

Electron Trapping Sites Near Oxygen Vacancies in Stabilized Zirconia

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Defects structures due to oxygen vacancies in stabilized zirconia are analyzed focusing on their electron trapping power under reducing conditions: the electrons released during reduction reactions give rise to electronic centers which immobilize the oxygen vacancies involved in the defects. The effective decrease of the migrating oxygen vacancies caused by this process may affect the ionic conductivity of the material. Thermal stability and dependence on yttria concentration of these defect complexes, investigated by means of electron paramagnetic resonance spectroscopy, are reviewed to determine composition and possible regeneration treatments which minimize the number of these electronic centers.

1. Introduction

Y-stabilized ZrO_2 is used extensively for electrochemical sensors.⁽¹⁾ As with other oxygen sensors, its relevant features depend mainly on bulk properties: the stabilization of the cubic phase achieved by the introduction of trivalent Y^{3+} ions induces in the material a high concentration of oxygen vacancies which allow the ionic conduction of O^{2-} ions from one vacancy to another. The physical and chemical processes which take place may be very complex, involving the motion and the redistribution of ionic and electronic carriers in the solid. Moreover, the concentration of oxygen vacancies may change under the conditions of a reducing atmosphere at high temperatures.⁽²⁾ In this case, electronic carriers resulting from the reduction reaction may be trapped, forming very stable defect com-

plexes comprising oxygen vacancies, which partially immobilize a fraction of anionic carriers.⁽³⁾

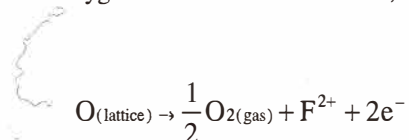
Several works have been devoted to the structural characterization of these types of defect and their energy level structure.⁽³⁻¹⁴⁾ Crystalline samples have been investigated to obtain detailed defect-structure information and to enable optical analysis of the electronic transitions between defect states. A variety of defect complexes has been identified, giving an idea of the possible environments of oxygen vacancies which may constitute electron traps. Electron paramagnetic resonance (EPR) measurements provide evidence that the main defect (named T center from its trigonal axial symmetry) should consist of two oxygen vacancies along a $\langle 111 \rangle$ direction at the sides of a Zr^{3+} ion arising from the trapping of an electron.⁽¹⁰⁾ This type of defect represents an electron trap constituted by sixfold-coordinated zirconium ion. In contrast, no evidence has been shown for electrons trapped at sevenfold-coordinated zirconium ions. This may be an indirect confirmation of the recently proposed sevenfold coordination of cations in the structure of stabilized zirconia since, in this case, the sevenfold-coordinated sites should not appear as electron traps.^(15, 16) Other types of defects seem to be associated with electron trapping in anionic vacancy sites as F- or F⁺-like color centers. The paramagnetic variant of this type of center should arise from high symmetry sites, indicating the absence of trivalent yttrium ions as nearest neighbors of the oxygen vacancies, with the oxygen vacancy surrounded by four Zr^{4+} ions. In fact, the F⁺ centers are associated with an isotropic EPR signal without hyperfine structure due to the $I = 1/2$ nuclear spin of yttrium. The F center should be diamagnetic, but its optical absorption features seem to be in the near UV region.

T- and F-like defects constitute the final states of the sites within the oxygen vacancy reservoir which may be filled by electrons if reduction processes take place. All these defects, together with their EPR and optical spectral features, appear to be effective probes of the association among oxygen vacancy sites and of the rearrangement of the anionic sublattice around the oxygen vacancies. By looking for these centers it is possible to verify, in specific cases, the expected abundance of particular types of oxygen vacancy associations and to determine indirectly the presence of unexpected effects, such as segregated components and clusters,⁽¹⁷⁾ or ordered regions.⁽¹⁴⁾ In fact, the analysis of the EPR defects in sintered tetragonal yttria-zirconia polycrystals enabled identification of oxygen vacancy sites inside unwanted yttria aggregates, while the absence of the EPR signal attributed to sixfold-coordinated Zr^{3+} ions confirmed an oxygen vacancy concentration lower than that expected in the zirconia structure. Similarly, in single crystals of cubic stabilized zirconia, the observed densities of paramagnetic vacancy centers (T and F⁺ centers), obtained by scaling differently from those predicted for a random distribution of oxygen vacancies in different stoichiometries, suggested the presence of ordered sequences of vacancies (charge compensated by yttrium ions) with no significant electron trapping power. Here we will consider the analysis of the defect creation yield and thermal stability as tools for the identification of the stoichiometry and/or regeneration annealing processes which minimize the content of these electronic centers.

2. Defect Creation Process

Different types of treatment (such as chemical reduction, electrodiffusion, X-ray irradiation, UV laser exposure) may create electron centers associated with oxygen vacancies. Typical reducing treatments consist of annealing at 950°C for 3 h in a flowing mixture of argon with 5% H₂ after a stepwise heating for 2 h, followed by a quick cooling to room temperature, all of which were conducted in reducing atmosphere. High-efficiency electrochemical reduction may be achieved at lower temperatures (about 600°C) in flowing nitrogen with less than 1 ppm of O₂ by applying an electric potential difference of 8–10 V for a few hours (*e.g.*, 4 h). The total charge migrated in the sample during such treatments ranges from less than 2 C to more than 20 C. While nearly homogeneous modifications of samples are observed (from optical measurements) with high-temperature reductions, electroreduced samples are characterized by a sharp defect gradient on the advancing front of the reducing process. Ionizing radiation treatments are characterized by low efficiency depending on the penetration depth of the radiation: 50 μm for X-rays from a W-target tube with an electron current of 20 mA at 38 kV, and about 0.2 mm for an excimer laser beam with λ = 308 nm.

We note that ionizing radiation does not cause atomic displacements in the crystal structures, rather, it generates electron-hole pairs which may recombine or become trapped. The EPR signal from trapped hole centers has indeed been observed after X-ray irradiation, but it decays at room temperature in about 24 h. In contrast, reducing treatments at high temperature create both oxygen vacancies and electrons, but no holes, according to the reaction:



where the electrons may be trapped giving rise to T- and F-like centers. We note that, while the center density is nearly a function of the dose alone in irradiated samples (it is weakly affected by changes in the oxygen vacancy concentrations⁽¹⁴⁾), it is strongly dependent on the composition in chemically treated samples:⁽³⁾ in fact, in the latter case, the number of trapped electrons is related to the number of oxygen atoms released during the reducing reaction, which decreases by increasing the stabilizing oxide concentration. The reducing reaction is indeed driven by ionic diffusion processes which, as with other transport properties of oxygen ion conductors, decrease above a critical value of oxygen vacancy density.⁽²⁾ Therefore, a heavily stabilized material is shown to possibly prevent the formation of electron trapping sites.

3. Defect Stability

The paramagnetic center stability has been studied by means of isochronal and isothermal pulsed annealings in samples with different compositions, and subjected to different

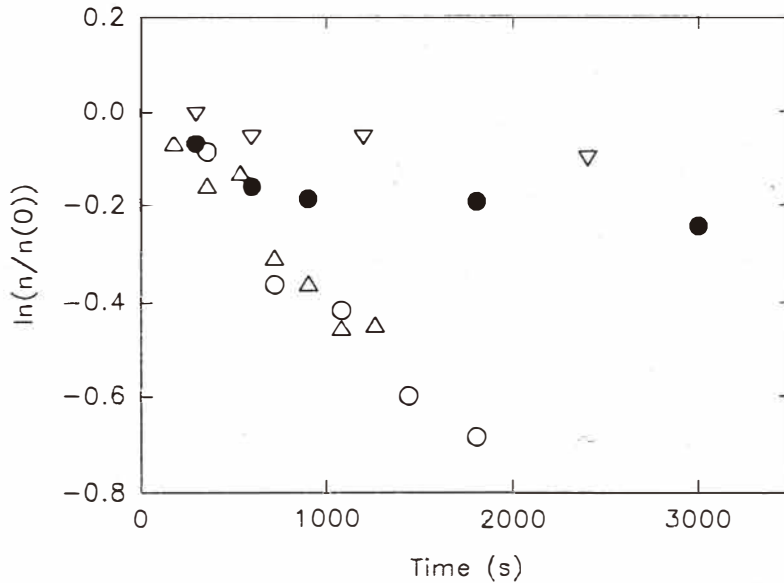


Fig. 1. Isothermal decay of T centers in X-ray irradiated (○) or reduced (●) 12% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and in X-ray irradiated (△) or reduced (▽) 24% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ at $T = 200^\circ\text{C}$.

treatments. In Fig. 1 pulsed annealing data of the T-center population in 12% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and 24% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ are reported in the case of $T = 200^\circ\text{C}$. The decay of T-centers created in a reducing atmosphere differs markedly from that observed in samples exposed to ionizing radiation. From an analysis of these measurements, the high stability of T centers created by reducing reactions appears not to be due to a higher detrapping energy with respect to the radiation-induced centers, but to a low density of the available empty traps constituted by the precursors of the paramagnetic and optical centers. In fact, the reducing reactions show a higher efficiency in filling oxygen vacancies with several types of electronic occupation with respect to ionizing radiation and no electronic hole is associated with the electrons arising from the chemical reaction.⁽⁷⁾ Thus, the annihilation process of reduction-created centers can efficiently take place only with oxidation at relatively high temperatures (higher than 600°C , where radiation-induced centers are completely annihilated). It is noteworthy that the annihilation kinetics of radiation-induced centers are similar in differently stabilized materials, but they differ for centers created by chemical reducing reaction, and also in the low-temperature range where oxidation processes are negligible. Since this type of difference seems to be due to different densities of empty traps,⁽⁷⁾ one can deduce from Fig. 1 that the higher the vacancy density, the fewer the empty traps.

This is not surprising, since high densities of stabilizing Y_2O_3 force the vacancies to associate with two yttrium ions (or to create oxygen vacancy superlattices in the case of a

single crystal), forming neutral sites which are not effective electron traps. This result should be considered in determining the optimum conditions, in minimizing the formation of electron trapping sites and in choosing the possible regeneration treatments in order to reduce the number of these centers; once again, high degrees of stabilization seem effective for inducing defect-damage hardness. In contrast, extended annealing time (or annealing at high temperatures) is necessary to oxidize the existing defects for material containing a low concentration of Y_2O_3 stabilizing oxide.

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