

Viewpoint Paper

Can we achieve significantly higher ionic conductivity in nanostructured zirconia?

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Abstract—Works on nanostructured ZrO_2 , including nanocrystalline ceramics, polycrystalline and epitaxial thin films, and heterostructures, are evaluated. Lower total conductivity has been achieved for nanocrystalline ceramics and polycrystalline thin films. Higher conductivity was reported for epitaxial films, but this might be an artefact of the substrate. The colossal ionic conductivity that was claimed for heterostructures has now been demonstrated to be electronic in origin. However, distinctively different properties may appear in ZrO_2 for grain sizes <5 nm.

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1. Introduction

ZrO_2 stabilized by, for example, Y_2O_3 , Sc_2O_3 or CaO is a pure ionic conductor, with oxygen vacancies being the charge carriers. The ionic conductivity of ZrO_2 is of prime importance in its role as the working electrolyte in solid oxide fuel cells (SOFCs) [1]. Owing to the relatively low mobility of oxygen vacancies, the ionic conductivity of ZrO_2 is small at low to intermediate temperatures; therefore, there is continued interest in enhancing the ionic conductivity of this material. Unlike electronic conductivity, which can be enhanced by orders of magnitude simply by increasing the electron or hole concentration, there exists a maximum ionic conductivity corresponding to an optimal vacancy concentration [2], such that increasing the vacancy concentration above the optimal value results in a decrease in ionic conductivity.

Decreasing the feature size (grain size or film thickness) from the micrometer to the nanometer scale usually results in a remarkable change in the transport properties of materials. In comparison with their microstructured counterparts, the most remarkable characteristic of nanostructured materials is the high interfacial density. This leads to two nano-effects [3–6]: the trivial size effect and the true size effect. The trivial size effect

is defined as the increased contribution of the interfacial properties to the overall materials properties, as a result of the increased interface to bulk fraction. When the spacing of interfaces becomes comparable with the Debye length, local properties change as a function of distance and the true size effect occurs. The CaF_2/BaF_2 heterolayer best embodies the true size effect [7]. The ionic conductivity of the CaF_2/BaF_2 heterolayer increases by two orders of magnitude when the heterolayer period (CaF_2 plus BaF_2 unit layer) decreases from 500 to 16 nm, because the neighboring space-charge layers overlap and the individual layers lose their bulk properties at a period of 16 nm. An important implication of this finding is that the materials properties can be tuned by varying the spacing of interfaces. In this context a fascinating question emerges: is it possible to achieve significantly higher ionic conductivity in nanostructured ZrO_2 ? In this work, up-to-date works on the ionic conductivity of nanostructured ZrO_2 bulk ceramics, thin films and heterostructures are evaluated, in order to find an answer to this question.

2. Ionic conduction in microcrystalline ZrO_2

Factors affecting ionic conductivity in microcrystalline ZrO_2 have been extensively reviewed and a conduction model has been established [8]; two key points are summarized in the following, and serve as a basis for understanding the behaviors of nanostructured ZrO_2 :

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(1) The grain-boundary core (i.e. the crystallographic mismatch zone between two grains) in stabilized-ZrO₂ is positively charged [9]; the enrichment of oxygen vacancies in the grain-boundary core is responsible for the positive potential [10,11]. The grain-boundary core expels oxygen vacancies, causing oxygen-vacancy depletion in the adjacent space-charge layers. The oxygen-vacancy concentration is described by [8,19]:

$$\frac{c_{V_o^{\bullet\bullet}}(x)}{c_{V_o^{\bullet\bullet}}(\infty)} = \exp \left[-\frac{1}{2} \left(\frac{x - \lambda^*}{L_D} \right)^2 \right] \quad (1)$$

For $x \geq \lambda^*$, $c_{V_o^{\bullet\bullet}}(x)/c_{V_o^{\bullet\bullet}}(\infty) = 1$. In Eq. (1), L_D is the Debye length, and λ^* the width of a space-charge layer. A typical λ^* value in stabilized-ZrO₂ is ~ 2.5 nm [12, 19,25]. The normalized oxygen-vacancy concentration, $c_{V_o^{\bullet\bullet}}(x)/c_{V_o^{\bullet\bullet}}(\infty)$, in the space-charge layer of 8 mol.% Y₂O₃-stabilized ZrO₂ (YSZ) at 500 °C, calculated from Eq. (1), is shown in Figure 1: oxygen vacancies are depleted by more than three orders of magnitude in the space-charge layer. The specific grain-boundary conductivity of stabilized-ZrO₂ is at least two orders of magnitude lower than the bulk conductivity [12–18]; oxygen-vacancy depletion in the space-charge layer is the physical origin of the low grain-boundary conductivity [19–25].

(2) The vacancy depletion gives rise to a back-to-back double Schottky barrier. The grain-boundary conductivity resulting from the Schottky barrier is given by [8,19]:

$$\frac{\sigma_{bulk}}{\sigma_{gb}} = \frac{\exp(2e\Delta\phi(0)/k_B T)}{4e\Delta\phi(0)/k_B T}, \quad (2)$$

and the activation energy for the grain-boundary conductivity, E_a^{gb} , by [8,19]:

$$E_a^{gb} - E_a^{bulk} = (2e\Delta\phi(0) - k_B T) \left[1 + \frac{1}{T\Delta\phi(0)} \frac{d\Delta\phi(0)}{d(1/T)} \right] \quad (3)$$

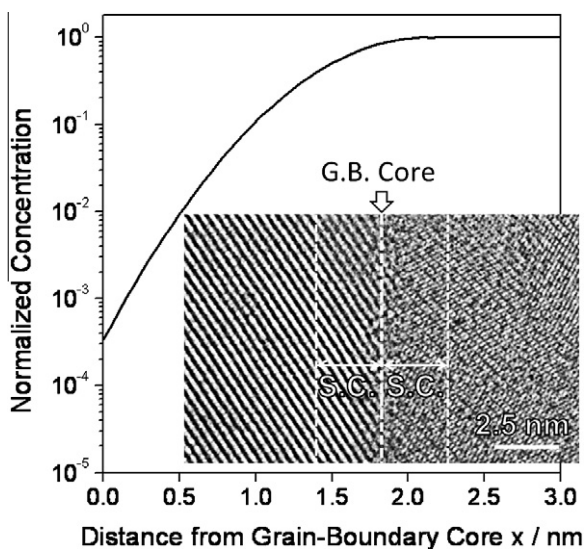


Figure 1. Normalized oxygen-vacancy concentration, $c_{V_o^{\bullet\bullet}}(x)/c_{V_o^{\bullet\bullet}}(\infty)$, in the space-charge layer of 8 mol.% Y₂O₃-stabilized ZrO₂ at 500 °C (SC: space-charge layer; GB: grain boundary) [19]. The inset is a high-resolution transmission electron microscopy image (HRTEM) of a grain boundary, showing a grain-boundary core and two adjacent space-charge layers.

As the bulk activation energy, E_a^{bulk} , is independent of $\Delta\phi(0)$, E_a^{gb} is determined by the Schottky barrier height. In Eqs. (2) and (3), $\Delta\phi(0)$ is the Schottky barrier height, σ_{bulk} the bulk conductivity, σ_{gb} the grain-boundary conductivity, e the elementary charge, k_B the Boltzmann constant and T the absolute temperature.

3. Ionic conduction in nanostructured ZrO₂

Nanostructured materials, in general, include bulk materials with nanometer-sized grains, thin films and heterostructures with nanoscale thicknesses. In the case of thin films, the very large surface/volume ratio makes such films vulnerable to the influence of ubiquitous water vapor, and the film–substrate interface also complicates the situation. Therefore, it is generally accepted that one can derive more reliable data from bulk materials than from thin films. In this section, ionic conductivity in bulk ZrO₂ is firstly analyzed.

3.1. Bulk ceramics: effect of decreasing grain size

As already mentioned, the oxygen-vacancy concentration in the grain-boundary core is higher [10,11]; it is therefore reasonable to expect that the transport of oxygen vacancies along the grain-boundary core might be faster: the ionic current could then flow exclusively along the core, short-circuiting the material. If this is the case, one could achieve significantly higher ionic conductivity in nanocrystalline ZrO₂. De Souza et al. [26] addressed this hypothesis by investigating ¹⁸O diffusion in 8 mol.% Y₂O₃-stabilized ZrO₂ with an average grain size of ~ 50 nm. Comparing with the tracer diffusion coefficient obtained for the nanocrystalline sample indicates that the grain boundaries actually hinder oxygen transport. Conclusive evidence was recently provided by Kim et al. [27], who demonstrated that oxygen vacancies in the surface region are nearly immobile even at temperatures as high as 600 °C, and that the fraction of immobile oxygen vacancies progressively increases with decreasing crystallite size. In view of the structure similarity between the surface region and the grain-boundary core, one can be confident that the oxygen vacancies in the grain-boundary core are also immobile. The accelerated ionic transport along the grain-boundary core in nanocrystalline ZrO₂ can thus be ruled out.

When the grain size decreases from the micrometer to the nanometer scale, the nano-effect appears. To illustrate the effect of decreasing grain size, the bulk conductivity, σ_{bulk} , and the specific grain-boundary conductivity, σ_{gb}^{sp} , for 3 mol.% Y₂O₃-stabilized ZrO₂ at 550 °C are compiled in Figure 2 as a function grain size [28], covering a grain size range of 41–1330 nm. Data for the 41 nm grain sample are taken from 2.9 mol.% Y₂O₃-stabilized ZrO₂ [29]. The relative densities of the samples are all above 94%. As shown in Figure 2, σ_{bulk} decreases but σ_{gb}^{sp} increases with decreasing grain size, but even for the finest grain size (41 nm) the specific grain-boundary conductivity remains more than one order of magnitude lower than the bulk conductivity. In addition, the total conductivity is lower when the grain size decreases to 41 nm.

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