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Synthesis of perovskite-type compounds by drip pyrolysis

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Lanthanum–transition metal mixed oxides, with the general formula $La_{1-x}M_xBO_3$, have been prepared, wherein M stands for Ca and Sr, and B stands for one or more transition metals selected from the group consisting of Cr, Mn, Fe, Co and Ni, where $0 \leqslant x \leqslant 0.50$. A drip pyrolysis method has been developed to synthesize the mixed oxides at low temperature (550 °C). As combustion fuel, glucose was added to the aqueous solution of metal salts. The prepared compounds have perovskite structures. This paper examines the possibilities of finding a simple and large scale procedure in order to produce a long list of perovskites necessary for fuel cell materials (air electrode and interconnect) and catalysts for oxidation catalysis. X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) measurements and determination of specific surface area, carbon content and particle size distribution have been carried out on the obtained perovskite powders.

1. Introduction

Solid oxide electrolyte fuel cells (SOFC) may offer a range of advantages for electrical power generation: high efficiency, simplicity of system design, and availability of useful by-product heat [1, 2]. However, there are still material problems with respect to the air electrode and interconnect components. Taking into account the high operating temperature (1000 °C) of SOFCs, these materials have to meet severe requirements from many points of view: chemical, thermomechanical, electrical, etc. [1]. Lanthanum manganites and chromites (undoped or doped with alkaline earths) are well known as materials for air electrodes and interconnects, respectively [2]. Other perovskites, such as $LaFeO_3$, $LaCoO_3$ and $LaNiO_3$, have been used in fuel cells as air electrodes [3].

Powders having high purity, phase homogeneity, controlled particle size distribution, and which are suitable for fabrication of components, are not easily obtainable via an economical, continuous process. Generally speaking, powder synthesis, based on the classic solid state reaction procedure, is not entirely satisfactory. Problems with poor chemical homogeneity demand high calcination temperatures, which on the other hand lead to aggregated, inactive powders. However, chemical homogeneity can be obtained by molecular mixing of the different constituents followed by calcination. Furthermore, controlled particle size distribution, in addition to fine crystallite size, can be maintained by using low calcination temperatures. The literature describes several attempts to improve the powder characteristics of mixed oxides based on various molecular mixing principles, such as spray pyrolysis [4] or organic precursor processes [5]. Whereas the first seems to rely upon development of complicated equipment, the latter appears to be successful for small scale laboratory production only, and may be difficult to control [6].

Recently it was shown that good results with respect to phase homogeneity, chemical purity and physical powder characteristics could be obtained by using a drip pyrolysis technique based on aqueous solutions of metal nitrates and acetates in preparing $La_{0.85}Sr_{0.15}MnO_3$ [7]. The powders were optimized for colloidal casting techniques, such as tape casting and slip casting. However, aiming at continuous powder synthesis, some inconveniences were discovered with respect to industrializing this procedure. For instance, the powder was not completely free flowing from the pyrolysis furnace, and it was difficult to establish optimal synthesis conditions corresponding to reasonably low furnace temperature for the pyrolysis.

Pederson *et al.* [8] and Chick *et al.* [9] recommended the use of a low molecular weight amino acid (glycine) as a complexing agent and combustion fuel in the pyrolysis. In this way low temperature sinterable chromites were obtained. Kingsley and Patil [10] and Martin *et al.* [11] used, besides glycine, other fuel additives: urea and carbohydrates (lactose, glucose and sucrose). In an earlier work, the complexing fuel combustion property of glycine was also applied in order to prepare $La_{1-x}Ca_xCrO_3$ with good sintering properties based on the drip pyrolysis technique [12].

It is well established that lanthanum chromite densifies poorly in air, even at elevated temperatures [13]. Therefore, several attempts to enhance the air sinterability at low temperatures have been carried out [14–16]. One of the most relevant attempts is the work of Sakai *et al.* [16], which demonstrated that

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a slight deficit in chromium, y, remarkably improved the air sinterability of calcium-doped lanthanum chromite ($La_{1-x}Ca_xCr_{1-y}Ca_yO_3$).

Koc and Anderson [17] and Nasrallah *et al.* [18] further attempted to enhance the air sinterability of lanthanum chromites by partly substituting Co for Cr (between 10 and 30 mol %). The intention of this work was to prepare such compounds by using a molecular mixing method and by adding a combustion fuel (glucose) in order to improve the pyrolysis conditions. The cobalt content was limited to 10 mol %, and it tried to compensate for the chromium deficit in the chemical formula by introducing a corresponding amount of cobalt.

The determination of sinterability, chemical stability and thermal expansion coefficient of the calcium and cobalt-doped lanthanum chromites is relevant for a fuel cell stack interconnect. The results are published elsewhere [19]. Seto *et al.* [20] prepared strontium-doped lanthanum chromites, doped on B sites with different metals (one or more cations). They obtained high electrical conductivities and high densities after sintering at 1600 °C, and the materials appeared to be promising for interconnect components in SOFCs. In an attempt to use the present method to synthesize a multicomponent perovskite, which could sinter at lower temperatures, calcium-doped lanthanum chromites have been prepared by introducing the transition metals, Fe, Co, Ni in minor amounts as B site dopants [21].

The catalytic properties of the perovskite oxides (ABO_3) are based on the presence of mixed valence B site ions and oxygen vacancies, which can be controlled by partial substitution of the basic elements (A, B) without affecting the fundamental structure [22]. Voorhoeve and coworkers investigated a long series of perovskites with catalytic properties [23]. The activities of perovskite-type oxides are strongly effected by the kind of foreign cation, as well as by its amount. The method presented is suitable for synthesizing such perovskite compounds.

For this study the following compositions have been prepared:

1. $La_{1-x}Sr_xMnO_3$, $0 \leqslant x \leqslant 0.5$;
2. $La_{0.70}Ca_{0.30}Cr_{1-y}Co_yO_3$, $0 \leqslant y \leqslant 0.10$;
   $La_{0.70}Ca_{0.30}Cr_{0.85}Co_{0.05}Fe_{0.05}Ni_{0.05}O_3$;
3. $La_{0.85}Sr_{0.15}Mn_{0.50}Cr_{0.50}O_3$;
   $La_{0.70}Ca_{0.30}Mn_{0.50}Cr_{0.50}O_3$; and
4. $LaFeO_3$, $LaCoO_3$, "$LaNiO_3$".

2. Experimental procedure

Stoichiometric compositions of the metal nitrates were dissolved in water, and glucose was added in a molar ratio of 1:1 with respect to total metal cation content. The concentration of stock solution was generally about 1 M. For the compounds containing manganese, manganese acetate was used instead of the nitrate, as this has been shown to have positive effects in a mixture with nitrates with respect to the pyrolysis and the resulting powder characteristics [7, 24]. For stock solutions containing manganese cations the pH was adjusted to 2.0 by adding nitric acid, ensuring a high stability (the stock solution could be stored for more than six months [7]).

The salt solutions were dripped through a feed tube into the hot zone of an SS-tube rotary furnace with a feed rate of 12 ml min^{-1}. The local temperature at the inner furnace wall was measured by thermocouples and was 550 °C.

Generally speaking, at least a half mole ($\sim$ 100 g) batch was produced from each perovskite-type oxide. A few larger batches of up to 1000 g have been produced in the case of $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.70}Ca_{0.30}Cr_{1-y}Co_yO_3$ ($0 \leqslant y \leqslant 0.10$) and batches of 5000 g for $LaMnO_3$. The powders were characterized by X-ray diffraction (Philips APD 1700), carbon analysis (Leco), particle size distribution (Malvern Mastersizer), surface area (Quantachrome Autosorp-6), and scanning electron microscope (SEM) (Jeol 100 CX). The crystallite size was calculated from the half-width of a diffraction peak using Scherrer's equation.

3. Results and discussion

The phase identification (by X-ray powder diffraction), crystallite size, carbon content and specific surface area are presented in Table I.

With one exception ("$LaNiO_3$"), all oxides have the expected perovskite-type structure. In the case of "$LaNiO_3$" the resulting product was mainly La_2NiO_4 and NiO.

In the case of manganites and chromites the perovskite compounds as synthesized could be indexed on the basis of a cubic cell as seen from Table I. After heat treatment at higher temperatures (sintering), manganites are rhombohedrally distorted, and the chromites (all doped with 30 mol % Ca) have an orthorhombic structure. Even undoped manganite (LM-1001) has a rhombohedral structure, which indicates a non-stoichiometric composition, $LaMnO_{3+\delta}$, where manganese is present both as Mn^{3+} and Mn^{4+} [25, 26].

The compound $La_{0.85}Sr_{0.15}Cr_{0.50}Mn_{0.50}O_3$ is a single phase with a rhombohedral structure after sintering at 1200 °C for 2 h, see Table I. Koc *et al.* [5] have shown that the composition $La_{0.85}Sr_{0.10}Cr_{0.50}Mn_{0.50}O_3$ has an orthorhombic structure (after sintering at 1475 °C). They obtained the same results in the case of a similar composition, $La_{0.89}Sr_{0.10}Cr_{1-x}Mn_xO_3$, with a substitution of less than 55% Mn for Cr. Furthermore, they obtained a single rhombohedral phase only for compounds with more than 60% Mn and a mixture of the two structures between 55 and 60% Mn. According to the results given here, an extra doping with 0.05% Sr was enough to obtain the rhombohedral structure when 50% of the Cr was replaced by Mn, i.e. less than 55% Mn. The other mixed chromite–manganite, $La_{0.70}Ca_{0.30}Cr_{0.50}Mn_{0.50}O_3$ (LCCM-1001, Table I) is orthorhombic, although it is highly doped with calcium.

The chromium based perovskites (LCC, LCCC and LCCC FN in Table I) show an orthorhombic structure in accordance with the results of Berjoan and Coutures on Ca-doped $LaCrO_3$ [27]. Apparently, minor doping with other elements (Co, Fe, Ni) does not change the type of crystalline structure.

The as synthesized $LaFeO_3$ and $LaCoO_3$ are orthorhombic and rhombohedral, respectively.

As extra phases, the Sr-doped manganites usually show $SrCO_3$, whose peaks in the XRD pattern grow as the strontium doping increases, correlating well with the measured C content (Table I). For low doping, however, ($\leqslant 15$ mol % Sr) the resulting manganite is a pure phase without any detectable (by XRD) $SrCO_3$, even though the pyrolysis furnace temperature in these experiments is low (~ 550 °C). Using

TABLE I Characteristics of powders produced by drip pyrolysis

Batch	Phase composition structure	Pseudocubic parameter (nm)	Crystallite size (nm)	Carbon content (%)	Surface area m^{2}g^{-1})
LM-1001	$LaMnO_3$, rhombohedral $a = 0.555$ nm $c = 1.338$ nm	0.390	19.2	0.38	27.2
LSM-1015	$La_{0.85}Sr_{0.15}MnO_3$, rhombohedral $a = 0.553$ nm $c = 1.350$ nm	0.391	25.2	0.45	27.3
LSM-1030	$La_{0.70}Sr_{0.30}MnO_3$, rhombohedral $a = 0.551$ nm $c = 1.343$ nm Extra phase: trace of $SrCO_3$	0.389	19.7	0.66	17.9
LSM-1050	$La_{0.50}Sr_{0.50}MnO_3$, rhombohedral $a = 0.549$ nm $c = 1.341$ nm Extra phase: very little $SrCO_3$	0.388	18.3	1.15	19.5
LSCM-1001	$La_{0.85}Sr_{0.15}Cr_{0.50}Mn_{0.50}O_3$, rhombohedral $a = 0.552$ nm $c = 1.333$ nm	0.388	18.7	0.56	29.4
LCCM-1001	$La_{0.70}Ca_{0.30}Mn_{0.50}Cr_{0.50}O_3$, orthorhombic $a = 0.546$ nm $b = 0.770$ nm $c = 0.544$ nm	0.385	19.2	0.42	37.7
LCC-1002	$La_{0.68}Ca_{0.35}Cr_{0.97}O_3$, orthorhombic $a = 0.545$ $b = 0.772$ $c = 0.546$ Extra phase: very little $CaCrO_4$ and La_2CrO_6	0.387	23.0	0.28	14.2
LCCC-1025	$La_{0.70}Ca_{0.30}Cr_{0.975}Co_{0.025}O_3$, orthorhombic $a = 0.542$ nm $b = 0.768$ nm $c = 0.544$ nm Extra phase: very little La_2CrO_6 and $CaCrO_4$	0.385	20.5	0.20	–
LCCC-1050	$La_{0.70}Ca_{0.30}Cr_{0.95}Co_{0.05}O_3$, orthorhombic $a = 0.543$ nm $b = 0.769$ nm $c = 0.545$ nm Extra phase: very little La_2CrO_6, $CaCrO_4$	0.386	23.5	0.33	–
LCCC-1100	$La_{0.70}Ca_{0.30}Cr_{0.90}Co_{0.10}O_3$, orthorhombic $a = 0.543$ nm $b = 0.768$ nm $c = 0.545$ nm Extra phase: trace of La_2CrO_6	0.385	21.5	0.31	17.4
LCCC-FN-1001	$La_{0.70}Ca_{0.30}Cr_{0.85}Co_{0.05}Fe_{0.05}Ni_{0.05}O_3$, orthorhombic $a = 0.548$ nm $b = 0.782$ nm $c = 0.555$ nm	0.388	26.0	1.30	22.5
LF-1001	$LaFeO_3$, orthorhombic $a = 0.556$ nm $b = 0.788$ nm $c = 0.555$ nm Extra phase: very little La_2O_3	–	19.2	0.91	21.7
LC$_0$-1001	$LaCoO_3$ rhombohedral $a = 0.545$ nm $c = 1.313$ nm Extra phase: very little La_2CO_5 and trace of Co_3O_4	–	27.0	0.65	19.4
LN-1001	La_2NiO_4, NiO, La_2CO_5	–	–	2.04	–

a citrate precursor process Baythoun and Sale recommend a much higher calcination temperature in order to remove $SrCO_3$ (1000 °C) [28].

In the case of the chromite-type perovskites the minor extra phases most frequently encountered are La_2CrO_6 and $CaCrO_4$ and occasionally $LaCrO_4$.

The minor extra phases present in these prepared perovskites usually amount to about 1 and 5% for LSM-1050, LCC-1002, LCCC-series, indicated as "trace of" and "very little", respectively (see Table I).

The crystallite size of the as synthesized compounds calculated from Scherrer's equation lies between 18 and 27 nm, and only small variations have been observed in relation to composition. The possible presence of lattice strains [4] and the low crystallite size resulting in broadened peaks makes it difficult to determine the true symmetry (rhombohedral and orthorhombic). Only after sintering at temperatures above 1200 °C is the true structure fully developed corresponding to the above-mentioned results (see Table I).

The carbon content appears to be below 1 wt %, whereas higher carbon content (1–2 wt %) has been found in powders with starting materials containing acetates, as in the case of manganites (especially highly doped LSM-1050), chromites (LCCCFN-1001) and the unsuccessful preparation of $LaNiO_3$.

Large specific surface area powders have been obtained via drip pyrolysis. The largest values have been found for mixed oxide manganite–chromite, LCCM-1001 ($37.7\ m^2\,g^{-1}$) and LSCM-1001 ($29.4\ m^2\,g^{-1}$). Generally speaking, starting from a mixture of nitrates–acetates larger specific surface areas have been obtained. Powders were prepared with specific surface area in the range between 14 and $38\ m^2\,g^{-1}$, which is similar to or larger than that of the freeze-dried powders obtained by Johnson *et al.* [29] or by the sol–gel method of Taguchi *et al.* [30], and much greater than that obtained by the citrate precursor method [6, 28]. Supposing equal spherical particles, an average particle diameter of 25 nm can be calculated from the specific surface area, reasonably close to the 19.2 nm determined from the Scherrer formula (LCCM, Table I).

Agglomerate size distribution of the powders has been measured using a particle size analyser based on laser light scattering. After 1 min in a dry shaking mixer containing zirconia balls, a mean agglomerate size of 4.2 μm for LM-1001 was found; whereas 24 h wet ball milled powder resulted in a value of 2.5 μm. In the case of LCCC, the mean agglomerate size, measured after 2 min of ultrasound treatment, was about 30 μm. A 24 h ball milled powder gave a 0.8 μm value for mean agglomerate size. This value is approximately 40 times the crystallite size (LCCC-1010 in Table I) which is in accordance with scanning electron micrographs (Fig. 1a, b) showing that these particles contain mesopores. Fig. 1a shows a micrograph of a chromite (LCCC-1010, as synthesized). The agglomerates reveal many cracks and are highly porous. The small grains (between 30 and 80 nm) are loosely bound together with many small pores and a few larger pores. This appears clearly from the more detailed picture in Fig. 1b. The agglomerates can easily be broken down to < 1 μm for the mean particle size by using wet ball milling. In the case of manganite powders, a more foam-like morphology appears (Fig. 2, $LaMnO_3$, as synthesized) which may be an optimal powder characteristic for SOFC electrodes or catalysts with controlled porosities.

All powders mentioned above have been synthesized continuously as a free flowing powder with

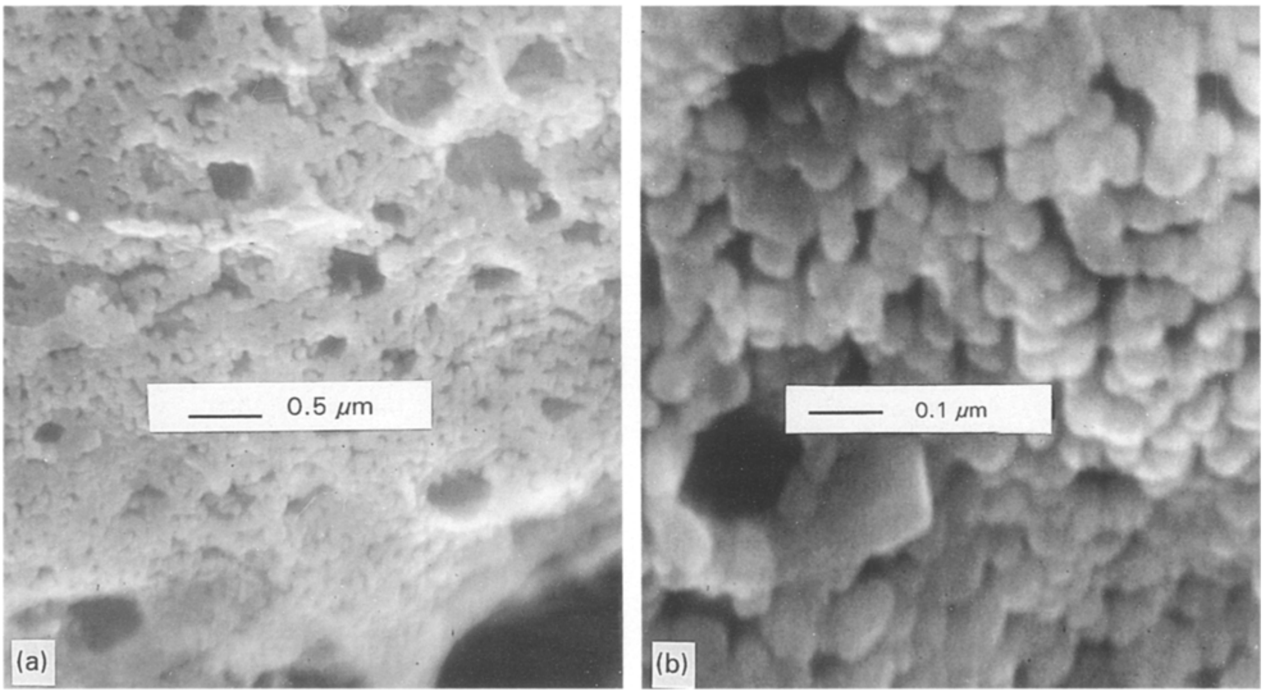

Figure 1 Scanning electron micrograph of $La_{0.70}Ca_{0.30}Cr_{0.90}\ Co_{0.10}O_3$ pyrolysed powder at (a) intermediate magnification and (b) high magnification.

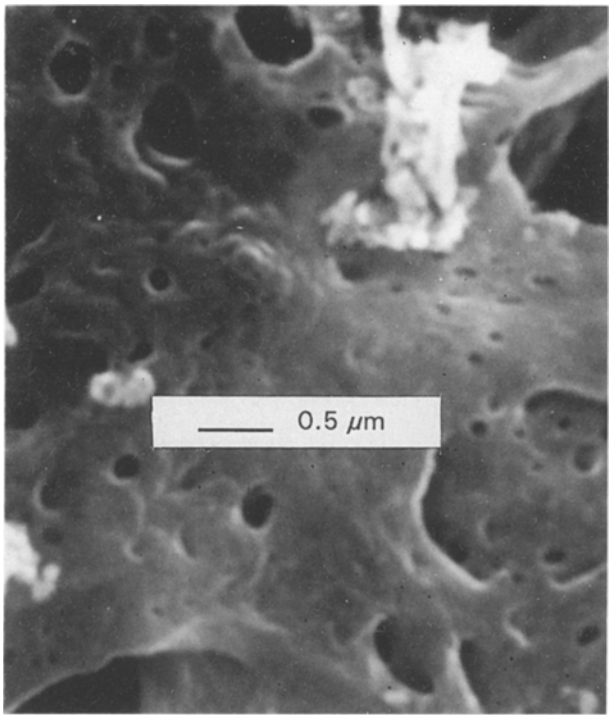

Figure 2 Scanning electron micrograph of $LaMnO_3$ pyrolysed powder.

a very high yield (more than 90%) directly from the rotary furnace.

4. Conclusions

Using a drip pyrolysis technique based on aqueous nitrate solutions a large spectrum of perovskites has been synthesized. Glucose as combustion fuel was added in the mole ratio 1:1 by means of which perovskite phases develop at low furnace temperature (550 °C), with high specific surface area.

Partially substituting acetates for nitrates as starting materials raised the surface area up to 38 $m^2 g^{-1}$ without increasing the carbon content significantly. The crystallite size seemed to be independent of composition for all the synthesized powders.

The minor phases present in the as prepared chromites (as chromates) seem to be useful in the sintering process (so called "transient liquid phase" [18]), and they seem to become incorporated in the perovskite lattice after heat treatment [19]. However, the presence of La_2O_3 in $LaFeO_3$ powder has to be avoided because of its hygroscopic and unstable nature.

In the case of $La(Sr)MnO_3$ samples, the residual carbon content increased with Sr-doping.

Rhombohedral perovskite structures were obtained for lanthanum manganites and *A* site Sr-doped lanthanum manganites as well as for *B* site Cr-doped manganites.

Chromites doped with 30% Ca had orthorhombic structure (LCC, LCCC, LCCC-FN) (see Table I).

The method used to synthesize the materials presented in this study has proven to be reproducible and suitable for upscaling.

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