Electron-beam damage and point defects near grain boundaries in cerium oxide

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Abstract

Cerium oxide is a technologically important ceramic with applications in catalysis and potentially as an electrolyte for solid-oxide fuel cells (SOFCs). The technological interest is largely due to the behavior of oxygen vacancies in this material. Grain boundaries play an important role in oxygen vacancy diffusion and, although not completely understood, the influence of grain boundaries has been attributed to both a space-charge effect and the segregation of impurities. In this paper, results from spatially resolved electron-energy-loss spectroscopy (EELS) near grain boundaries in doped CeO_2 in a transmission electron microscope (TEM) are reported. The data are interpreted as the result of beam damage that varies as the electron beam is scanned across grain boundaries and suggest a spatially varying concentration of oxygen vacancies near the grain boundaries.

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1. Introduction

Grain boundaries in solid-oxide electrolytes play an important role in the oxygen conductivity of the bulk material. Grain boundaries can be preferential locations for precipitates and can reduce the oxygen conductivity due to the presence of grain-boundary space-charge layers. It has been shown that for CeO_2 the presence of thick siliceous layers can account for the overwhelming majority of the oxygen ionic resistance,[1] but that even without siliceous impurities the grain boundaries still contribute a significant fraction of the ionic resistance.[2] Controlling the grain-boundary properties has been proposed as a method of improving the ionic conductivity of CeO_2 electrolytes.[3] In addition, the sintering behavior also strongly depends on the grain-boundary behavior. More generally, interfacial segregation and its influence on macroscale properties is an important problem for many ceramic materials[4] and in the case of CeO_2, a greater understanding of interfaces should enable improved performance for SOFCs and catalysts, where the interaction of oxygen vacancies and surfaces is critical.[5]

In CeO_2 polycrystals with low levels of Si impurities, the effect of grain boundaries on the oxygen conductivity has been attributed to the grain-boundary space charge.[2,6,7] At the grain boundary, the segregation of positively charged oxygen vacancies creates a charged boundary region; this charge is balanced in the crystal by the formation of neighboring regions of negative charge. These negatively charged space-charge layers are depleted in oxygen vacancies and enriched in defects such as Ce^{3+} ions or trivalent dopants (provided they are mobile). Because oxygen vacancies are the mobile defects necessary for oxygen conduction, the local depletion of vacancies will reduce the oxygen conductivity across the grain boundary. Alternatively, negatively charged substitutional defects from a high level of trivalent cation doping can segregate to the grain boundary and cause a negative charge which

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is balanced in the space-charge layer by a depletion of oxygen vacancies.

Several TEM studies of grain boundaries in CeO_2 have been performed, examining both structural and chemical features.[8,9] Particularly useful is the technique of electron-energy-loss spectroscopy (EELS) performed in scanning transmission electron microscopy (STEM) mode;[10] both composition and chemical-bonding information can be obtained at high spatial resolution. The Ce $M_{4,5}$ edge can be used to quantitatively measure the oxidation state of the Ce ions.[11,12]

In previous work STEM-EELS was used by Lei et al. to study grain boundaries in a polycrystalline CeO_2 doped with 20 mol% Gd.[9] Lei et al. measured simultaneous depletion in O, enrichment in Gd, and an increased fraction of reduced Ce ions at a grain boundary. In the same report, they also described STEM-EELS results on a c-ZrO_2 bicrystal stabilized with Y. They observed changes in the fine structure at the Zr M edge indicating increased electron density at the grain boundary; a decrease in the O concentration was also deduced from the EELS. At grain boundaries in two fluorite-structured oxides, the authors identified segregation of O vacancies, 3+ dopant ions and electrons (i.e., Ce^{3+} ions in the case of CeO_2). They did not directly observe any space-charge effect, i.e., depletion of charge carriers next to the grain boundary was not reported. This result could have been due to the very small concentration of defects.

STEM-EELS analysis of grain boundaries in both cubic and tetragonal Y-doped ZrO_2 by Backhaus-Ricoult and colleagues revealed segregation of various rare-earth and transition-metal dopants.[13] In the same work they reported evidence of a space-charge layer next to the grain boundaries, revealed by changes in the O K edge intensity and near-edge structure. The width of the space-charge layers was 3–5 nm.

Zhang et al.[14] investigated grain boundary chemistry in a polycrystal of Gd-doped CeO_2 that was also doped with Co. They also observed changes in the fine structure at the Ce M edge that indicated an increase in the fraction of Ce^{3+} at the grain boundary and O K edge changes that are consistent with increased oxygen vacancies at grain boundaries. From energy-filtering TEM (EFTEM) analyses combined with diffraction patterns, Zhang et al. identified Co precipitation in the form of either Co_3O_4 or CoO, depending on the temperature of heat treatment. Co segregation to GBs was also observed.

Although no grain boundaries were studied, the work of Gilliss et al.[12] is relevant as it describes EELS analysis of surfaces of CeO_2 particles with various impurities. Gilliss et al. performed STEM-EELS investigations on CeO_2 powders that contained La impurities and showed that the Ce charge state at the particle surfaces was significantly reduced while La simultaneously segregated to the surfaces.

Several other research groups have also investigated reduction at surfaces of CeO_2 particles, especially for nanoparticles. Wu et al.[15] combined HRTEM and EELS to measure deviations in lattice parameter and the oxidation state of Ce as a function of particle size. Consistent with measurements from other techniques, the authors showed that the lattice parameter increases with smaller particle sizes and that smaller particles are reduced. Nanoparticles of diameter as small as ∼3 nm were studied; these

particles were determined to be $CeO_{1.5}$ (i.e., Ce_2O_3). Spatially resolved EELS was used to study the same batch of nanoparticles and the authors reported that the surfaces were significantly reduced, but when the electron beam was in the center of the particle the Ce M edge ELNES indicated Ce^{4+} ions were the main species. Although the lattice parameter data from HRTEM showed significant scatter, the results were not inconsistent with a structural model of the particles that assumed a shell of reduced Ce_2O_3 material and an oxidized core. The dimensions of the reduced shell were deduced from the EELS data.

Recently, Turner et al.[16] studied cerium oxide particles using atomically resolved STEM-EELS in a monochromated and aberration-corrected STEM. They combined high-resolution spectrum imaging with model-based quantification to determine the spatial distribution of reduced cerium ions. Confirming earlier results,[15] the particles had reduced surfaces and the smaller particles (∼5 nm or smaller) appeared to be fully reduced. Their results also showed that, when imaging down the ⟨1 1 1⟩ zone axis, the first atomic layer at the surface was fully reduced to Ce^{3+} and the second and third layers were partially reduced. The spatial extent of reduction was dependent on the crystallographic orientation of the particle surface. A key result relevant to the current work is that the reduction can be highly localized (the first few atomic layers), although it is still an open question as to how surface reduction relates to reduction at grain boundaries.

X-ray diffraction and X-ray photoelectron spectroscopy (XPS) have also been used to study the variation in lattice parameter and oxidation state by a number of researchers.[17,18] The results consistently show an increase in the lattice parameter and a reduction of the Ce ion to the 3+ state as the particle size decreases.

Avila-Paredes and Kim[3] also studied CeO_2 polycrystals that had been doped with both Gd and Fe using STEM-EELS. However, they did not analyze the Ce M or O K edge ELNES features to identify any changes in oxidation state near grain boundaries. They did identify Fe- and Si-rich phases at triple junctions, but no segregation of any elements to the grain boundaries. They also did not detect any amorphous phases at the grain boundaries using HRTEM. These authors performed impedance spectroscopy on specimens with Cu, Mn, Co and Fe dopants in addition to the Gd. Their results showed lower grain-boundary resistivities for Co and Fe dopants and lower oxygen conductivity activation energies. They interpreted these results as showing that the grain-boundary electrostatic potential was considerably lower for Co and Fe dopants. They attributed these observations to the Fe and Co segregating to the grain boundary and thereby reducing the positive grain-boundary charge, similar to a suggestion from Guo[19] for using segregation to reduce the grain-boundary resistivity. They did not detect Fe segregation to the boundaries, however, and suggested that the Fe content was below the detection limits.

Jasper et al.[8] combined structural characterization of boundaries using HRTEM with impedance spectroscopy for a set of CeO_2 polycrystals with different concentrations of Gd and trace impurities. They studied polycrystals with the same nominal Gd content (10 at%) from three different commercial suppliers and