



Review

Invited Review: Some recent developments in the atomic-scale characterization of structural and transport properties of ceria-based catalysts and ionic conductors



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ABSTRACT

Ceria-based materials are utilized as automotive exhaust catalysts for the removal of noxious compounds, as catalysts for reforming ethanol and methane to produce hydrogen in fuel cells, as materials for solar-energy-to-fuel conversion, and as cathode, anode, and electrolyte materials in solid oxide fuel cells (SOFCs). The present paper is a critical review on the atomic-scale characterization of oxide-ion diffusion pathway, the existing phases, the phase transformations, “metastable” and stable phase diagrams, and oxygen storage capacity (OSC) of ceria-based materials. “Metastable,” compositionally (x) homogeneous t' - and t'' -ceria–zirconia $Ce_xZr_{1-x}O_2$ solid solutions ($0.2 < x < 0.9$) are key materials to obtain a high OSC, leading to high catalytic activity. Here, the t' - and t'' -forms are unstable compared to the two-phase mixture of stable ZrO_2 -rich tetragonal and CeO_2 -rich cubic (or t'') phases, but are stable in the partitionless, compositionally homogeneous phases. The axial ratio, c/a_F where the subscript F represents the pseudo-fluorite lattice, of the t' -form is larger than unity, while the c/a_F ratio of the t'' -form equals unity. Formation of the t' - and t'' - $Ce_xZr_{1-x}O_2$ is depicted in the “metastable” phase diagram consisting of allotropic phase boundaries in the CeO_2 – ZrO_2 system and is explained using the schematic Gibbs energy–composition (G – x) diagram. The composition (CeO_2 content x)-induced t' – t'' transition in $Ce_xZr_{1-x}O_2$ is discrete and of first order. The c – t'' phase transition of $Ce_xZr_{1-x}O_2$ is induced by the oxygen displacement from the regular fluorite position $1/4, 1/4, 1/4$ along the c -axis. The c – t'' transition is continuous and might be of higher order. The c – t'' phase boundary at room temperature is located at around $x = 0.85$ – 0.9 in both bulk and nanocrystalline $Ce_xZr_{1-x}O_2$. The tetragonal symmetry of compositionally homogeneous nano-sized $Ce_{0.5}Zr_{0.5}O_2$ in air is retained up to 1176 K. The c/a_F ratio, and the oxygen displacement are smaller in the nanocrystalline $Ce_{0.5}Zr_{0.5}O_2$ than in bulk $Ce_{0.5}Zr_{0.5}O_2$. Bulk oxide-ion diffusion is an important step of oxygen storage and release in ceria-based catalysts, and the oxide-ion diffusivity is essential for high OSC and efficiency of the SOFCs and the solar-energy-to-fuel conversion. The present paper reviews the atomic-scale characterization of ion diffusion in ceria-based catalysts and fluorite-type ionic conductors and discusses the correlation between their bulk ion diffusivity and structural properties. The spatial distributions of neutron scattering length density, bond valence sum (BVS), and bond-valence-based energy (BVE) in the unit cell of tetragonal ceria–zirconia compounds, cubic fluorite-type ceria-based materials, and other fluorite-structured compounds such as $Ce_{0.5}Zr_{0.5}O_2$, CeO_2 , ceria–yttria $Ce_{0.97}Y_{0.07}O_{1.96}$, bismuth oxide solid solution δ - $Bi_{1.4}Yb_{0.6}O_3$, and copper iodide α - CuI indicate the three-dimensional network of curved $\langle 100 \rangle_F$ ion diffusion pathways and anisotropic $\langle 111 \rangle_F$ thermal vibration of mobile ions, which are responsible for the bulk ion diffusion and conduction. Here, the subscript F denotes the pseudo-fluorite lattice. The BVE distributions of $Ce_{0.5}Zr_{0.5}O_2$ and CeO_2 indicate lower activation energy and higher mobility of oxide ions in $Ce_{0.5}Zr_{0.5}O_2$ compared with CeO_2 .

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1. Introduction

Ceria-based materials such as CeO₂, Ce_xZr_{1-x}O₂, and Ce_{1-x}R_xO_{2-x/2} (*R*: rare earth) are of vital importance as (1) automotive exhaust catalysts for the removal of noxious compounds, (2) catalysts for reforming ethanol and methane to produce hydrogen in fuel cells, (3) materials for solar-energy-to-fuel conversion, and (4) cathode, anode, and electrolyte materials in solid oxide fuel cells (SOFCs) [1–19]. The success of ceria-based materials is mainly ascribed to the unique combination of high oxide-ion diffusivity coupled with the ability to shift easily between reduced Ce³⁺ and oxidized Ce⁴⁺ states. The oxygen storage/release and redox properties of ceria-based catalysts are considered to play key roles in their catalytic activity. Fig. 1 shows the steps in the oxygen storage/release process [18,19]. The bulk oxide-ion diffusion in ceria-based catalysts is an important step in the oxygen storage/release process (fourth step: (4) in Fig. 1). The bulk oxide-ion conductivity in ceria-based materials for the cathode, anode, and electrolyte of SOFCs is essential for the energy conversion efficiency. Therefore, atomic-scale understanding of the oxide-ion diffusion mechanism in ceria-based materials is required for further developments of ceria-based catalysts and SOFC materials [20–23].

In conventional structure analyses such as Rietveld refinements, the unit-cell parameters, occupancy factors, atomic coordinates, and atomic displacement parameters (ADPs) are refined (see

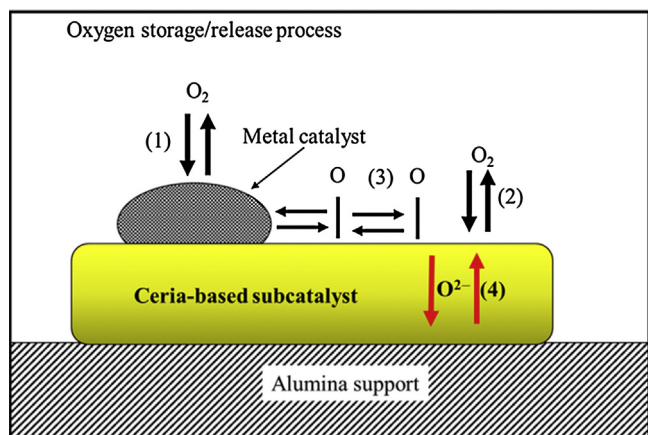


Fig. 1. Steps in the oxygen storage/release process of ceria-based catalysts. Step (1): Adsorption and dissociation of O₂ on the metal particles. Step (2): Direct exchange of O₂ from the gas phase with the O atoms of the ceria-based catalyst. Step (3): Diffusion and spillover of O atoms on the surfaces of ceria-based catalyst and on the metal catalyst. Step (4): Bulk oxide-ion diffusion in the ceria-based catalyst.

Table 1 as an example [23]). In the conventional structure analysis, the thermal vibration of an atom is usually approximated by the isotropic and/or anisotropic ADPs (thermal ellipsoid) with a Gaussian distribution. However, this is not sufficient to express the positional disorders and diffusion pathways of mobile ions, which are important for understanding the ion-diffusion mechanism at the atomic scale (Fig. 2a). On the contrary, the precise structure analysis of neutron and X-ray powder diffraction data by the maximum-entropy method (MEM) enables the determination of the continuous and complicated spatial distribution of mobile ions in the crystal lattice of ceria-based materials and of other ionic conductors (Fig. 2b) [17,20–22,24] (see the details in Section 6.1).

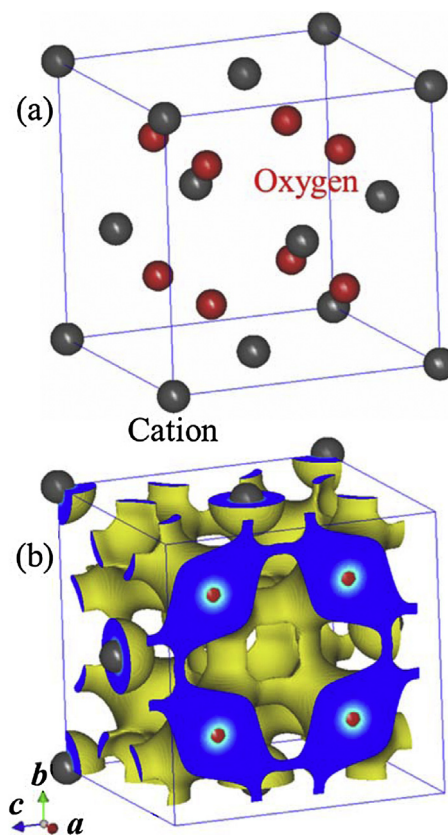


Fig. 2. (a) Refined crystal structure of Ce_{0.927}Y_{0.073}O_{1.962} at 1434 °C [17,20]. (b) Iso-surface of the neutron scattering length density distribution of Ce_{0.927}Y_{0.073}O_{1.962} at the same temperature [17,20]. Reprinted from Refs. [17,24] with permission from Imperial College Press and Ceramic Society of Japan.

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