3}CrO_3$ sintered ceramics with exceptionally high electrical conductivity is reported here.

The powder of $La_{0.7}Ca_{0.3}CrO_3$ (hereafter LCC-30) was prepared by a modified spray pyrolysis process using lanthanum nitrate hexahydrate (Indian Rare Earth, 99.9%), calcium nitrate tetrahydrate (S. D. Fine Chem. Limited, 99%), chromium (III) nitrate (Loba Chem. Limited, 98.5%), glycine (Qualigens Fine Chemicals, 98.5%), and citric acid monohydrate (Merck Limited, 99.5%). The precursor solution used for spray pyrolysis was prepared from an aqueous mixture of lanthanum nitrate, calcium nitrate, and chromium (III) nitrate in the molar proportion La/Ca equal to 0.7:0.3 and (La + Ca)/Cr equals unity. To the mixed metal solutions, a calculated amount of glycine and citric acid monohydrate was added slowly so as to maintain a glycine to metal nitrate ratio of 0.60 and a citrate to metal nitrate ratio of 0.05. The solution was allowed to evaporate slowly by maintaining a temperature of ~85−90 °C with continuous stirring. The precursor solution thus obtained was atomized through a double fluid nozzle into a hot spray pyrolyzer chamber maintained at a temperature of 450 °C. The as-sprayed powder was calcined at 1150 °C for 6 h. The calcined powder was pressed into a 25 mm × 10 mm × 5 mm bar at pressures of 137, 258, and 482 MPa, respectively, by uniaxial pressing. The pressed samples were heat treated in an electrically heated furnace in the temperature range of 1300−1500 °C for 6 h.

Thermogravimetric analysis (TGA) plot of the 1150 °C calcined powder did not indicate any weight loss (figure not shown) confirming complete decomposition of the precursor. X-ray powder diffraction (XRD) data collected at a scan rate of 2° per minute on a Philips PW 3207 diffractometer with Cu Kα radiation of the 1150 °C calcined and 1500 °C sintered samples are

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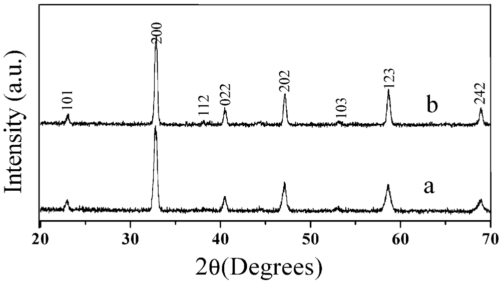

Figure 1. XRD patterns of LCC-30 sample (a) calcined at 1150 °C/6 h and (b) sintered at 1500 °C/6 h.

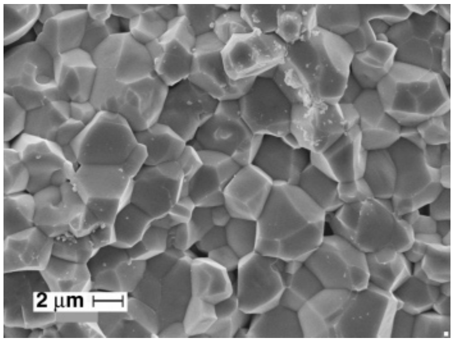

Figure 2. Fracture surface of 1500 °C sintered LCC-30 sample.

shown in Figure 1. The powder diffraction data confirm the formation of single-phase perovskite $La_{0.7}Ca_{0.3}CrO_3$ after calcination at 1150 °C for 6 h. The refined lattice parameter of the 1150 °C calcined powder is $a = 5.44 \pm 0.06$ Å, $b = 7.67 \pm 0.02$ Å, $c = 5.46 \pm 0.01$ Å, and the calculated unit cell volume is 228.40 ± 0.10 Å^3, which is in very good agreement with the report of Sakai et al.[19] for $La_{0.7}Ca_{0.3}CrO_3$ sample (228.05 Å^3). The particle size distribution of the as-calcined powder exhibited a bimodal distribution with an average agglomerate size of around 10.5 μm. Ball milling, on the other hand, reduced the average agglomerate size to around 1.8 μm indicating the presence of softly agglomerated particles. The percentage densification achieved as a function of sintering temperature for different compaction pressures was compared (data not shown). Irrespective of the initial compaction pressure, all the samples exhibited a density of more than 94% of theoretical density at 1500 °C. A fully dense LCC sample compacted using a pressure of 482 MPa and sintered at 1500 °C exhibited a density of around 97.79 ± 0.5% of theoretical density. The scanning electron micrograph (Leo 430i scanning electron microscope) of the fracture surface of such a sintered bar confirmed (Figure 2) a well-compacted dense ceramic with clearly defined well-connected grains of 1−3 μm. Moreover, there was no evidence of any secondary phase in the microstructure. Our sintering studies with pure $La_{0.7}Ca_{0.3}CrO_3$ perovskite powder clearly establish a diffusion-controlled sintering mechanism in contrast to a liquid-phase-assisted sintering as reported earlier by other investigators.[4,17,18] The electrical conductivity of the sintered samples in air by four-probe measurement technique using HP multimeter (model 3458A) provided a maximum conductivity of 69.75 ± 0.50 Scm^{-1}, the highest so far reported for sintered $La_{0.7}Ca_{0.3}CrO_3$ samples.[5,11,12,20] To ascertain and understand the effect of atmosphere (oxygen partial pressure) on the electrical conductivity of dense $La_{0.7}Ca_{0.3}CrO_3$, measurements were also performed in flowing air, argon, and reducing atmospheres (mixture of 3% hydrogen and 97% argon and 20% hydrogen and 80% argon) at 1000 °C and the data are shown in Figure 3. We have observed that there is a substantial reduction in the conductivity with decrease in the oxygen partial pressure in the order air (69.75 Scm^{-1}), argon (17.00 Scm^{-1}), 3% hydrogen (6.64 Scm^{-1}), and 20% hydrogen (3.36 Scm^{-1}) at 1000 °C.[4] Nevertheless, the conductivity in the reducing atmosphere is still within the limit for its application as an interconnect material. The sintered sample exhibited a three point bending strength of around 118 MPa.[21]

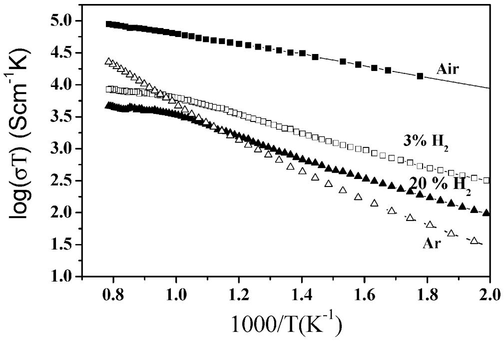

Figure 3. Arrhenius plots of the electrical conductivity of LCC-30 sample sintered at 1500 °C in different atmospheres.

Mori et al.[10] achieved ~94% theoretical density only after sintering $La_{0.9}Ca_{0.1}CrO_3$ samples at 1900 °C in a reducing (Ar + CO) atmosphere. On the other hand, Sakai et al.[11] observed more than 90% density from chromium deficient samples at 1600 °C. The latter authors[17] also observed calcium rich phases at the grain boundaries due to liquid-phase sintering. Surprisingly, $La_{1-x}Ca_xCrO_3$ reactive powder prepared by a complex polymerization exhibited only 74.7% densification at 1700 °C.[12] On the contrary, Chakraborty et al. [20] reported a density of around 98% at 1250 °C by using citrate−nitrate synthesized powder, but they observed a conductivity of only 43 Scm^{-1}.

To conclude, in contrast to the available literature on sintering of Ca-doped $LaCrO_3$ ceramics, the idea of sintering using pure $La_{0.7}Ca_{0.3}CrO_3$ starting powders rather than using mixed chromite and calcium chromate powders has promoted diffusion-controlled sintering in air at a relatively lower temperature (1500 °C) yielding dense (97.79%) $La_{0.7}Ca_{0.3}CrO_3$ ceramic with exceptionally high conductivity (69.75 Scm^{-1}) for SOFC applications.

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