Journal of the European Ceramic Society 17 (1997) 1027–1031
PII: S0955-2219(96)00182-3
Printed in Great Britain. All rights reserved
0955-2219/97/$17.00

Sol–Gel Synthesis of Lanthanum Chromite Powder

S. Bilger, G. Blaß & R. Förthmann

Forschungszentrum Jülich GmbH, Institute for Materials in Energy Systems (IWE), PO Box 1913,
D-52425 Jülich, Germany

(Received 9 May 1996; revised version received 20 August 1996; accepted 29 August 1996)

Abstract

Alkaline earth-doped $LaCrO_3$ *is a satisfactorily conducting ceramic material for the interconnector of Solid Oxide Fuel Cells (SOFC). For the synthesis of highly sinterable* $LaCrO_3$ *powders spray-drying of adequate precursors like sols based on alkoxides has been used. Lanthanum chromium hydroxide sol was prepared by hydrolysis of synthesized methoxide complexes. The chemical reactions during hydrolysis and peptization of the precursors are described. The crystalline phase formation during heat treatment of spray-dried amorphous gel consisting of hydroxides and contaminant chloride ligands was characterized by thermal analysis methods (TG, DTG, DTA) and X-ray diffraction analysis. The progressive oxidation of Cr(III) by thermal dehydroxylation transforms the powder into fine crystallized La(III)Cr(V)hydroxo-oxychloride at 450°C. A thermal treatment permits complete chlorine removal forming sinterable crystalline* $LaCrO_3$ *perovskite powder at temperatures above 720°C. The same sol–gel process also can be applied to chlorine-free nitrate-containing alkoxide sols. The properties of sinterable lanthanum chromite powders obtained from these sols are compared with powders made by direct spray-drying of lanthanum-chromium nitrate solutions. © 1997 Elsevier Science Limited.*

1 Introduction

The solid oxide fuel cell (SOFC) represents a promising way of converting chemical energy of gaseous fuel directly into electric energy.[1] The current status of the development of a cell unit is based on an yttria-stabilized zirconia (YSZ) solid electrolyte and electrodes consisting of Sr-doped $LaMnO_3$ (cathode) and Ni/YSZ cermet (anode). A suitable ceramic material to be used to interconnect the air and fuel electrodes of adjacent cells is an alkaline earth-doped $LaCrO_3$. For long-term reliability the interconnector has to meet the following requirements: high density, i.e. gas tightness, high electronic conductivity, and sufficient chemical and mechanical stability in oxidizing and reducing atmospheres.

In 1992 we demonstrated the preparation of a homogeneous perovskite powder for the cathode using a newly developed sol–gel peroxide process.[2] Metal alkoxide chemistry has attracted considerable attention as a precursor for ceramic synthesis. The first lanthanide alkoxide $La(OCH_3)_3$ was prepared by Bradley and Factor in 1958.[3]

In this paper the synthesis of a lanthanum-chromium methoxide complex is reported which can be used as a sol–gel precursor for preparing sinterable $LaCrO_3$ perovskite powders.

2 Experimental

Lanthanum trichloride heptahydrate and chromium trichloride hexahydrate (99·9% both) were dissolved by stirring in a large excess of methanol corresponding to a ratio of $CH_3OH/(La+Cr) \approx 150$. After complete dissolution the mixture was refluxed for 30 min at the boiling point of the solvent (65°C) obtaining a dark green alcoholic solution. The exothermic precipitation of lanthanum-chromium methoxide occurred by adding gaseous ammonia. The soluble ammonium chloride was removed by hot filtration at 40°C, and the precipitate was washed Cl^--free by methanol. The blue-gray methoxide residue was hydrolysed in cold water by vigorous stirring and peptized by adding hydrochloric acid for stabilizing the sol. The flowsheet for the alkoxide sol preparation and the powder preparation is shown in Fig. 1.

The sol was directly spray-dried at 175°C. Calcination of the green dried gel powder followed at 800°C before pelletizing and sintering. The chemical composition of the perovskite obtained was investigated by ICP-AES resulting in

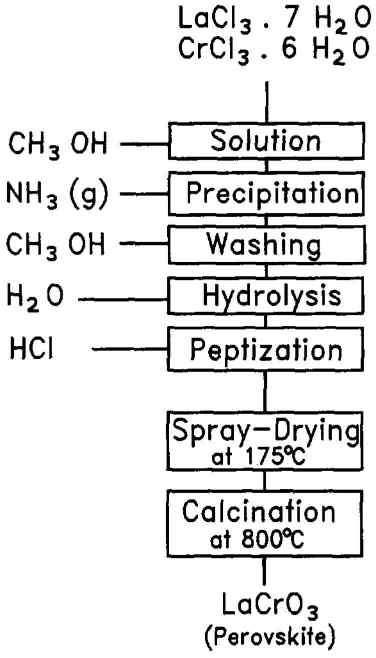

Fig. 1. Flowsheet of the $LaCrO_3$ powder preparation by the sol–gel process.

56·0 wt% La and 21·3 wt% Cr corresponding to an atomic ratio of La/Cr = 1.

Simultaneous thermogravimetric and differential thermoanalysis measurements were performed in air (flow rate 3 l/h) at a heating rate of 6 K/min (Netzsch thermo-analyser STA 409). For X-ray diffraction analysis samples of about 75 mg were heated in open platinum crucibles to different temperatures and, after reaching these temperatures, quickly cooled to room temperature. X-ray diffractograms were recorded by using a SIEMENS X-ray diffractometer with Cu K_α radiation (voltage: 45 kV, tube current: 45 mA).

3 Results

The first step of the process is the formation of a homogeneous solution of the hydrated chlorides in methanol. Probably this solution contains solvated complexes of La^{3+} and Cr^{3+} ions with water molecules and Cl^--ligands in the first coordination sphere and a number of loosely bonded CH_3OH molecules at a larger distance. It is also to be expected that ligand exchange reactions occur in the solvated shell.[4,5]

The precipitation of the alcoholate complex by gaseous ammonia probably forms lanthanum/chromium chloro-methoxide complexes. Alkoxide complexes of chromium and lanthanum have been described in the literature.[6–9] In addition, several reports have mentioned chloride contamination especially of organolanthanide complexes.[10,11] One example is the reaction of $NdCl_3$ with $NaOCH(CH_3)_2$ resulting (by X-ray analysis) in the hexametallic cluster $[Nd_6(OCH(CH_3)_2)_{17}Cl]$ with Cl^- replacing one of 18 $-OCH(CH_3)_2$ ligands.[12] Some new isopropoxide derivates of lanthanum and zirconium of the type $[La(Zr_2(OCH(CH_3)_2)_9)_nCl_{3-n}]$ and $[La(Zr_2(OCH(CH_3)_2)_9)_n(OCH(CH_3)_2)_{3-n}]$ with n = 1, 2 or 3 were synthesized and characterized.[13]

It may be assumed that the lanthanum/chromium methoxide polynuclear complex prepared in this work has a rather complex structural composition. The sol obtained from the washed precipitate is formed by hydrolysis of methoxide groups followed by oligomerization reactions which link the metal centres through oxo or amino bridges. The sol is stabilized by adsorption of protons (H^+) at the surface of the colloidal particles causing a positive charge which prevents agglomeration. The sol obtained is stable for several months. It was converted by spray-drying to form a dehydrated gel powder.

The gel powders were investigated by simultaneous TG/DTA recording. The result for the Cl^--containing sols is shown in Fig. 2. There is a broad endothermal peak between 100 and 280°C corresponding to the release of the volatile compounds H_2O and NH_3. At 400 ± 50°C an exothermal peak is attributable to the combustion of residual methoxide groups ($-OCH_3$) as well as to further dehydroxylation processes. This stage of the thermolysis corresponds to the formation of a lanthanum chromium oxohydroxo-chloride phase which was confirmed by X-ray diffraction analysis. At 750°C the perovskite phase $LaCrO_3$ is formed by thermal decomposition of the Cl^--containing $LaCrO_4$ phase; at this temperature oxygen is partially released.

The TG curve shows at temperatures above 450°C three weight changes characterized by three minimum peaks of the DTG curve. From the observed weight losses and from chemical analysis

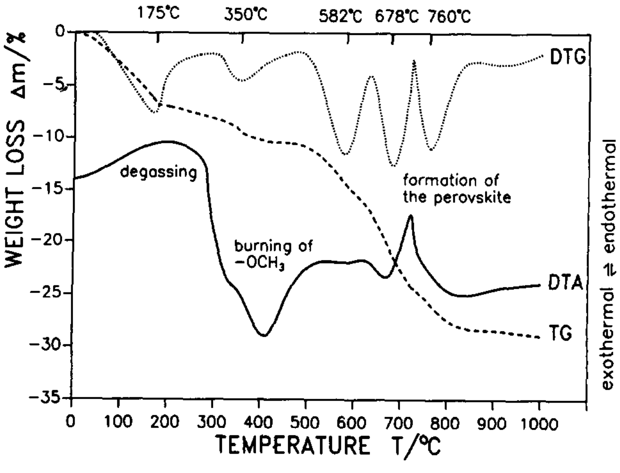

Fig. 2. TG/DTA measurement of spray-dried $LaCrO_3$ powder prepared from alkoxide sol.

of the chlorine content the following compositions were calculated:

450°C: $LaCrCl_{1\cdot15}O_{2\cdot50}(OH)_{1\cdot85}$,
630°C: $LaCrCl_{0\cdot70}O_{3\cdot20}(OH)_{0\cdot9}$,
675°C: $LaCrCl_{0\cdot19}O_{3\cdot91}$,
760°C: $LaCrO_3$.

The results of X-ray diffraction analysis confirm these compositions. The spray-dried powder (at 175°C) was amorphous and had green colour due to the presence of Cr^{3+} cations. After thermal treatment at 450°C the X-ray pattern showed some crystallinity attributable to a hydroxo-oxo chloride phase similar to LaOCl which crystallizes in the tetragonal P4/nmm structure.[14] At 675°C a new crystalline phase was observed which can be attached to the composition $LaCrCl_{0\cdot19}O_{3\cdot91}$ calculated from TG results and chemical analysis. This composition has the monoclinic monazite-type structure of $LaCrO_4$.[15] At 710°C the formation of crystalline $LaCrO_3$ phase becomes detectable. Above 760°C the powder consisted of the pure Cl^--free $LaCrO_3$ perovskite phase.

The same sol–gel process can also be applied by using lanthanum and chromium nitrates as starting materials. Chlorine-free alkoxide sols were prepared by using the same flowsheet, but nitrates (and nitric acid) instead of chlorides. From the TG/DTA measurements of powders from such nitrate-containing alkoxide sols and powders obtained directly from spray-dried nitrate solutions the following two results are important:

(1) At 500°C all volatile compounds and all decomposition products are completely removed from the powder.
(2) At 760 ± 10°C the formation of the perovskite phase occurs; at this temperature some further weight loss is observed due to oxygen release. The total weight loss of both powders was found to be equal with an average value of 45·9 ± 1·1%, corresponding to a composition of $LaCr(ONO_3)_2.5\ H_2O$ for the freshly spray-dried powder. It can be concluded that the precursors of both powders have, independent of the details of the preparation route, nearly the same decomposition characteristics.

X-ray diffraction analysis shows that after calcination at 500°C in air the two powders contain mainly $LaCrO_4$ with very small amounts of La_2CrO_6 and traces of $CaCrO_4$. At temperatures above 800°C the powder consists of the pure rhombohedral $LaCrO_3$ perovskite phase.

The freshly spray-dried powders consist of spherical droplets which are transformed during calcination into agglomerates containing grains of submicron size. A typical example is shown in Fig. 3. The grain size distribution was measured by using the sedimentation method following recommended IEA practices for the suspension preparation. The median grain size of all powders calcined at 500°C is about 4 μm (d_{50}) ranging from 1 μm (d_{10}) to 8 μm (d_{90}). After calcining at 800°C a bimodal grain size distribution was observed with 3–4 μm median grain size and about 20% of particles with sizes below 1 μm (Fig. 4). After five hours wet milling the grain size was reduced to 0·6 μm (d_{50}) ranging from 0·3 μm (d_{10}) to 3·8 μm (d_{90}).

Fig. 3. SEM image of spherical $LaCrO_3$ agglomerates consisting of smaller grains (sol–gel, calcined at 800°C).

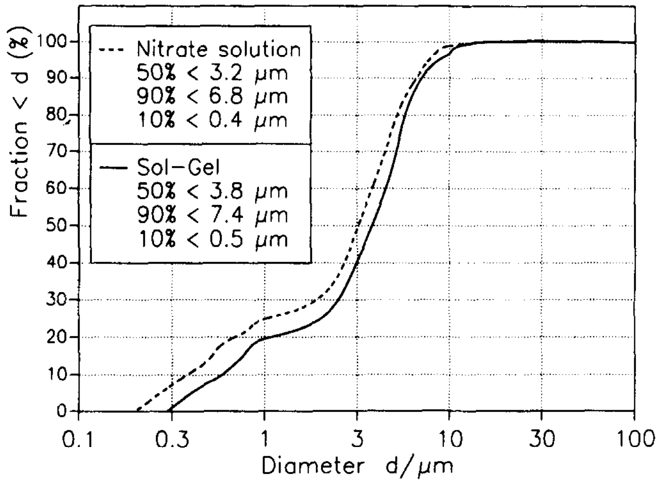

Fig. 4. Bimodal particle size distribution of spray-dried $LaCrO_3$ powders prepared from nitrate-containing alkoxide sol and directly from nitrate solutions after calcination in air at 800°C.

BET measurements of $LaCrO_3$ powders with 10% La replaced by Ca and 10% Cr substituted by Co (composition: $La_{0\cdot9}Ca_{0\cdot1}Cr_{0\cdot9}Co_{0\cdot1}O_3$) after calcining at 500 and 800°C gave very similar results for powders obtained by the sol–gel process and by directly spray-drying of nitrate solutions:

Powder	500°C	800°C
Sol–gel	11·3 $m^2\ g^{-1}$	3·0 $m^2\ g^{-1}$
Nitrate	12·6 $m^2\ g^{-1}$	3·4 $m^2\ g^{-1}$

The lattice parameters of the sol-gel perovskite powder calcined at 800°C were

$$a = 0{\cdot}5452 \pm 0{\cdot}0001 \text{ nm},$$
$$b = 0{\cdot}5485 \pm 0{\cdot}0001 \text{ nm},$$
$$c = 0{\cdot}7720 \pm 0{\cdot}0002 \text{ nm}.$$

The unit cell volume calculated from these lattice parameters is $V = 0{\cdot}231 \pm 0{\cdot}015$ nm^3. The unit cell contains four $LaCrO_3$ units. From these data the theoretical density was calculated: $\rho_{TD} = 6{\cdot}62 \pm 0{\cdot}01$ g cm^{-3}. This agrees with the theoretical density of $6{\cdot}61 \pm 0{\cdot}03$ g cm^{-3} obtained from data of Koc and Anderson[16] for the same composition.

From the calcined powders small pellets were made by uniaxial pressing (55 MPa) followed by cold isostatic pressing at 300 MPa. The pellets were sintered at 1400°C in air and in a H_2/H_2O mixture with 1 mbar H_2 and 29 mbar H_2O calculated for an oxygen equilibrium partial pressure of 2×10^{-7} bar O_2. Vapour pressure measurements by Knudsen cell/mass spectrometry technique of different gaseous chromium species over $LaCrO_3$ resulted in a minimum of the chromium vapour pressures at about 10^{-7} bar O_2.[17] After 5 h sintering densities of 6·4–6·5 g cm^{-3} were reached in air and 6·50–6·55 g cm^{-3} in H_2/H_2O corresponding to 97–98% TD and 98–99% TD respectively.

The electrical conductivity of specimens sintered at 1400°C in air was found to be somewhat higher than previously published data[18] for the composition $La_{0{\cdot}9}Ca_{0{\cdot}1}Cr_{0{\cdot}9}Co_{0{\cdot}1}O_3$ which was pressed and sintered from powders made by the Pechini process.[19] At 1000°C the electrical conductivity was $30{\cdot}3 \pm 1{\cdot}3$ S cm^{-1} (sol–gel) and $26{\cdot}3 \pm 0{\cdot}9$ S cm^{-1} (nitrate solution). From the slope of the Arrhenius plots

$$\log\sigma T = \log A - \frac{E_A}{RT\ln 10}$$

the activation energy of the electrical conductivity was determined to be equal for specimens sintered from both types of powder: $E_A = 26{\cdot}1 \pm 0{\cdot}4$ kJ mol^{-1}.

4 Discussion and Summary

Lanthanum chromite powders with sufficient sinterability at 1400°C for the ceramic interconnector of solid oxide fuel cells were obtained by spray-drying of lanthanum chromium alkoxide sols. The results of the powder characterization have shown that spray-dried powders from alkoxide sols have very similar properties compared with spray-dried powders obtained directly from nitrate solutions. This surprising result may be explained by considering the chemistry of the two processes.

The alkoxide sol is made by hydrolysis of $(La,Cr)(OCH_3)_3$ and subsequent peptization by adding hydrochloric or nitric acid forming a positively charged colloidal solution with $[(La,Cr)(H_2O)_4(OH)_2]^+$ cations and Cl^- or NO_3^- anions. This sol is converted during the spray-drying step to a gel powder of nearly the same composition. By direct spray-drying of nitrate solutions partial decomposition of the nitrates occurs and, consequently, hydrolysis in the droplets forms possibly a very similar gel composition:

$$[(La,Cr)(H_2O)_4(NO_3)_2]^+ + NO_3^- + 2\ H_2O \rightarrow$$
$$[(La,Cr)(H_2O)_4(OH)_2]^+ + NO_3^- + 2\ HNO_3.$$

The gel droplets lose part of their water, forming a lanthanum-chromium oxynitrate hydrate $LaCr(ONO_3)_2.5\ H_2O$ in agreement with the observed weight loss of about 46%. This colloidal chemical process in the droplets during the spray-drying step is the reason for the similar properties of the spray-dried powders obtained from alkoxide sols and from nitrate solutions.

References

1. Riley, B., Solid oxide fuel cells — The next stage. *J. Power Sources*, **29** (1990) 223–238.
2. Bilger, S., Syskakis, E., Naoumidis, A. & Nickel, H., Sol–gel synthesis of strontium-doped lanthanum manganite. *J. Am. Ceram. Soc.*, **75** (1992) 964–970.
3. Bradley, D. C. & Faktor, M. M., Preparation of lanthanum alkoxides. *Chem. Ind. [London]* (1958) 1332.
4. Cossy, C. & Merbach, A. E., Recent developments in solvation and dynamics of the lanthanum(III) ions. *Pure Appl. Chem.*, **60** (1988) 1785–1796.
5. Mehrotra, R. C., Bharara, P. C. & Mahendra, K. N., Alcoholate complexes of chromium(III) chloride. *Trans. Met. Chem.*, **2** (1977) 161–163.
6. Brown, D. A., Cunningham, D. & Glass, W. K., Studies of chromium(III) alkoxides. *J. Chem. Soc. (A)* (1968) 1563–1568.
7. Mehrotra, R. C., Transition-metal alkoxides. In *Advances in Organic Chemistry and Radiochemistry*, ed. H. J. Emeleus & A. G. Sharpe, Vol. 26 (1983) 269–335.
8. Bradley, D. C., Mehrotra, R. C. & Gauer, D. P., *Metal Alkoxides*. Academic Press, London, 1978.
9. Evans, W. J. & Sollberger, M. S., Synthesis and X-ray crystal structure of a soluble pentametallic organoyttrium alkoxide oxide complex. *J. Am. Chem. Soc.*, **108** (1986) 6095–6096.
10. Misra, S. N., Misra, T. N. & Mehrotra, R. C., Organic compounds of lanthanide elements. *Aust. J. Chem.*, **21** (1968) 797–800.
11. Mehrotra, R. C. & Batwara, J. M., Preparation and some reactions of alkoxides of gadolinium and erbium. *Inorg. Chem.*, **9** (1970) 2505–2510.
12. Anderson, R. A., Temleton, D. H. & Zalkin, A., Synthesis and crystal structure of a neodymium isopropoxide chloride $Nd_6[OCH(CH_3)_2]_{17}Cl$. *Inorg. Chem.*, **17** (1978) 1962–1965.
13. Upendra Tripthi, M., Singh, A. & Mehrotra, R. C., Synthesis and characterization of some heterobimetallic isopropoxides of lanthanum with zirconium. *Polyhedron*, **10** (1991) 949–954.

14. Brixner, L. H. & Moore, E. P., Single-crystal refinement of the structure of LaOCl. *Acta Cryst.*, **C39** (1983) 1316.
15. Mauca, S. G. & Baron, E. J., Crystal data for lanthanum chromate(V). *J. Appl. Cryst.*, **15** (1982) 102–103.
16. Koc, R. & Anderson, H. U., Liquid phase sintering of $LaCrO_3$. *J. Eur. Ceram. Soc.*, **9** (1992) 285–292.
17. Peck, D. H., Miller, M., Kobertz, D., Nickel, H. & Hilpert, K., Vaporization studies of $LaCrO_3$ — Thermodynamic activities and thermodynamic properties for the formation. *J. Am. Ceram. Soc.*, (submitted).
18. Nasrallah, M. M., Carter, J. D., Anderson, H. U. & Koc, R., Low temperature air-sinterable $LaCrO_3$ and $YCrO_3$. *Proc. 2nd International Symposium on SOFC*, Athens, 2–5 July 1991, pp. 637–644.
19. Pechini, M., US Patent 3.330.697 (July 1967).