Temperature-Programmed Reduction and Dispersive X-Ray Absorption Spectroscopy Studies of CeO$_2$-Based Nanopowders for Intermediate-Temperature Solid-Oxide Fuel Cell Anodes

Marina S. Bellora$^{1,2}$, Joaquín Sacanell$^{2,3,*}$, Cristián Huck-Iriart$^1$, Analía L. Soldati$^3$, Susana A. Larrondo$^{4,5}$, Diego G. Lamas$^1$

$^1$CONICET/Laboratorio de Cristalografía Aplicada, Escuela de Ciencia y Tecnología, Universidad Nacional de General San Martín, San Martín, Argentina
$^2$Departamento de Física de la Materia Condensada, Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energia Atómica, San Martín, Argentina
$^3$Instituto de Nanociencia y Nanotecnología (INN), CNEA-CONICET, San Martín and San Carlos de Bariloche, Argentina
$^4$UNIDEF-CONICET-MINDEF, Departamento de Investigaciones en Sólidos, CITEDEF, Villa Martelli, Argentina
$^5$Instituto de Investigación e Ingeniería Ambiental, Universidad Nacional de General San Martín, San Martín, Argentina

Email: *sacanell@tandar.cnea.gov.ar

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1. Introduction

Cerium oxide (CeO$_2$) has been studied for many years and it is still the focus of...
great attention due its wide range of possible applications. It is used in three-way catalysts (TWCs) for the elimination of toxic auto-exhaust gases [1] [2] low-temperature water-gas shift (WGS) reaction [3] [4], oxygen sensors [5] [6], oxygen permeation membrane systems [7] [8] and solid-oxide fuel cells (SOFCs) [9] [10] [11] [12], among others.

In all the aforementioned applications, there is a growing interest in the study of nanostructured materials, in which an improved surface-to-volume ratio can be obtained. This interest is founded in the consequent substantial reduction in the energy for defect formation occurs in nanocrystalline CeO$_2$, that leads to a high degree of non-stoichiometry and electronic carrier generation [13] both beneficial for redox, catalytic and transport properties. For example, CeO$_2$-based nanoceramics exhibit enhanced ionic conductivity [14], which is very important for their application as SOFC electrolytes.

Although the benefit of the use of nanostructured materials has already been pointed out by several authors, the studies of this type of materials from the basic point of view to understand the mechanisms underlying the different processes of catalysis are scarce. In recent years, our research groups have investigated CeO$_2$-based and NiO/CeO$_2$-based catalysts by dispersive X-ray absorption spectroscopy (DXAS) under different atmospheres and reaction conditions [15] [16] [17] [18]. Samples with different morphologies were analyzed, finding that CeO$_2$-based materials with small average crystallite size and high specific surface area exhibit the best properties, reaching high reducibility and excellent methane conversion for intermediate temperatures [19].

In this work, we analyzed the redox behavior of nanocrystalline Gd$_2$O$_3$, Sm$_2$O$_3$ and Y$_2$O$_3$-doped CeO$_2$ (GDC, SDC and YDC, respectively) powders. We used conventional laboratory temperature programmed reduction (TPR) and combined those results with an in-situ DXAS study under diluted hydrogen atmosphere, in order to gain further insight on the redox properties of the systems. The samples were treated at different temperatures, between 400˚C and 900˚C to analyze the influence of the crystallite size.

2. Experimental Procedure

Samples were prepared from nanocrystalline commercial (Nextech Materials) Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ (GDC), CeO$_2$-10 mol% Sm$_2$O$_3$ (Ce$_{0.9}$Sm$_{0.1}$O$_{1.9}$, SDC) and CeO$_2$-10 mol% Y$_2$O$_3$ (Ce$_{0.82}$Y$_{0.18}$O$_{1.9}$, YDC) powders. They were calcined at 400˚C, 650˚C and 900˚C in order to study the influence of the average crystallite size.

X-ray powder diffraction (XPD) was performed in a Bruker D8 Discover DaVinci diffractometer (Institute of Physics, University of Sao Paulo, Brazil) operated with Cu-K$\alpha$ radiation at 40 kV and 30 mA, a Ni filter and a Lynx-eye detector, in Bragg-Brentano configuration. Experimental data were collected in the angular $2\theta$ range of 20˚ - 140˚ with a step size of 0.02˚ and a time per step of 1 s. The average crystallite sizes of the crystalline phases were determined for all the samples using the Scherrer equation.
Specific surface area was evaluated by means of N\textsubscript{2}-physisorption with a Quantachrome Corporation Autosorb-1 equipment. Samples were previously degassed with pure He at 90°C during 12 h. Results were obtained using the five-point Brunauer-Emmett-Teller (BET) method.

Transmission Electron Microscopy (TEM) experiments were performed using a Philips CM 200 UT microscope operated at 200 kV. The microscope was equipped with ultratwin objective lens and an EDAX spectrometer for chemical analysis by EDS. Powdered samples were suspended in isopropyl alcohol, ultrasonicated for 2 minutes and deposited in Cu/ultrathin hollow carbon TEM grids (Ted Pella).

Hydrogen temperature programmed reduction (TPR) experiments were performed in a Micromeritics Chemisorb 2720 equipment to study sample reducibility. The mass employed for each experiment was of 80 mg. Prior to TPR tests, samples were pretreated in He at 300°C during 30 min to remove any adsorbed species on the solid surface. TPR was carried out with a 50 cm\textsuperscript{3} (STP) min\textsuperscript{-1} (5 vol.% H\textsubscript{2}/Ar) flow from room temperature up to 800°C following a heating ramp of 10°C min\textsuperscript{-1}. Hydrogen uptake was estimated using a Thermal Conductivity Detector (TCD) previously calibrated.

Dispersive X-ray absorption spectroscopy (DAXS) study was performed at the D06A-DXAS dispersive beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). A Si (111) monochromator was used altogether with a CCD detector to collect the absorption spectrum in transmission mode. Self-supporting discs were prepared by mixing the sample powder with boron nitride that has no significant absorption in the energy ranges used. The catalyst mass in the discs was calculated in order to obtain a total absorption ratio of 1.5. Sample discs were located in a sample-holder with a thermocouple attached to it. The sample holder was placed in a quartz reactor, with inlet and outlet gas lines, and located in a furnace with temperature control. Inlet gas composition was set with a gas-mixing station provided with mass flow controllers and exit composition was assessed with a Pfeiffer Omnistar mass spectrometer.

We followed the evolution of DXAS spectra as function of temperature at the L\textsubscript{3}-edge of Ce under diluted H\textsubscript{2}(5% in He), in order to determine the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} proportion. The temperature range was of 400°C - 800°C. CeO\textsubscript{2} and Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O were also measured as standards. Ce\textsuperscript{3+}/Ce\textsuperscript{4+} proportion was obtained by means of linear least square procedures using Python scripting.

3. Results and Discussion

X-ray diffraction patterns for the samples calcined at 400°C are presented in Figure 1. All of them display the expected fluorite-type crystal structure with no sign of any impurity. The nanostructured character of the powders is evidenced by their wide Bragg peaks.

Samples of the three compounds were treated at different temperatures, in order to obtain powders with different particle sizes. Figure 2 displays the X-ray
Figure 1. X-ray diffraction patterns for all compounds treated at 400°C.

As expected, the broadening of Bragg peaks decreases for increasing calcination temperature because samples treated at higher temperatures are formed by larger crystallites. The average crystallite sizes ($D$) determined from the Scherrer equation for all samples are summarized in Table 1. Crystallite sizes range from around 5 to ~50 nm. In particular, the SDC sample treated at 900°C, is formed by crystallite significantly larger than GDC and YDC samples calcined at the same temperature.

Figure 2. X-ray diffraction patterns for YDC powders compounds treated at 400°C, 650°C and 900°C.

diffraction patterns for YDC nanopowders treated at 400°C, 650°C and 900°C. From those images, it can be observed that particle sizes are of the same order of magnitude of crystallite sizes (Table 1), thus indicating that particles...
Table 1. Average crystallite size in nm determined using Scherrer equation for all the samples studied in this work.

| Sample | 400°C | 650°C | 900°C |
|--------|-------|-------|-------|
| GDC    | 4.5(2) | 14(1) | 36(3) |
| SDC    | 4.6(2) | 13(1) | 48(4) |
| YDC    | 4.6(2) | 14(1) | 36(3) |

Figure 3. TEM images of the samples calcined at 650°C: (a) GDC, (b) SDC, (c) YDC.

are single crystals. This feature was also observed for samples treated at 400°C and for samples treated at 900°C, as exemplified in Figure 4 for the SDC system. From the morphological point of view, it can be seen that the particles display polygonal shapes in samples treated at higher temperatures.

The dependence of the average crystallite size as a function of calcination temperature is presented in Figure 5, where it can be seen that crystallite growth is less significant in GDC and YDC compared to SDC. In any case, in undoped ceria the effect is more prominent than that observed in the present work [20] [21]. This is a consequence of the inhibition produced by the solute drag model due to a space charge effect [22]. Y₂O₃ is known as one of the most efficient inhibitors of grain boundary mobility [20], here we show that Gd₂O₃ has a very similar effect.

The values of BET specific surface area of the samples are summarized in Table 2. As it can be observed in Figure 5, there is a marked correlation between SSA and average crystallite size, showing inverse trends for increasing calcination temperature.

The temperature-programmed reduction (TPR) profiles of samples calcined at
Figure 4. TEM images for the SDC samples treated at (a) 400˚C, (b) 650˚C, (c) 900˚C.

Figure 5. Average crystallite size and BET specific surface area as functions of calcination temperature.

Table 2. BET specific surface area in m²/g for all samples.

| Sample | 400˚C | 650˚C | 900˚C |
|--------|-------|-------|-------|
| GDC    | 170   | 53    | 24    |
| SDC    | 170   | 54    | 16    |
| YDC    | 170   | 55    | 26    |

650˚C are shown in Figure 6. The TPR signal, directly related with hydrogen consumption, is presented as a function of the temperature of the sample. The
Figure 6. (a) TPR profile and (b) hydrogen consumption, for samples calcined at 650°C.

Curves do not present the same shape, position and height of the maximum. It is clearly observed that the main peak for all samples is close to 500°C, while a secondary peak is detected around 770°C. The main peak corresponding to the GDC sample, notably occurs at a lower temperature than those corresponding to YDC and SDC, indicating that the first is more efficient for hydrogen oxidation than the other two. Besides, SDC sample is slightly better than YDC one considering their reducibility, in view of the lower temperature at which hydrogen consumption is triggered. No significant difference is observed between the secondary peak of the three samples. The same trend was observed for samples treated at 400°C and 900°C. In Figure 6(b) we show the hydrogen consumption as a function of temperature in which the overall picture is clarified. Indeed, hydrogen consumption of GDC triggers at significantly lower temperature and is higher in the whole temperature range, than that corresponding to SDC and YDC, which are both very similar.

We also studied the influence of the average crystallite size on the reducibility of the samples. Figure 7(a) displays the TPR profiles for the YDC system as an example. It can be observed that the temperature of the main peak decreases with increasing calcination temperature, thus indicating that samples of lower
The above results regarding the influence of crystallite size and dopant oxide on the reducibility of the samples were further confirmed by using the DXAS technique under diluted H₂ atmosphere (5 mol% H₂/He). The experimental procedure was designed in order to mimic the conditions of the laboratory TPR experiments. For example, DXAS data taken at the Ce L₃-edge for the SDC nanopowder calcined at 400°C is shown in Figure 8, displaying the evolution as a function of temperature. At room temperature, two peaks characteristic of Ce⁴⁺ are detected, while one peak corresponding to Ce³⁺ becomes more prominent at high temperatures. By measuring DXAS data corresponding to Ce³⁺ and Ce⁴⁺ standards and using a linear combination procedure, it was possible to determine the Ce³⁺ fraction as a function of temperature for all the samples.

Figure 9 displays the Ce³⁺ fraction (α_{Ce³⁺}) as a function of temperature for GDC, SDC and YDC samples treated at 400°C (Figure 8(a)) and 650°C (Figure 8(b)). As it can be observed that the largest values of α_{Ce³⁺} were exhibited by
Figure 8. DXAS data at the Ce L$_3$-edge collected upon heating under 5 mol% H$_2$/He up to 600˚C for SDC nanopowder calcined at 400˚C.

Figure 9. Ce$^{3+}$ fraction ($\alpha_{\text{Ce}^{3+}}$) for the GDC, SDC and YDC samples, treated at (a) 400˚C and (b) 650˚C, obtained from DXAS analysis.
GDC for both sets samples (calcined at 400˚C and 650˚C), clearly indicates its higher reducibility compared to SDC and YDC systems, in excellent agreement with TPR results.

4. Conclusions

In this work, we analyzed by the effect of average crystallite size and dopant oxide on the reducibility of CeO₂-based nanopowders by temperature-programmed reduction and dispersive X-ray absorption spectroscopy techniques.

We obtained samples formed by single-crystalline particles of controlled grain size, ranging between 4 to around 50 nm of diameter. The addition of Gd₂O₃ or Y₂O₃ has shown to inhibit grain growth more efficiently than Sm₂O₃.

Our results obtained from combined TPR and in situ DXAS, evidenced that:
- Gd₂O₃-doped ceria display better reducibility than Y₂O₃- and Sm₂O₃-doped ceria.
- Reducibility is enhanced in the samples formed by small sized crystallites.

Even though all the materials studied in this work exhibited good properties and, therefore, are likely to be used as anodes of intermediate-temperature SOFCs, Gd₂O₃-doped CeO₂ nanopowders presented the best performance and are more promising for applications.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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