



# Leaching effect in gadolinia-doped ceria aqueous suspensions for ceramic processes



A. Caldarelli <sup>a,b</sup>, E. Mercadelli <sup>b,\*</sup>, S. Presto <sup>c</sup>, M. Viviani <sup>c</sup>, A. Sanson <sup>b</sup>

<sup>a</sup> CERTIMAC s.r.l., Via Granarolo 62, Faenza, Italy

<sup>b</sup> ISTE-CNR Institute of Science and Technology for Ceramics, Via Granarolo 64, Faenza, Italy

<sup>c</sup> IENI-CNR Institute for Energetics and Interphases, Via De Marini 6, Genova, Italy

## HIGHLIGHTS

- Furoic acid results as a good dispersant for CGO water-based suspensions.
- Suspension pH and ball-milling time change CGO surface electrochemical properties.
- Furoic acid leads unexpectedly to CGO surface ionic leaching.
- Ionic leaching lowers grain boundary resistance improving ionic conductivity.

## ARTICLE INFO

### Article history:

Received 21 January 2016

Received in revised form

11 June 2016

Accepted 14 June 2016

Available online 6 July 2016

### Keywords:

Gadolinium doped ceria

Water-based suspensions

Furoic acid

Ionic leaching

Electrical conductivity

## ABSTRACT

Gadolinium doped ceria (CGO) is a commonly used electrolytic material for Solid Oxide Fuel Cells (SOFCs) and for this reason different shaping methods for its deposition are reported in literature. Most of these processes are based on the use of organic-based CGO suspensions, but water-based processes are acquiring increasingly interest for their economical and environmental friendly properties. In this paper we reported how the components of water-based suspension and some unexpected process parameters can deeply affect the functional properties of the final powder. In particular, we observed that CGO powders are strongly affected by ionic leaching induced by furoic acid used as dispersant: the extent of this leaching was related to the dispersant concentration and suspension's ball-milling-time; the phenomenon was confirmed by ICP-AES analyses on suspensions supernatant. Most importantly, ionic leaching affected the electrical properties of CGO: leached powder showed a higher ionic conductivity as a consequence of a partial removal of Gd ions at the grain boundaries.

This work is therefore pointing out that when considering water-based suspensions, it is extremely important to carefully consider all the process parameters, including the organic components of the ceramic suspension, as these could lead to unexpected effects on the properties of the powder, affecting the performance of the final shaped material.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Gadolinium doped ceria ( $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ , CGO) due to its electrical conductivity noticeably higher at low temperature than the one of the most common yttrium doped zirconia (YSZ), is considered an alternative electrolytic material for solid oxide fuel cells (SOFCs) [1–5]. CGO electrolytes permit therefore to lower the operational temperature of the fuel cell at intermediate value

(773–973 K), allowing minor costs and increasing materials durability.

The electrical conductivity of gadolinium doped ceria (CGO) is due to partial substitution of cerium ions ( $\text{Ce}^{4+}$ ) by gadolinium ions ( $\text{Gd}^{3+}$ ) in cerium dioxide ( $\text{CeO}_2$ ) fluorite structure, accompanied by the generation of oxygen vacancies ( $\text{O}^{2-}$ ) that keep electrical neutrality of the material; these defects are mainly responsible for the high ionic conductivity [6] of these materials, even if other phenomena can influence the CGO electrical properties.

Generally speaking, the electrical conductivity for doped ceria materials is affected by several factors: i) the type and the amount of the dopant [3,7], ii) the nature and concentration of impurities

\* Corresponding author.

E-mail address: [elisa.mercadelli@istec.cnr.it](mailto:elisa.mercadelli@istec.cnr.it) (E. Mercadelli).

(ions, segregated phases, insulating amorphous layers, sintering aids, etc.) [8–11] and iii) the microstructure of the sintered material, which is a consequence of the shaping process and sintering parameters used for its manufacturing [12] as well as the physical-chemical characteristics of the starting powders [13,14]. Moreover, the conductivity of CGO is also function of temperature and oxygen partial pressure: cerium dioxide is a mixed ionic-electronic conductor and the electronic conduction predominates during operation at high temperatures (>1273 K) and at low oxygen partial pressure, where  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  reduction is favored [15]. This last condition must be avoided in order to prevent SOFC short circuiting [16].

For the above reasons many papers dealing with electrical characterization of CGO electrolyte with the same composition (Gd mol. %) report disaccoring results. Sometimes the comparison of results is also complicated by the lack of information, e.g. physical-chemical characteristics of electrolyte powder and of the sintered electrolyte material.

In the present research we report that another source of variability can be introduced when this material is used in water-based suspension with specific dispersing agents. The use of CGO suspension is quite common for producing electrolyte layers by wet ceramic techniques (e.g. wet powder spray, spin or dip coating, etc.) and a suitable composition must be identified in order to get a stable suspension to correctly perform the deposition process.

In this work, the influence of furoic acid, the most effective deflocculant able to disperse the CGO powder, onto water-based suspensions properties was deeply investigated. In particular the effects of the dispersant concentration and of the ball-milling time were evaluated onto the chemical-physical CGO properties of the powders. Finally, the sintered pellets resulting from final recovered powders, were characterized in terms of composition, morphology and electrical conductivity.

## 2. Experimental

### 2.1. Starting materials

A commercial gadolinium doped ceria powder –  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (ssa =  $32.6 \text{ m}^2 \text{ g}^{-1}$ ,  $d_{50} = 0.37 \mu\text{m}$ , Fuel Cells Materials, USA) was used for the present investigation. Different dispersants were tested for the preparation of doped ceria (CGO) suspensions: furoic acid (98%, Sigma-Aldrich), Duramax D-3005 (35%, Rohm and Haas), triethanolamine ( $\geq 99\%$ , Sigma-Aldrich), benzoic acid (99%, Sigma-Aldrich), 4-hydroxy benzoic acid ( $\geq 99\%$ , Fluka), 4-amino benzoic acid (99%, Sigma-Aldrich) and PVP K15 ( $M_r = 10,000$ , Fluka). Distilled water was used as solvent for CGO suspensions.

### 2.2. Sedimentation tests

The suspensions used for sedimentation tests (33 vol% of the dispersant in respect to CGO; 4 wt% of CGO to total weight) were ball-milled for 24 h with zirconia grinding media of different size, in order to get powder disaggregation. Suspensions were successively poured into 25 ml graded cylinders: the height of the sediment, visible at the bottom, and that one corresponding to deflocculated suspension were recorded for few days for evaluating suspension stability.

### 2.3. Zeta potential analyses

The Zeta Potential ( $\zeta$ ) analyses of CGO ball-milled aqueous suspensions (4 wt% of CGO to total weight; 40 h of ball-milling) were performed by Acoustosizer II (Colloidal Dynamics, USA) electroacoustic spectroscopy. The suspensions were prepared in the

absence of any added electrolytes. The titration of a CGO suspension was performed automatically by the instrument, collecting simultaneously pH and Zeta Potential.

### 2.4. Chemical composition analyses: Raman and UV–visible spectroscopy

The dried powders recovered from the suspensions (untreated and leached samples) were analyzed by Raman Spectroscopy (Renishaw 1000, laser source Ar ion 514 nm, equipped with Leica DMLM microscope) and UV–visible spectroscopy (Perkin Elmer Lambda 35), to check possible differences in surface and bulk chemical compositions.

### 2.5. Field emission scanning electron microscopy analyses (FESEM)

Powders' aggregates and particles size and morphology, were investigated using a field emission scanning electron microscope (FESEM, Gemini Columns SIGMA Zeiss, Germany). The analyses were carried out by preparing a very diluted suspension of CGO commercial powder in ethanol (0.1 wt% of CGO to total mass), sonicated for few minutes and then nebulized several times over SEM analysis stub. The sample was not coated to make it conductive but it was directly analyzed. Cross-section micrographs on sintered powder pellets were carried out to detect grains dimensions and morphology: each sample was polished and then thermally etched at 1373 K. Elementary analyses were performed by energy dispersive X-ray analyses (EDX).

### 2.6. Inductively coupled plasma atomic emission spectroscopy analyses (ICP-AES)

Elemental analyses were performed by ICP-AES spectrometry (Liberty 200 Varian, Australia) on powders and surnatants of different CGO suspensions, with or without dispersant, in order to measure Gd and Ce atomic concentrations. The prepared suspensions (4 wt% of CGO to total weight; 0–33 vol% of furoic acid) at the end of the ball-milling time (40–90 h), were first centrifuged (6000 rpm, 20 min), then the recovered wet powders were dried at ambient conditions for few days while the corresponding liquids (surnatants) were again centrifuged (3000 rpm, 15 min) by using specific filtration units (30,000 MCWO filtering units, Millipore): this procedure was carried out in order to assure the analysis merely of the liquid part. The obtained solutions were subjected directly to ICP analysis to check the presence of Ce and Gd ions while samples of each recovered powder (0.04 g) were dissolved in a mixture 1:1 vol of concentrated acids (HCl,  $\text{H}_2\text{SO}_4$ ) by using a microwave digestion system, adding water to reach 100 ml of total volume. The instrument response was first calibrated by analyzing two solutions with known content of Gd and Ce ions (standard solutions).

### 2.7. Electrical characterization: impedance spectroscopy measurements

The electrical analyses were performed on CGO pellets prepared with recovered powders (untreated and leached samples) by cold isostatic pressing at 150 MPa and sintered at 1673 K for 4 h. The relative density of the different pellets were measured by Archimede's method, considering  $7.23 \text{ g cm}^{-3}$  as CGO theoretical density [17]. Platinum electrodes (Platinum ink 6926, Metalor) were brushed on each side of pellets and cured at 1273 K.

Impedance Spectroscopy measurements were carried out in a high-temperature rig (Norecs, Probostat) in 4-wire configuration by a Frequency Response Analyser (Solartron, SI1260) and dielectric

Download English Version:

<https://daneshyari.com/en/article/7727900>

Download Persian Version:

<https://daneshyari.com/article/7727900>

[Daneshyari.com](https://daneshyari.com)