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Manufacture of a non-stoichiometric LSM cathode SOFC material by aqueous tape casting

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Abstract

This work deals with the manufacture of non-stoichiometric strontium-doped lanthanum manganite (LSM) as a cathode material by aqueous colloidal processing. This requires some knowledge of the processability and sinterability of this material. The stability of aqueous suspensions of a fine non-stoichiometric LSM powder was studied by measuring the zeta potential as a function of pH and deflocculant content. Concentrated suspensions were prepared to solids loadings as high as 50 vol.%. The best dispersing conditions and the influence of binders and tape casting performance were determined by means of rheological measurements. LSM cathode tapes were characterized in the green state and after sintering at 1500 °C/2 h, leading to high density compacts. Maximum sintering rate is achieved at 1350 °C. Once the sintering behavior is known a porous material can be easily designed using a sintering temperature compatible with the other components of the semi-cell.

Keywords: Suspensions; Tape casting; Shaping; Fuel cells; Perovskites

1. Introduction

In recent years, there has been a continuous interest in developing new materials with perovskite structure. Perovskite oxides have the general formula ABO_3, where the B-site cation occupies the interstitial site of an octahedron of oxygen anions and the A-site cation fits in the large cavity at the center of the 12 coordination site.[1,2] Showing a wide range of oxygen stoichiometry, these materials have been attracting much attention due to the existence of mixed ionic and electronic conductivity.[3–5]

Rare-earth manganites are perovskites with a great potential for use in a wide range of applications, such as sensors, permanent magnets, catalysts and pigments,[6,7] but recent effort focuses on the wide variety of interesting electrical and magnetic properties,[8] and their possible use as electrode materials for solid-oxide fuel cells (SOFCs).[3–5,9–11]

There is a broad body of work dealing with the processing of different parts of the SOFCs by colloidal routes, mostly referred to the electrolyte layer or to the anode materials.[12–14] However, facing the manufacture of the stack, it is also necessary to study the colloidal behavior of the other components to allow global integration. In this sense, there is very scarce work dealing with the processing and, in particular, with the colloidal behavior of the interconnection and cathode materials.[15–18] This can be explained considering the composition of such materials, being doped manganite the most widely used up to now. A typical cathode material for SOFC applications should be porous and well adhered to a dense electrolyte material. LSM is used as a cathode material in SOFCs because it displays appropriate electronic and ionic conductivity, high thermal and chemical stability, and an adequate coefficient of thermal expansion as well as an appropriate compatibility with YSZ electrolyte.[11,16,19,20] These materials have a complex colloidal behavior in water due to the possible dissolution of some of the cations forming the material at certain pH conditions and other problems related to the preparation of concentrated suspensions suitable for slurry consolidation. For instance, Ramanathan and Kakade[21] prepared aqueous slurries of LSM powder prepared by a gel combustion method. Those slurries showed pseudoplasticity, i.e., decrease in viscosity with increasing shear rate. However, available information about processing and sintering of this material is scarce.

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The present work deals with the preparation and optimization of concentrated aqueous suspensions of non-stoichiometric Sr-doped-$LaMnO_{3-\delta}$ powders and their processing by a tape casting route. The influence of suspension parameters, such as the binder system content, on the rheological behavior of the suspensions, the tape casting performance and the characteristics of the green and the sintered tapes, was studied.

2. Experimental procedure

2.1. Starting materials

Commercial submicronic powder of a non-stoichiometric strontium-doped lanthanum manganite, $(La_{0.85}Sr_{0.15})_{0.98}MnO_{3-\delta}$ (LSM85, Inframat Advanced Materials, USA) was used as starting material. The physicochemical characteristics of these powders and the stability of the suspensions were studied. Characterization of the as-received powder was performed by measuring the particle size distribution by laser diffraction (Mastersizer S, Malvern, UK), the specific surface area using the single-point BET method (MonosorbTM Surface Area Analyzer MS-13, Quantachrome Corporation, USA) after degassing at 150 °C, the density by He-picnometry (Multipycnometer, Quantachrome Corporation, USA), the morphology by field emission scanning electron microscopy (FE-SEM Hitachi S-4700, Japan), and the phases through X-ray diffraction analysis (Bruker D8 Advance, USA). The powder was dispersed in water using an ultrasounds probe (UP 400S, Dr. Hielscher GmbH, Germany). Differential thermal and thermogravimetric analyses (DTA-TGA) were carried out by using a thermoanalyzer (Netzsch STA-409, Germany) under air, employing a platinum crucible and a heating and a cooling rate of 10 °C/min in order to observe the processes involved. As a reference substance finely powdered alumina was used.

2.2. Preparation and characterization of suspensions

The solubility of the powders in water was studied preparing two sets of suspensions at different pH values. In the first series, suspensions were maintained undisturbed and pH was measured after 1, 2, 24, 48, 72 h and 1 week. In the second series of samples suspensions were prepared at pH values of 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 and adjusting continuously these pHs during 24 h. The final suspensions of the two series (after 1 week in the first and 24 h in the second) were then centrifuged and the liquid-phase was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Iris Advantage, Thermo Jarrel-Ash, USA) in order to determine the concentration of soluble species. The error of the ICP-OES measurements was below 1% of measured value. The average of three measurements is always given.

The colloidal stability of aqueous suspensions of LSM was studied by measuring the zeta potential (ζ) as a function of both deflocculant content and pH using a Zetasizer NanoZS instrument (Malvern, UK), based on the laser Doppler velocimetry technique. HCl and KOH were used to change the pH, and KCl 10^{-2} M was used as an inert electrolyte. A commercial polyacrylic acid-based polyelectrolyte, PAA (DURAMAX^{TM} D-3005, Rohm & Haas, USA) was used as a deflocculant with additions ranging from 0.5 to 2.0 wt% (on a dry solids basis). Suspensions for zeta potential measurements were prepared to a powder concentration of 0.1 g/l and sonicated for 1 min in order to prevent agglomeration.

The rheological behavior of all prepared slurries was studied with a rheometer (MARS, Thermo, Germany) operated at controlled shear rate (CR) conditions. The sensor system consisted on a double-cone rotor and a stationary cylindrical plate. The chamber is protected with a solvent trap to reduce evaporation phenomena. Measurements were performed by increasing the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 2 min and returning to 0 in 5 min. Temperature was maintained constant at 25 °C.

Concentrated LSM suspensions were prepared to solids loading ranging from 20 to 55 vol.% with different PAA contents (up to 2 wt%) and sonication times (up to 4 min). Tape casting slips were prepared adding 10 wt% of an acrylic emulsion (Duramax B-1000, Rohm & Haas, USA) binder, which has an active matter content of 55 wt%. The different suspensions were cast in a home-made tape casting machine with a moving deposit at a casting speed of 5 cm/s and a single-blade system. Different tapes were produced fixing the blade height at 200 and 100 μm.

2.3. Sintering and microstructure

Dynamic shrinkage as a function of temperature was measured until 1600 °C (5 °C/min heating and cooling rates) using a dilatometer with alumina rod (Model Adamel Lhomargy, DI-24 model, Brie France) on a reference sample prepared by isostatic pressing the as-received powder at 200 MPa. Samples were treated up to 1500 °C at a heating and a cooling rate of 5 °C/min, and keeping a dwell time of 2 h. The microstructure of the sintered samples was analyzed on polished (down to 1 μm) and thermally etched surfaces (1480 °C for 6 min, heating and cooling rates of 10 °C/min) by means of a Scanning Electron Microscopy (SEM, Zeiss DSM-400, Germany). Green and sintered densities were measured by immersion method in mercury and water, respectively. A reference tape was also sintered with a similar thermal schedule, which included a plateau at 500 °C during 1 h in order to evaluate the difference of density with respect to pressed samples.

3. Results and discussion

Fig. 1a shows the morphology of the as-received powder. It consists of non-spherical, faceted powders with diameters ranging from 1 to 3 micrometers with the presence of hard agglomerates of up to 5 ~μm. The microstructure of the as-received powder reveals that they have been thermally treated to high temperatures as needed to form the complex perovskite phase. This is clearly observed in Fig. 1b, which shows an aggregate formed by several particles sintered together; these clusters are distributed along the entire sample. The average particle size measured by laser diffraction is 2.5 ± 0.5 μm, as can be seen in Fig. 2. This size reduces with the presence of deflocculant and