

Nano-scale Compositional Heterogeneity in Pr-doped CeO₂

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Rare-earth doped cerias have properties which make them suitable anode materials for solid oxide fuel cells (SOFC's) [1]. The redox behavior of the anode material in an SOFC is critical for the efficient conversion of chemical energy (oxidation of hydrogen or hydrocarbons at the anode) to electrical energy. Chemical heterogeneity at the nanoscale is an inherent problem in ceria-zirconia mixed oxides and can modify the performance [2]. In-situ observations have shown that the redox behavior of these oxides depends on the heterogeneity at the atomic level. Here, we report the heterogeneity observed in Pr-doped CeO₂ anode material at the nano-scale.

Pure CeO₂ and 3% Pr-doped CeO₂ powders were synthesized by drying a 0.05M solution of Ce(NO₃)₃·6H₂O and Pr(NO₃)₃·6H₂O, in 1-3SCFM air flow at 350°C, using a home-made spray drying system. A part of the sample was calcined at 700°C in air. X-ray powder diffraction showed the resulting powder to contain nanoparticles with 7nm average diameter and a fluorite structure. High resolution imaging and electron energy-loss spectroscopy were performed using FEI-TECNAI F20 environmental TEM and JEOL 2010F microscopes, operated at 200kV. The contribution from Pr in doped oxide samples was obtained using the spectra from pure CeO₂ for calibration. All spectra were collected, under the same conditions, in diffraction mode with 1ev/channel dispersion and a 2mm spectrometer aperture size.

HREM images from pre-calcined (Figure 1a) and calcined (Figure 1b) Pr-doped CeO₂ samples show that the particle size increases after calcination. EELS spectra collected from individual grains were processed to determine the compositional heterogeneity by measuring relative intensity ratios of Pr to Ce signals. Several steps were required in the Pr background removal procedure because of the overlap between the Ce (at 890eV) and Pr (at 920 eV) signals. First, an inverse power law (AE^{-r}) was fitted to the region in front of the Ce edge and extrapolated to remove the background under both the Ce and combine Pr and Ce signals (Fig 2a). The integrated intensity over two regions of the remaining signal, a low energy window I₁ (width 10 eV) involving only the Ce signal and a higher energy window, I₂, which contained contributions from both Pr and Ce (width 30eV) was measured. Similar low and high energy integrals, I₃ and I₄, were determined for the pure ceria sample (Figure 2b). The Pr signal I_{Pr} can then be determined from $I_{Pr} = I_2 - \alpha I_1$ where $\alpha = I_4/I_3$. The best internal consistency was achieved by not including the Ce white lines in the low energy window. Higher variation in the distribution of Pr was observed in the pre-calcined sample (Figure 3a) compared to the calcined sample (Figure 3(b)). It can be concluded that the samples became more homogeneous after calcination. In situ measurements will be used to correlate local composition of the individual particles to their redox property.

References:

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[2] Ruigang Wang, P.A. Crozier, Renu Sharma, James B. Adams, *Journal of Physical Chemistry B*, 2006. **110**: p. 18278-18285.

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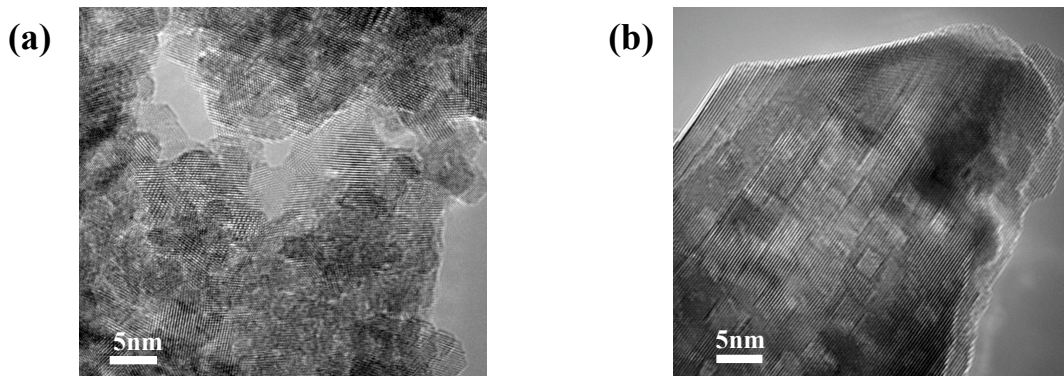


Fig.1. Typical HREM images recorded from (a) pre-calcined and (b) post-calcined (700°C) Pr-doped CeO₂ sample showing an increase in particle size after calcination.

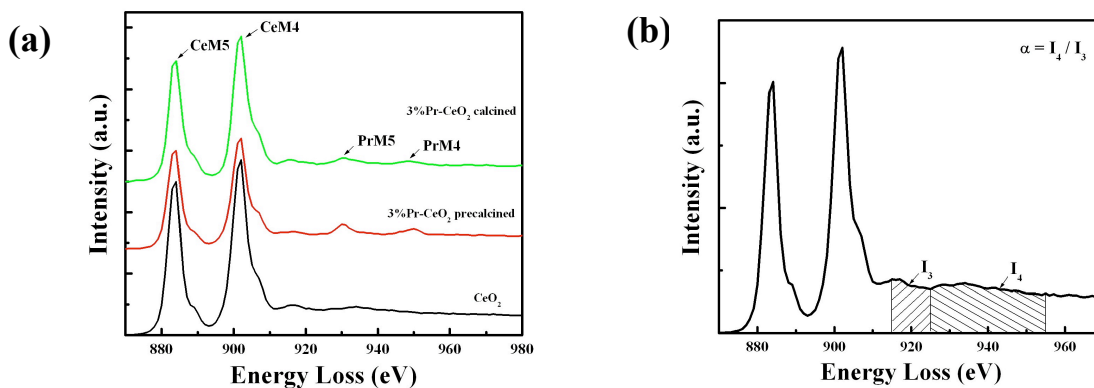


Fig.2. (a) EELS spectra from individual particles of pure CeO₂, precalcined and calcined Pr-doped samples respectively, (b) energy windows used to obtain intensity ratios.

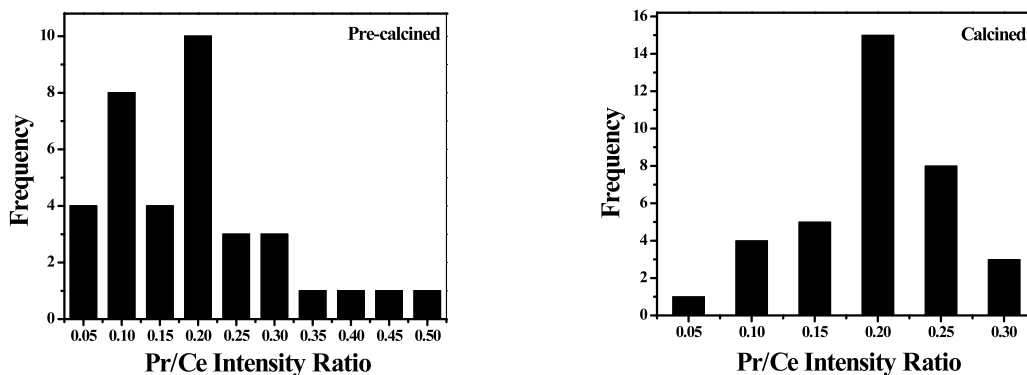


Fig.3. (a) Pr/Ce intensity ratio in individual particles from (a) pre-calcined and (b) post-calcined sample.