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Stability of Calcium Substituted Lanthanum Chromites used as SOFC Anodes for Methane Oxidation

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Abstract

$La_{0{\cdot}7}Ca_{0{\cdot}32}CrO_3$, $La_{0{\cdot}75}Ca_{0{\cdot}15}Sr_{0{\cdot}1}Cr_{0{\cdot}95}Mg_{0{\cdot}05}O_3$, $La_{0{\cdot}85}Ca_{0{\cdot}15}CrO_3$ and $La_{0{\cdot}85}Ca_{0{\cdot}15}Cr_{0{\cdot}9}Mg_{0{\cdot}1}O_3$ compounds were studied in reducing atmospheres containing hydrogen, methane and CO/CO_2. They were found to exhibit liquid phase sintering except for $La_{0{\cdot}85}Ca_{0{\cdot}15}CrO_3$. Mg enhanced the densification of stoichiometric $LaCrO_3$. Current was found to affect the stability of the heavily doped samples, whereas the reducing atmospheres did not have a detectable impact. Calcium and or strontium and chromium enriched secondary phases were detected on current treated $La_{0{\cdot}7}Ca_{0{\cdot}32}CrO_3$ and $La_{0{\cdot}75}Ca_{0{\cdot}15}Sr_{0{\cdot}1}Cr_{0{\cdot}95}Mg_{0{\cdot}05}O_3$ samples. $La_{0{\cdot}85}Ca_{0{\cdot}15}Cr_{0{\cdot}9}Mg_{0{\cdot}1}O_3$ did not degrade under current, at least for 100 h. A current enhanced demixing could be responsable for the segregation. The solubility limit of calcium in $LaCrO_3$ is thought to be low at 800°C (around 15%). © 1999 Elsevier Science Limited. All rights reserved

Keywords: surface reaction, perovskites, fuel cells.

1 Introduction

Calcium substituted lanthanum chromites (LCC), used as interconnects[1] for solid oxide fuel cells (SOFC), were previously explored as alternative anodes to the conventional Ni-yttria stabilized zirconia (YSZ)-cermet.[2] Thermochemical and electrocatalytical properties of these anodes were assessed in wet hydrogen and methane fuels at different temperatures.[2] During the electrochemical tests under fuel cell conditions, a rapid degradation of the cell performance was observed. SEM analysis revealed the formation of an interfacial reaction layer between LCC and YSZ. This thin layer was found to be a poor conductor. EDX and ESCA analyses showed that under these reducing conditions, the LCC anodes were enriched with calcium and chromium at the surface. Calcium chromate phases were believed to exsolve from these materials and decompose to $CaCr_2O_4$ and CaO which eventually reacts with the YSZ electrolyte to form $CaZrO_3$. This phase segregation is also thought to affect the activity of these anodes towards the fuel oxidation.

In order to ascertain these observations and to follow the possibility of stabilizing these materials against reduction, we investigated the behaviour of some LCCs with different doping levels in different atmospheres and under current.

2 Experimental

$La_{0{\cdot}7}Ca_{0{\cdot}32}CrO_3$ (LCC1) powder was acquired from EMPA, Switzerland. $La_{0{\cdot}75}Ca_{0{\cdot}15}Sr_{0{\cdot}1}Cr_{0{\cdot}95}Mg_{0{\cdot}05}O_3$ (LCSCM), $La_{0{\cdot}85}Ca_{{\cdot}15}CrO_3$ (LCC2) and $La_{0{\cdot}85}Ca_{{\cdot}15}Cr_{0{\cdot}9}Mg_{0{\cdot}1}O_3$ (LCCM) powders were prepared following the citrate procedure from nitrate precursors (Fluka, >99% purity except for the $Cr(NO_3)_3.9H_2O$, >97%) and 1 M aqueous citric acid solutions. The gels obtained were precalcined at 110°C for 24 h then 200°C for 2 h and the resulting powders crushed to size by dry ball-milling. Subsequently, high temperature calcination at 1100 to 1200°C was necessary to get the pure perovskite structures as confirmed by XRD. Residual, low intensity (<2%), unidentified peaks, not matching the usually admitted orthorhombic lattice structure of these perovskites were detected. However, compounds such as $CaCrO_4$, CaO, Cr_2O_3, β-$CaCr_2O_4$, $Ca_3(CrO_4)_2$, $Ca_5(CrO_4)_3$, $Ca_5(CrO_4)_3O_{0{\cdot}5}$ or La_2CrO_6, could not be accounted for these small

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intensity peaks. At lower temperatures, secondary phases such as $CaCrO_4$ and α-$CaCr_2O_4$ were detected by XRD.

Ball-milled, these powders had a specific surface area between 2 and 4 $m^2 g^{-1}$ and a particle size distribution centred at 3·6, 1·4, 0·9, and 2·1 μm for LCC1, LCSCM, LCC2 and LCCM, respectively. Rods of $13\times6\times5\,mm^3$ were pressed at 100 kPa and sintered at 1550°C for 4 h. Densities varied between 95 and 97% of theoretical for LCC1, LCSCM and LCCM whereas LCC2 pellets were quite porous (72% dense). It was observed that the addition of Mg enhanced noticeably the sinterability of stoichiometric lanthanum chromites [Fig. 4(c) and (d)], also in the case of Sr doping (not presented here). Subsequently, they were polished to the μm scale and some were cut in length into two or three pieces and ultrasonically washed with ethanol.

dc four probe technique conductivity measurements were carried out at 800°C for 100 h on some rods (except for the LCC2) in air and reducing conditions, especially in $H_2+3\%H_2O$, to analyse the effect of current and gas atmosphere on the stability of these materials. Silver-paint was applied as electrodes and silver or platinum wires were used as contacts. Constant currents of 10 to 30 mA were applied corresponding to about 100 to 300 $mA\,cm^{-2}$ in fuel cell mode, and the voltage monitored with time. The oxygen partial pressure was measured simultaneously by a YSZ sensor placed near the sample.

Other rods were subjected for 100 h to different atmospheres like air, $80\%CO/20\%CO_2$, $CH_4+3\%H_2O$ or $H_2+3\%H_2O$ without current treatment. All rods were later examined by SEM and EDX and some also by XRD.

3 Results and Discussion

By substitution of elements such as Ca, Sr and Mg on the La or Cr sites in $LaCrO_3$ (LC), electronic compensation occurs by the formation of holes at high oxygen partial pressure, i.e. the oxidation of Cr^{III} to Cr^{IV}, or of oxygen vacancies at low pO_2. In our measurements at 800°C, the conductivities in air increased with the dopant concentration and amounted to 24, 11 and 7 $S\,cm^{-1}$ for LCC1, LCSCM and LCCM, respectively. After passing from air to wet hydrogen ($pO_2=10^{-21}$ atm) and applying a current to the samples, the conductivities decreased over a period of 20 h, then increased again to stabilize at an intermediate value. In this atmosphere they reached only 0·8, 0·5 and 1 $S\,cm^{-1}$, respectively. As expected,[3,4] there is no big difference in conductivities at low oxygen partial pressures.

From post-mortem analysis, LCC1 and LCSCM exhibited cracks and were found to be fragile when compared to the initial material. SEM analysis showed [Fig. 1(b)] that these two materials broke rather intragranularly. LCCM did not display a similar behaviour.

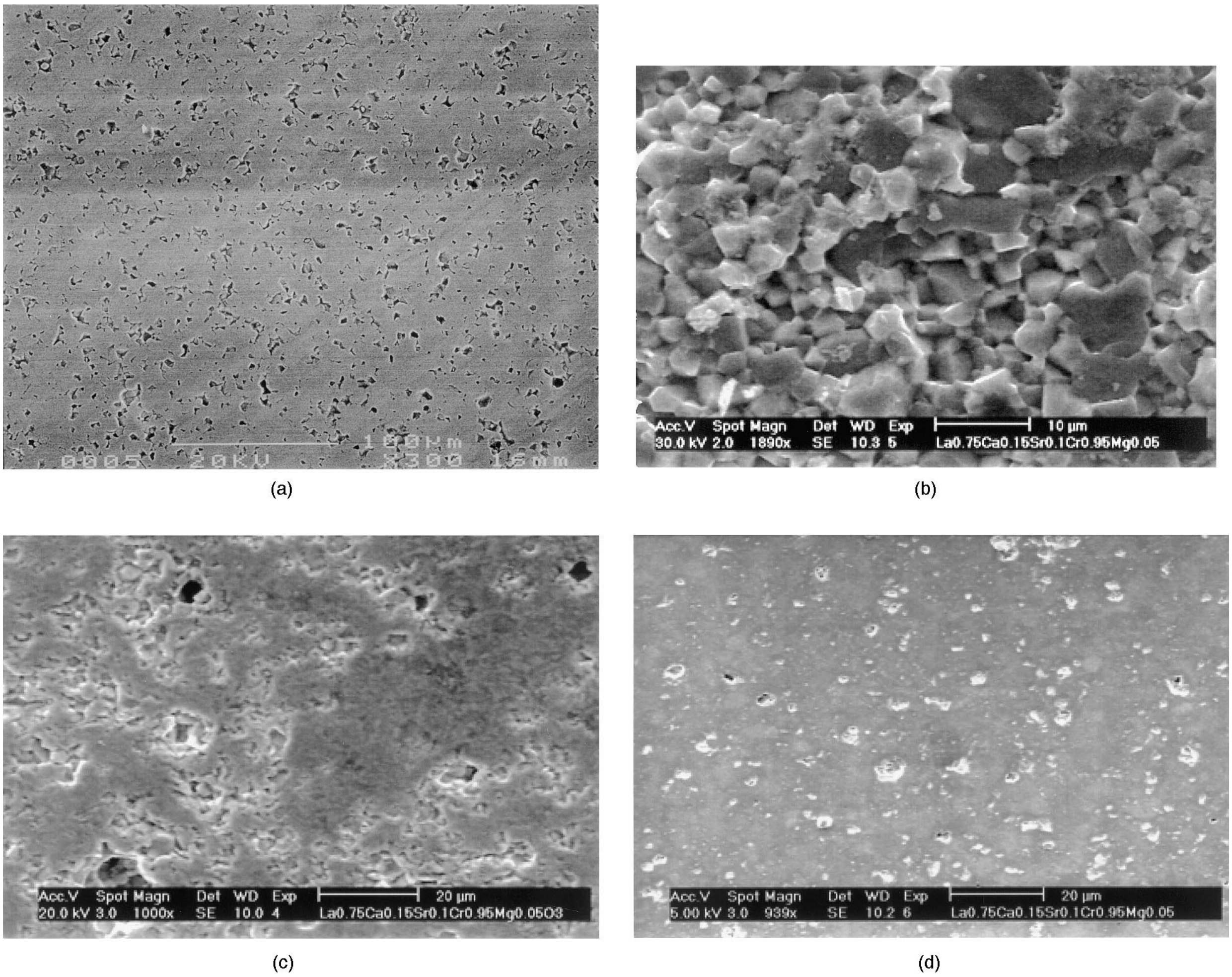
SEM micrographs of the LCC1 and LCSCM conductivity rods showed also the presence of exsolved phases as depicted in Fig. 2. Semi-quantitative EDX analysis revealed secondary phases enriched with calcium, strontium and chromium with only small amounts of lanthanum which might stem from the underlying bulk. Si impurities were also detected. The exact nature of these phases is not yet confirmed as XRD analysis did not reveal any extra phase. Figure 3 show two different EDX spectras, one for a freshly polished LCSCM surface and the other for the conductivity test rod. After a further thermal treatment in air, we observed a melt-like form covering the surface. As to LCCM, the conductivity sample had a different behaviour and no secondary phases were detected [Fig. 2(e) and (f)].

Further EDX investigations on cross-sections and on repolished bar surfaces did not reveal any particular phase segregation within the bulk. This behaviour might confirm our previous observations on porous LCC1 anodes where a superficial calcium and chromium excess was detected by ESCA within a few nm depth.

Other polished LCSCM rods were subjected to different gas mixtures. The results presented in Fig. 1(c) and (d) and Fig. 4(b) indicate no detectable secondary phase exsolution when the polished rods were only thermally treated in wet methane, CO/CO_2 and wet hydrogen. No indication of carbonates growth was evidenced. Similarly, LCC1, LCCM and LCC2 did not degrade when treated in wet hydrogen [Fig. 4(a), (c) and (d)]. These materials are thus quite stable even under such reducing atmospheres.

Surface analysis on fresh unpolished samples revealed however melt-like layers within the grain boundaries (see Fig. 5) suggesting a liquid phase sintering process. High levels of Ca, Sr and Mg along with some Si were found there. Obviously, these layers are cleaned away when the samples are polished.

The behaviour just described indicates that the current treatment should have an impact on the stability of these materials. We previously observed that screen-printed substituted $LaCrO_3$, sintered at 1100°C on YSZ sheets, did not generate any relevant topotactic reaction, even when treated for 100 h at 800°C in wet hydrogen. In a fuel cell test however, a rapid degradation was noticed and related to the formation of a melt-like interfacial



(a) (b) (c) (d)

Fig. 1. SEM micrographs of $La_{0\cdot75}Ca_{0\cdot15}Sr_{0\cdot1}Cr_{0\cdot95}Mg_{0\cdot5}O_3$ (LCSCM) rods: (a) as such, polished surface; (b) cross-section of a current treated rod in wet hydrogen at 800°C; (c) surface of a wet methane treated rod at 800°C; (d) surface of a CO/CO_2 treated rod at 800°C.

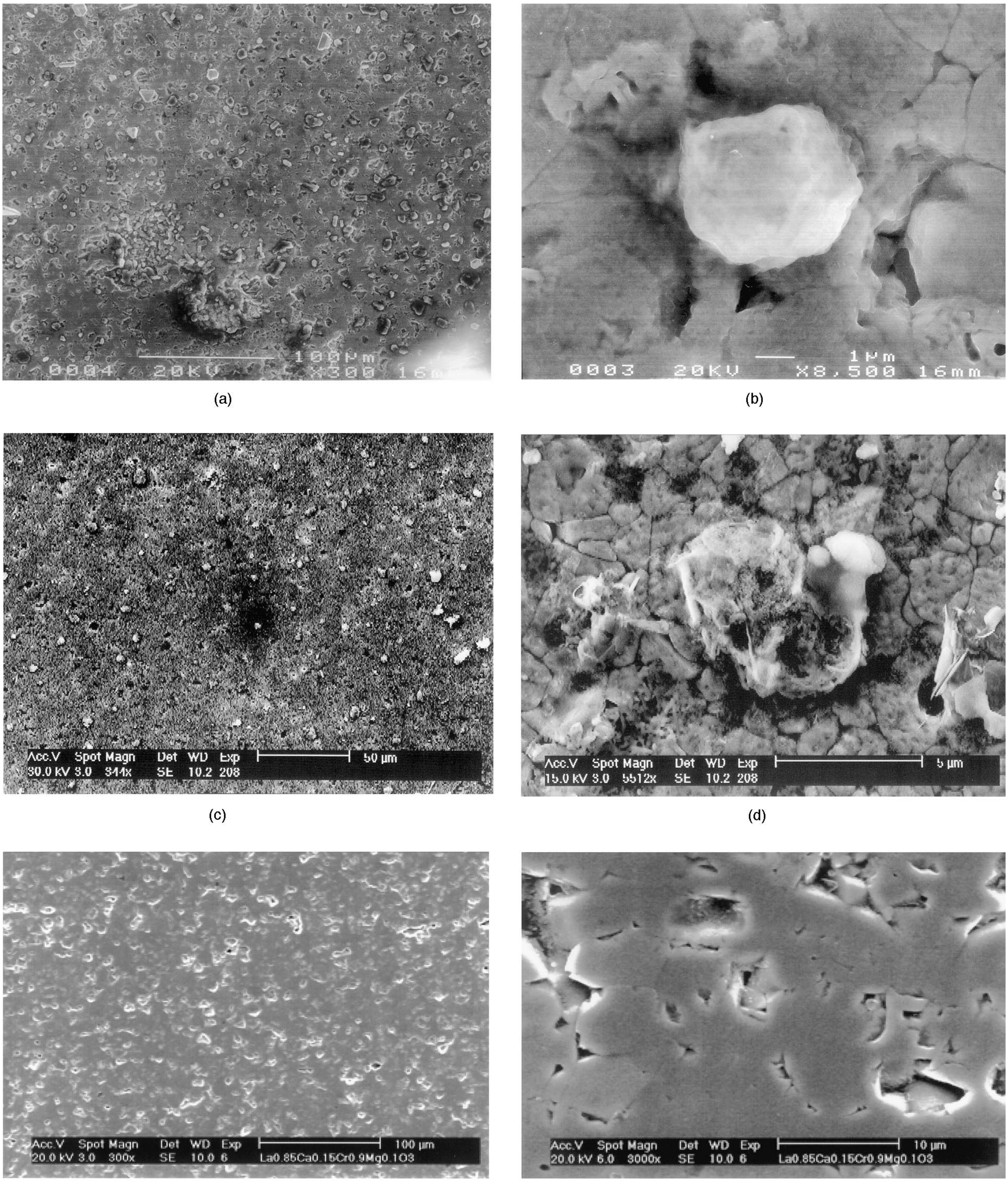
layer.[2] We suspected the exsolved secondary phases $(Ca_m(CrO_4)_n$ and CaO to react with YSZ and to form the poor conductor $CaZrO_3$ as evidenced by the overlaping of SIMS analyses for Ca and Zr.

Doped LCs were already reported[5,6] to degrade in reducing atmospheres due to a destabilizing effect of the used dopants. Also, Sakai *et al.* and Nishiyama *et al.*[7,8] observed phase segregations in $La(Ca,Sr)Cr(Co)O_3$ compounds under an oxygen potential gradient and current flow at 1000°C. This phenomena may be related to a demixing effect[9] and is also observed in some mixed ionic-electronic membrane materials. For the LC materials, Sakai *et al.*[8] report that within a few nm (~5 nm) of the surface, a calcium rich region exists at grain boundaries as evidenced by AES measurements. A compositional change in such a thin region would however be undetectable by EDX, which explains our results. $(Ca,Sr)_m(CrO_4)_n$ phases are known to be present in highly doped LCs[10,11] and to be responsible for their dense sintering, but they ultimately redissolve in the material which make them quite difficult to detect by XRD. By lowering the annealing temperature, these phases could segregate. However, as no detectable degradation was observed on polished rods thermally treated in reducing gas mixtures, the demixing should be slow. The fact that current, more than reducing conditions, seems to affect the stability might be related to current enhanced demixing. Secondary phases might also originate from grain boundaries as the cations diffusivity there is known to be quite large when compared to the bulk.[12]

The fact that LCCM material did not present any phase exsolution indicates that the solubility limit of calcium is quite low at least at 800°C (around 15%). Carter *et al.*[13] reported a solubility limit of 20% for calcium at 900°C, and Sakai *et al.*[14] observed a phase segregation using XRD measurements in the $La_{0\cdot7}Ca_{0\cdot32}CrO_3$ system.

4 Summary

The present results indicate liquid phase sintering of $La_{0\cdot7}Ca_{0\cdot32}CrO_3$, $La_{0\cdot75}Ca_{0\cdot15}Sr_{\cdot1}Cr_{0\cdot95}Mg_{0\cdot05}O_3$ and $La_{0\cdot85}Ca_{\cdot15}Cr_{0\cdot9}Mg_{0\cdot1}O_3$. Exsolved secondary phases, enriched with calcium and/or strontium



(a) (b)

(c) (d)

(e) (f)

Fig. 2. Surface SEM micrographs of: (a) and (b). $La_{0.7}Ca_{0.32}CrO_3$ (LCC1); and (c)–(d). $La_{0.75}Ca_{0.15}Sr_{0.1}Cr_{0.95}Mg_{0.05}O_3$ (LCSCM); (e)–(f). $La_{0.85}Ca_{0.15}Cr_{0.9}Mg_{0.1}O_3$ (LCCM) rods subjected for 100 h to current treatment in wet hydrogen ($T = 800$°C). Only LCC1 and LCSCM exhibited secondary phase exsolution.

and chromium oxides, were observed on sintered bars. Mg was found to enhance the densification of these materials.

These materials appear to be stable in reducing atmospheres such as wet hydrogen and methane. No carbonates growth were evidenced. Current flow, more than reducing conditions, seems to affect the stability of these materials when subjected to low oxygen partial pressures. Secondary phase exsolution was observed at the surface of polish sintered rods when current treated at 800°C, in the case of the heavily doped materials. However, no bulk segregation was observed in polished surfaces and in cross-sections. This indicates a possible demixing effect enhanced by current. Equally, the solubility limit of calcium in $LaCrO_3$ appears low. $La_{0.85}Ca_{0.15}Cr_{0.9}Mg_{0.1}O_3$ compound, with a low Ca concentration, did not exhibit such exsolutions.

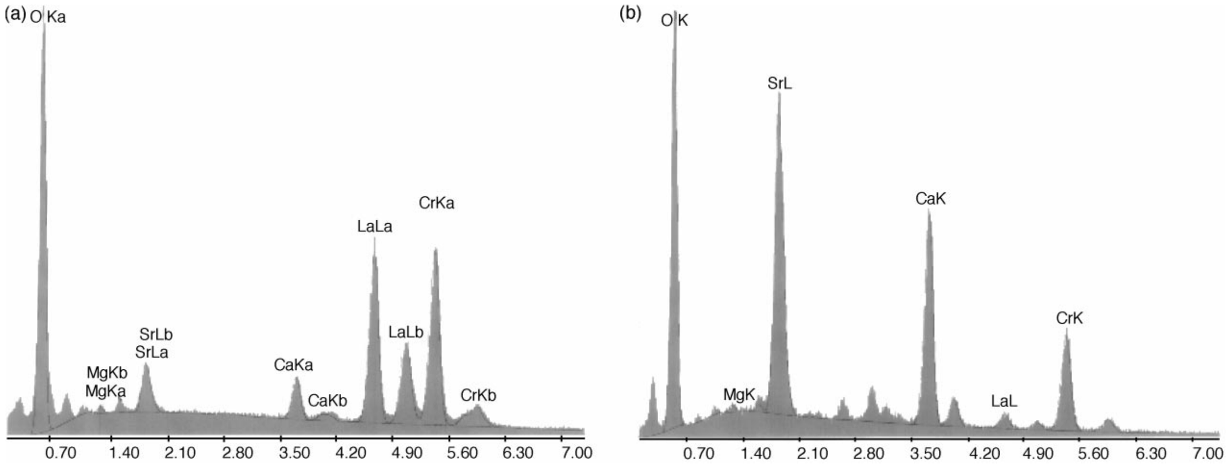
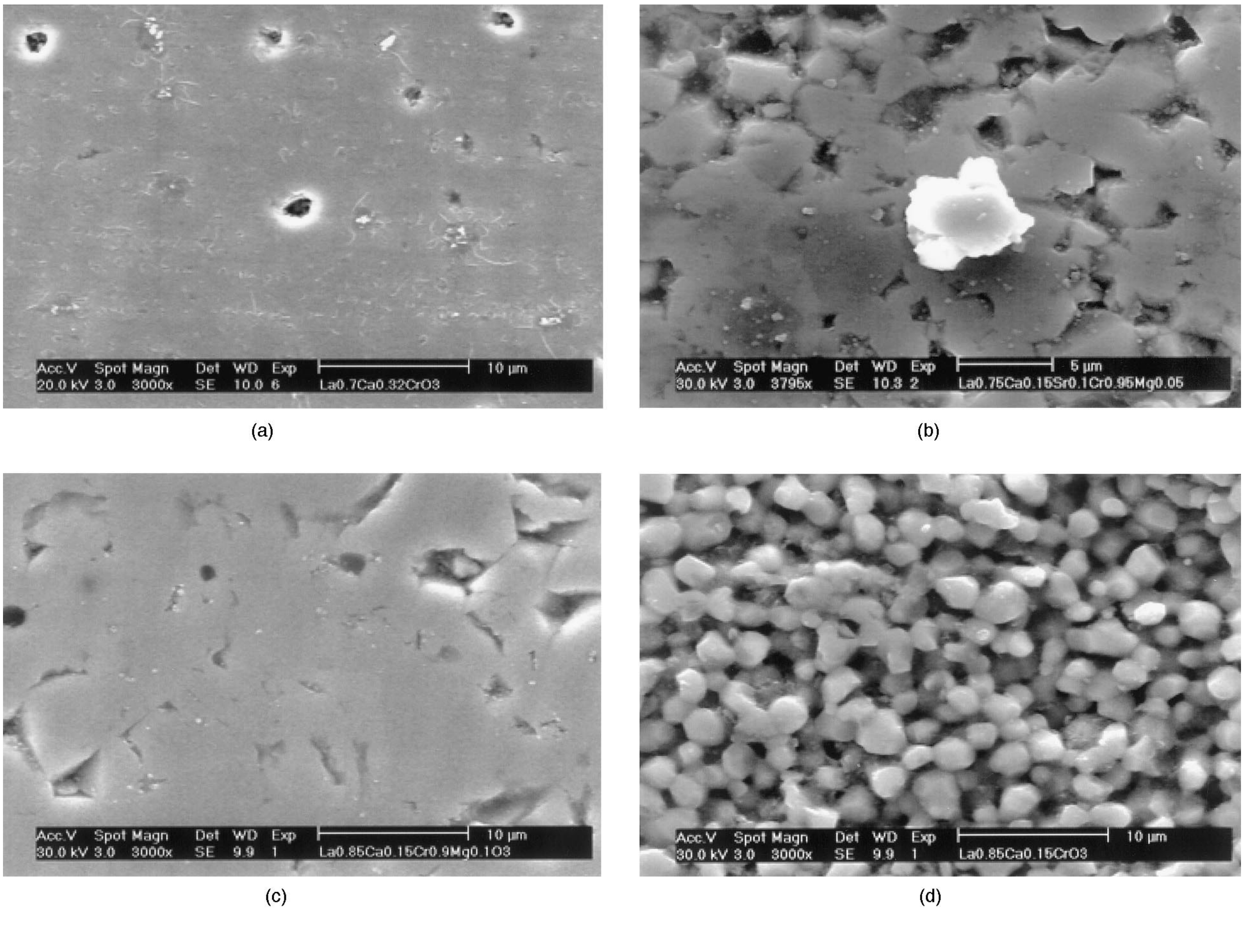


Fig. 3. EDX analysis on (a) an as such, polished LCSCM surface, as seen in Fig. 1(a) and (b) a current treated LCSCM in wet hydrogen and corresponding to the structure of Fig. 2(d).



(a) (b)

(c) (d)

Fig. 4. Surface SEM micrographs of wet hydrogen treated rods of: (a) $La_{0.7}Ca_{0.32}CrO_3$ (LCC1); (b) $La_{0.75}Ca_{0.15}Sr_{0.1}Cr_{0.95}Mg_{0.05}O_3$ (LCSCM); (c) $La_{0.85}Ca_{0.15}Cr_{0.9}Mg_{0.1}O_3$ (LCCM); and (d) $La_{0.85}Ca_{0.15}CrO_3$ (LCC2). The addition of 10% Mg on the B-side enhanced the sinterability of $La_{0.85}Ca_{0.15}CrO_3$.

Globally, the behaviour described above gave evidence on the surface reactions which could occur between a porous LC anode and YSZ. The exsolution, and thus the surface reaction, might be enhanced in a porous structure. Lowering the dopant amount, whose concentration does not affect the conductivity of $LaCrO_3$ at low oxygen partial pressures, is thus needed to reach a more stable anode.

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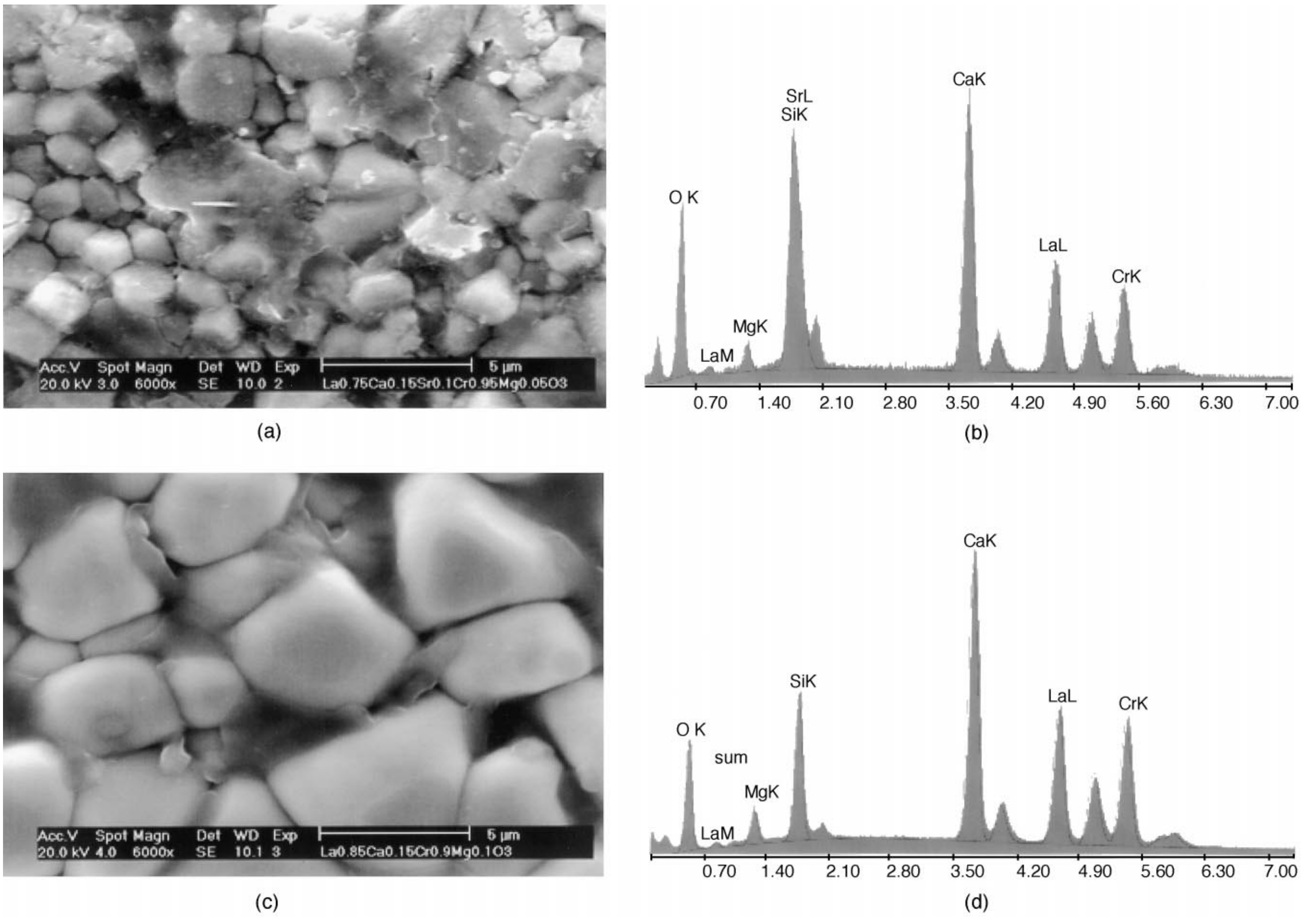

Fig. 5. SEM micrographs and subsequent EDX analyses of (a) and (b). LCSCM and (c) and (d). LCCM unpolished rods sintered at 1550°C. Melt-like structures can be seen corresponding to enriched Ca, Sr, Mg, Cr and Si phases. The shown EDX are taken in the cross-marked section of the micrographs.

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