

*In-situ DXAS Study of NiO/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> nanocomposites for IT-SOFC anodes*

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Fuel cells are promising devices for environmentally clean energy production by directly converting chemical energy into electricity. Among them, solid-oxide fuel cells (SOFCs) have the unique capability to use different fuels such as hydrogen or hydrocarbons. However, several issues have to be solved in order to improve their efficiency and reduce their costs. The reduction of their operating temperature, typically around 900-1000°C, is one of the most important problems to be addressed. For this reason, the development of novel materials for intermediate-temperature SOFCs (IT-SOFCs), which operate in the range of 500-800°C, is a subject of major importance in this field.

CeO<sub>2</sub>-based anodes exhibit excellent performance. These materials are mixed ionic/electronic conductors (MIECs) under reducing atmosphere and, therefore, fuel oxidation can take place on its entire surface, while it only occurs in the [anode/electrolyte/gas] interface (triple-phase boundaries) for electronic conductors. In recent years, our research groups investigated the performance of nanostructured CeO<sub>2</sub>-based anodes for IT-SOFCs [1-3]. Nanomaterials are not employed in conventional SOFCs since grain growth is expected to occur at the high operating temperatures of these devices. However, their use in IT-SOFCs is currently under evaluation. Anodes based on nanostructured MIECs are very interesting because the number of active sites for fuel oxidation is expected to increase dramatically.

The aim of this work was to investigate the influence of the grain size on the reducibility of NiO/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> nanocomposites under diluted hydrogen by means of the Dispersive X-ray Absorption Spectroscopy (DXAS) technique. These experiments at the Ni-K and Ce-LIII edges were carried out at the D06A-DXAS beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil).

NiO/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> nanocomposites were prepared by impregnation of commercial CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> nanopowders (Nextech Materials, USA, average crystallite size: 5 nm) with Ni nitrate. Different calcination treatments, with final temperatures between 400 and 1100°C, were used in order to prepare materials with different grain sizes. They were characterized by X-ray powder diffraction, scanning and transmission electron microscopies and temperature-programmed reduction techniques.

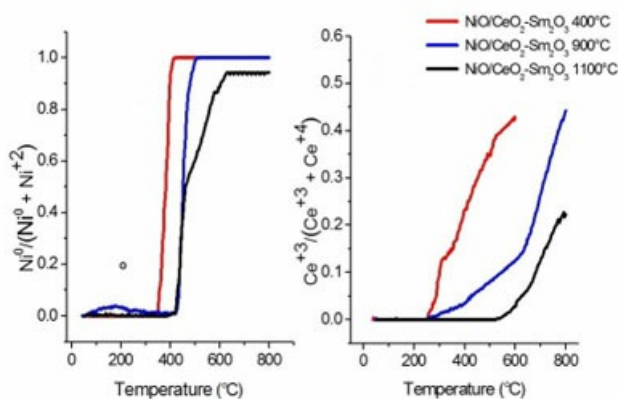
For DXAS analysis, samples were measured in the form of thin discs prepared by mixing and pressing the NiO/CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> nanopowder with boron nitride (its absorption is negligible for the energy ranges considered in this work). The disc was placed in a special sample holder inside an oven with controlled temperature. The reduction experiments were performed by heating the sample in a flow of hydrogen (5 mol%) in helium. The study was performed for temperatures up to 800°C and the heating rate was of 10°C/min. NiO and metallic Ni were used as Ni<sup>+2</sup> and Ni<sup>0</sup> standards, respectively, while Ce(III) nitrate and CeO<sub>2</sub> were used for Ce<sup>+3</sup> and Ce<sup>+4</sup>, respectively.

Our DXAS study showed that NiO reduction to metallic Ni is almost complete in diluted hydrogen for all samples, while Ce<sup>+4</sup> partially reduces to Ce<sup>+3</sup> in the same temperature range. In both cases, the reducibility strongly increases with decreasing crystallite size. The reduction process starts at lower temperature in the samples with smaller crystallite size and, in addition, the reduction rate increases with decreasing crystallite size.

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**Keywords:** [IT-SOFCs](#), [DXAS](#), [CeO<sub>2</sub>-based anodes](#)