



# Protons in cubic yttria-stabilized zirconia: Binding sites and migration pathways

A.G. Marinopoulos

CFisUC, Department of Physics, University of Coimbra, Coimbra P-3004-516, Portugal



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## ABSTRACT

Despite the fact that unusually high power generation attributed to proton conduction has been reported recently for nanostructured yttria-stabilized zirconia (YSZ) little is known about the atomistic mechanisms of proton transport and corresponding activation energies, namely the factors that dictate proton mobility. Important issues to be examined include the energetics of proton incorporation in the YSZ host, the binding of protons to intrinsic structural defects and the role of grain boundaries in proton conduction. The present study reports calculations based on density-functional theory (DFT) of defect-formation energies and energy barriers for proton migration in cubic YSZ for an yttria doping in the 10–12 mol% range. For the bulk-crystalline lattice representative migration pathways are identified and the corresponding energy barriers for proton migration are calculated using the nudged elastic-band method. The feasibility for the grain boundaries to act as fast diffusion pathways for protons is also examined. For the high-angle  $\Sigma 5(310)$  grain boundary DFT calculations were undertaken so as to determine the segregation propensity of protons as well as the magnitude of energy barriers for selected proton migration pathways at the core of this extended defect. The present calculations outline the importance of oxygen vacancies for proton migration in the bulk crystal and the ability of localized cation clusters at the grain-boundary core to act as strong obstacles to proton motion.

## 1. Introduction

Zirconia is an oxide with extensive applications in the ceramics technology [1]. It is routinely used as a thermal-barrier coating [2] and is an integral part in oxygen-sensor and abrasive components [3]. Zirconia is also commonly employed in its cubic phase as the solid electrolyte in fuel-cell technology and related applications in electrochemistry [4,5]. In these cases the cubic phase of zirconia is stabilized at lower temperatures by suitable aliovalent doping with metal oxides. The stabilization mechanism entails the formation of oxygen vacancies in the anion sublattice as charge-compensating defects [6]. Yttria-stabilized cubic zirconia (YSZ), in particular, is the zirconia-yttria solid solution most widely used in solid-oxide fuel cells owing to exceptional mechanical and chemical stabilities and high ionic conductivity.

Recent experimental studies initiated a strong interest in dense nanostructured YSZ as a proton conductor in solid-oxide fuel cells at low and intermediate temperatures [7–11]. Observations of the proton conductivity rapidly rising with decreasing grain size in nanostructured YSZ samples led to propositions that grain boundaries (GBs) are highly conductive paths for proton transport [8,11]. Other studies, however, contested such a point of view. Proton conduction was not observed through GBs in nanostructured YSZ [12]; instead it was found to mainly

take place through the inner surface areas of the YSZ porous material [12]. Surface proton conduction was also documented to be much larger with respect to conduction in the bulk interior of YSZ or its internal GBs [13,14].

These findings present a serious challenge for computational methodologies. Clearly, there is a need to have a consistent view of the proton-migration processes at the atomic level for both the bulk-crystalline phase and the GBs of YSZ. GBs are intrinsic extended defects within polycrystalline and nanocrystalline YSZ and it is vital to understand their role. The question is whether these defects are trapping regions for the protons, thus impeding their motion or, alternatively, whether they are fast-conduction pathways making proton migration easier.

The presence of protons dissolved in oxides has been well known since the early work by Stotz and Wagner [15]. Wagner [16] also studied the hydrogen solubility and diffusivity in zirconia-yttria solid solutions at 900 °C and 1000 °C. The corresponding solubility was found to be proportional to the square root of the water partial pressure. The mole fraction of the protons in the oxide was determined to be about  $2 \times 10^{-4}$  at 1000 °C and 1 atm of H<sub>2</sub>O vapor. More recently, hydrogen configurations in YSZ have been studied by means of muonium spectroscopy [17,18] and first-principles approaches [19] based on density-

E-mail address: [marinop@teor.fis.uc.pt](mailto:marinop@teor.fis.uc.pt).

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functional theory (DFT) [20,21]. Hydrogen in its positively-charged state  $H^+$  (namely the proton defect) adopted exclusively hydroxide O-H configurations with the proton forming a short dative bond with the oxygen ions. From the calculated charge-transition levels it was deduced that hydrogen is a deep donor and an amphoteric impurity in YSZ with the pinning level,  $E(+/-)$ , positioned in the upper part of the band gap [19].

Proton transport in oxides is known to be accomplished through two distinct mechanisms [22,23]. First, via proton transfer whereby a proton initially bound to an oxygen ion hops to a neighboring oxygen ion forming a new O-H configuration. Secondly, via rotational diffusion of the protonic defect accomplished through a reorientation of the O-H bond. This mechanism does not contribute directly to macroscopic diffusion since the proton remains bound to the same oxygen ion. Theoretical calculations of proton migration in crystalline phases of zirconia have been rare. For the monoclinic phase first-principles molecular dynamics calculations [24] showed that proton motion at lower temperatures is exclusively of the reorientation type. Proton hopping between neighboring oxygen ions was observed at higher temperatures (990 K) and an activation energy of 0.32 eV for individual proton jumps was deduced [24]. DFT-based metadynamics calculations [25] were also employed to study proton-diffusion events and trajectories in tetragonal zirconia at 1500 K. For the cubic phase first-principles calculations of proton-migration barriers were only recently performed [26] and were restricted to the ideal fluorite structure, with an yttrium atom introduced substitutionally in the cation sublattice. The obtained energy barriers were mostly in the range from 0.32 to 0.42 eV for selected proton diffusive jumps along certain prescribed pathways in the lattice.

Despite this initial progress at the atomistic level, important aspects of proton migration in YSZ are still unresolved: foremost of all the effect of oxygen vacancies to proton migration and secondly the magnitude of the reorientation step. Oxygen vacancies, in particular, are intrinsic structural defects of the equilibrium cubic YSZ phase and their effect on proton transport needs to be taken into account. The aim in the present study was to determine the relevant energetics of proton incorporation, the preferred binding sites of protons and the magnitude of their migration barriers in cubic YSZ from first principles. Similarly to earlier studies [19,27–32] YSZ was structurally modeled by special quasi-random structures simulating a stable zirconia-yttria solid solution with a 10.3 mol%  $Y_2O_3$  doping. Representative migration paths for the proton were identified and the corresponding energy barriers were determined. The impact of the intrinsic structure of YSZ, in particular of the oxygen vacancies and local ionic environment and coordination was examined and discussed.

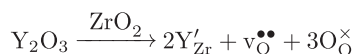
In order to assess the relevance of GBs in proton conduction further calculations were also performed. The aim in this case was to determine the segregation propensity of the protons at the core region of a high-angle GB in this oxide and also to determine the magnitude of the energy barriers for proton migration. The  $\Sigma 5(310)$  GB was chosen for this purpose. This is a high-energy interface which has been frequently studied in the past experimentally by high-resolution electron microscopy and Z-contrast imaging [33] and theoretically by empirical [34,35] and first-principles [36–38] approaches. These studies resolved important structural patterns of the interfacial structure of this GB, in particular, the symmetry and projection of the cation sublattice along the [001] axis and the interface-plane termination.

## 2. Theoretical background and preliminaries

The calculations in the present study were based on spin-polarized DFT [20,21] within the generalized-gradient approximation (GGA) for exchange and correlation, and the projector-augmented wave (PAW) method [39,40]. More specifically the semilocal PBE (proposed by Perdew, Burke and Ernzerhof) functional [41] was used. For this purpose, the corresponding implementations of the VASP code [42–44] were employed. The crystalline wavefunctions were expanded in a

plane-wave basis limited by a cutoff energy of 470 eV. For both zirconium and yttrium atoms the semicore  $4s$  and  $4p$  electrons were included in the valence states. For the defect calculations, a Monkhorst–Pack [45]  $2 \times 2 \times 2$  k-point mesh was chosen for the Brillouin-zone integrations.

The bulk-crystalline YSZ cubic phase was modeled by 96-atom quasi-random supercells with a lattice parameter twice as large as that of the primitive fluorite cell. The calculated magnitude for the latter ( $a_{\text{latt}}$ ) was equal to 5.149 Å after energy minimization with the PBE functional. An yttria doping of 10.3 mol% was achieved by a suitable incorporation of yttria units in the ideal fluorite lattice. In the present case, six yttrium atoms were introduced substitutionally at random sites of the cation sublattice. These defects (denoted as  $Y'_{\text{Zr}}$  in Kröger-Vink notation) are negatively charged. Therefore, three oxygen vacancies were also created as charge-compensating defects of positive effective charge ( $v_{\text{O}}^{\bullet\bullet}$ ). The incorporation reaction in Kröger-Vink notation is the following:



with  $O_{\text{O}}^{\times}$  denoting oxygen atoms at normal lattice sites.

Similarly to earlier atomistic calculations of YSZ [27–32] a number of different supercells were constructed starting with various vacancy-vacancy distances and different vacancy-yttrium associations. Fifteen distinct supercells were finally obtained following energy minimization (see the Appendix). The lowest-energy supercell was then taken in order to perform the defect calculations. In this supercell the closest-spaced oxygen vacancies were fifth-nearest neighbors.

For the GB calculations the high-angle  $\Sigma 5(310)$  tilt GB was chosen. This is a high-energy interface with short in-plane periodicities and with the rotation (tilt) axis parallel to the [001] direction. A supercell of orthorhombic shape was constructed using periodic boundary conditions containing two equivalent GBs of alternating misorientations and totalling 228 atoms. The size of the supercell along the interface-normal vector was sufficiently large (equal to  $2\sqrt{10} a_{\text{latt}}$ ) to minimize spurious interactions between the two GBs. Yttria units were introduced corresponding to 11.3 mol% doping, thus approaching as close as possible the doping magnitude of the bulk-crystalline supercells. The incorporation of these units was done on a plane-by-plane basis ensuring a uniform distribution of yttrium atoms and oxygen vacancies in the whole supercell [38].

The formation energies,  $\Delta E_{\text{def}}^f$ , for the point defects studied, namely hydrogen and oxygen vacancy, were obtained as a function of the electron chemical potential  $\mu_e$  (Fermi energy) and of the chemical potentials  $\mu_i$  of the species involved. The corresponding expression is

$$\Delta E_{\text{def}}^f = E_{\text{def}}^{\text{tot}} - E_{\text{bulk}}^{\text{tot}} + (\Delta n)\mu_i + q(\mu_e + E_V) \quad (1)$$

where  $E_{\text{def}}^{\text{tot}}$  is the total energy of the defect supercell and  $E_{\text{bulk}}^{\text{tot}}$  the total energy of the bulk supercell.  $E_V$  is the energy of the valence-band maximum and sets the reference for the positions of the Fermi level  $\mu_e$  in the gap. The magnitude of the latter,  $E_{\text{gap}}$ , was found equal to 3.91 eV.  $\Delta n$  takes the value of  $-1$  or  $+1$  for the hydrogen or the vacancy defect, respectively. Finally,  $q$  is the effective charge of the defect. A uniform compensating background charge was also added to the supercell when charged defects were studied. This allowed to describe such defects while enforcing the overall charge neutrality of the periodic supercells, both for bulk YSZ and the GB. The treatment of charged GBs would instead require a different approach and it was beyond the scope of the present study. Such GBs are always associated with adjoining space-charge layers [46] which provide charge compensation. The thickness of these layers can even reach up to several hundred nanometers; thus, it would require a large number of atoms to be properly described at the atomistic level.

The energy profiles for proton migration along several representative migration pathways in bulk YSZ and the GB were determined by means of the nudged elastic-band (NEB) method [47].

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