Review

Nanocrystals of zirconia- and ceria-based solid electrolytes: Syntheses and properties

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Abstract

Nano-effect on solid electrolytes that appears as a conductivity enhancement is expected as a way to develop or improve practical solid ionic devices, such as solid oxide fuel cells. Interfaces play a major role in the enhanced conductivity. Using nanocrystals (NCs) as the starting material, the nanostructured materials containing many interfaces, i.e., grain boundaries, can be simply made by forming the NCs with successive sintering without grain growth. The past decade has seen significant advances in the syntheses of solid electrolyte NCs and understanding the nano-effects on the ionic conductivity. In the present paper, the syntheses of zirconia- and ceria-based NCs, which are important constituent materials of solid oxide fuel cells, and their grain size-dependent conductivity due to the nano-effect are briefly reviewed.

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1. Introduction

Since the discovery of the significantly higher ionic conductivity of the nanocomposite of LiI and porous Al2O3 than that of bulk LiI [1], the enhancement of the ionic conductivity at the interfaces and/or near interface regions has been drawing the attention as nano-effects appearing in solid electrolytes. The ionic conducting properties in the nanometer region around the interfaces have been experimentally and theoretically studied, and several important developments have occurred as a result of these efforts. The discovery of the strongly enhanced ionic conductivity in the multilayered BaF2/CaF2 thin film

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and the development of the space charge theory, which explains the conductivity enhancement, are such examples [2]. Today, it is expected that the study of the nano-effect is the next phase, which focused on developing the strongly enhanced conductivity due to nano-effects in practical materials.

Nanocrystals (NCs) are expected as suitable starting materials for developing nanostructured practical devices, in which many interfaces play a major role in the nano-effect, because of their cost efficiency and mass productivity. Therefore, the synthesis of solid electrolyte NCs can be regarded as the starting point in order to develop practical nanostructured solid-state ionic devices.

The solid oxide fuel cell (SOFC) is an attractive target for application of the nano-effect. When the conductivity of the solid electrolytes and the electrodes consisting of SOFCs is enhanced by the nano-effect, the effect on our life is significant. From the viewpoint described above, the recent advances in the syntheses of NCs of zirconia- and ceria-based materials, which are the major constituent materials of SOFCs, and the size-dependent conductivity caused by the nano-effect are briefly reviewed in this paper.

2. Syntheses of NCs and their characterization

2.1. Zirconia-based materials

Various methods have been developed for the syntheses of less agglomerated zirconia-based NCs. Among them, inert gas condensation (IGC) using thermal evaporation has a merit that the as-synthesized powder has a crystalline form [3,4]. The typical experimental setup is described in Ref. [3]. For the ZrO₂ NCs, zirconium monoxide evaporated in a UHV-chamber is condensed as ZrO₂ on a cold plate cooled by liquid nitrogen. The average particle size of the obtained powder is approximately 10 nm. The powder is completely crystallized, and its defect concentration, such as dislocations, is very rare [3]. The particle size and its distribution depend on the cooling rate during the condensation. When the cooling rate is high, small NCs are obtained. However, the particle size and its distribution are not exactly controllable, because the crystallization, i.e., the condensation, rate is extremely high. Instead of Joule heating, gas condensation applied by DC magnetron sputtering using Zr metal as the sputtering target was reported [3]. By applying the sputtering, purer ZrO₂ NCs can be obtained. Combustion syntheses also result in well-crystallized ZrO₂ NCs; however, the as-synthesized NCs are strongly agglomerated [6–8].

The chemical solution routes, such as precipitation [9–13] and sol–gel [14,15] techniques, are generally used for the zirconia-based NCs. Typical procedures for these techniques are as follows. For the precipitation technique, zirconium oxychloride (ZrOCl₂) or zirconium oxynitrate (ZrO(NO₃)₂) is dissolved in water, and then an aqueous ammonium solution is added dropwise until the pH becomes sufficiently high. For the sol–gel technique, the zirconium iso-propoxide (Zr(OPr)₄) propanol complex is dissolved in dry propanol, and water is then added dropwise. For the synthesis of the Y₂O₃-stabilized ZrO₂ (YSZ), yttrium nitrate (Y(NO₃)₃) or yttrium chloride (YCl₃) as well as the zirconium source are dissolved in the starting solution for both techniques. The as-synthesized powders obtained by these chemical solution routes are amorphous complex oxyhydroxides, and the particle size and their distributions are not exactly controllable due to their high reaction rate. However, many researchers have employed these techniques due to the simplicity and easiness. The as-synthesized amorphous oxyhydroxide is crystallized by post-annealing above 300 °C. Crystallization is complex and usually leaves the hydroxyl-group, i.e., interstitial protonic defects, in the resulting NCs. Chadwick et al. [16] studied in detail the crystallization by X-ray absorption and NMR spectroscopies. According to their study, crystallization is basically represented as dehydroxylation and cross-linking [17], but dehydroxylation is not complete prior to crystallization; the composition is not accurately described as ZrO₂ until > 500 °C. In order to obtain small NCs, the amorphous oxyhydroxides are frequently annealed at ~300 °C. The properties of the obtained NCs should be described by taking the remaining protonic defects into consideration. The size of NCs is usually > 10 nm after crystallization [9,10,16], while well-crystallized NCs with a single nm particle size cannot be obtained by these techniques.

The hydrothermal process results in crystalline NCs without post-annealing [18–22]. For example, 80 °C and subsequent 180 °C hydrothermal treatment of the aqueous solution of ZrO(NO₃)₂, Y(NO₃)₃ and urea results in well-crystallized YSZ NCs with ~10 nm particle size [18]. However, the obtained NCs may involve significant protonic defects, because the NCs are crystallized from the aqueous solution.

In contrast to the aqueous solution route, which results in amorphous oxyhydroxides, the non-hydrolytic sol–gel reaction reported by Joo et al. [23] results in well-crystallized NCs. The overall reaction, termed alkylhalide elimination, is described as follows:

$$Zr(OPr)₄ + ZrX₄ \rightarrow 2ZrO₂ + 4PrX,$$

(1)

where Zr(OPr)₄ is a zirconium iso-propoxide and ZrX₄ is a zirconium halide. The organic solvent with a high boiling temperature, e.g., tri-octylphosphineoxide (TOPO) and oleylamine, are usually used for the reaction solvent [24–27]; the starting solution, i.e., the mixture of Zr(OPr)₄ and ZrX₄ in the organic solvent, reacts at 300–350 °C. Unlike the sol–gel reaction using an aqueous solution, the non-hydrolytic sol–gel technique does not involve water as the solvent and/or by-product; therefore, the protonic defect, i.e., the OH-group, in the resulting NCs should be negligible. The solvent, such as the TOPO and oleylamine, behaves as a surfactant. These surfactant molecules coat the surfaces of the NCs, termed capping; therefore, the agglomeration of the NCs is suppressed, and the NCs are
obtained in a colloidal solution form. Because the crystal growth is kinetically suppressed by surface capping, the size of the obtained NCs is several nanometers. Figs. 1(a) and (b) show the high-resolution transmission electron microscope (HRTEM) image and the particle size distribution evaluated from the small angle X-ray scattering (SAXS) of the ZrO2 NCs [27], which are synthesized by the non-hydrolytic sol–gel technique. These figures indicate that the obtained NCs are well-crystallized and highly monodispersed. Y2O3 can be easily doped into ZrO2 by adding Y(OPr)3 or YX3 into the starting solution [28]. The non-hydrolytic condensation reaction (1) usually results in a hydrogen halide (HX) as the by-product. Therefore, the process is not suitable for the materials, which easily react with the HX. For such cases, the ester elimination reaction described by the following overall reaction (2) is suitable because a highly reactive by-product is not generated.

\[
\begin{align*}
\text{M}_2\text{O}_2\text{CO}_2\text{R} + \text{R}^\prime\text{O}_2\text{M} & \rightarrow \text{M}_2\text{O}_2\text{M} + \text{R}^\prime\text{O}_2\text{CO}_2\text{R}, \\
\text{where R and R}' & \text{ are alkyl groups. Details of this process are described in another review paper [29].}
\end{align*}
\]

The powder X-ray diffraction (XRD) profiles of the NCs are highly broadened due to their small crystalline size; therefore, it is very hard to detect any structural change in the zirconia NCs upon Y2O3-doping, i.e., transformation from the monoclinic to the tetragonal and cubic forms. Fig. 2(a) shows the XRD profiles of the 3 and 8 mol% Y2O3-doped ZrO2 NCs synthesized by co-precipitation and subsequent calcination at 650 °C [11]. The 3 and 8 mol% Y2O3-doped zirconias should have the tetragonal and cubic forms, respectively, under equilibrium condition. For the tetragonal form, diffractions at \(2\theta = 25^\circ\) and \(50^\circ\) and \(60^\circ\) become doublets; however, distinct peak splitting cannot be observed due to the broadened profile, and the profile appeared to be identical to that of the 8 mol% Y2O3-doped NCs. It is very difficult to identify by XRD whether the obtained phase is the tetragonal or cubic form. In contrast to the XRD profiles, a distinct difference in the number of peaks is observed in the Raman spectra (Fig. 2(b)) [11]. The changes in the Raman bands depending on the structural change upon Y2O3-doping into ZrO2 have been established [30–34]. The 641, 613 and 473 cm\(^{-1}\) bands observed for the 3 mol% Y2O3-doped NCs are attributable to the Raman active modes for the tetragonal form, and the asymmetric 625 cm\(^{-1}\) band and weak 464 cm\(^{-1}\) hump observed for the 8 mol% Y2O3-doped NCs are attributable to the Raman active and normally inactive modes for the cubic form, respectively. Thus, Raman spectroscopy gives information that can distinguish the crystal form of the zirconia-based NCs.

2.2. Ceria-based materials

Ceria-based NCs, whose sizes are less than several tens of nanometers, can be synthesized by IGC [35], precipitation [36–43], combustion [44–46], hydrothermal [47,48] and non-hydrolytic sol–gel methods [27,49,50] as in the case of the zirconia-based NCs. Among them, the precipitation method of NH4OH addition into a Ce(NO3)3 aqueous solution is generally used. Unlike the zirconia-based case,
the as-precipitated powder crystallizes by aging of the product solution below 80 °C or by drying of the product powder. The reaction is generally understood as oxidation from the as-precipitated Ce^{3+}(OH)_{3} to Ce^{4+}(OH)_{4} by the dissolved oxygen and subsequent dehydroxylation during aging [37]. The oxidation from Ce^{3+} to Ce^{4+} was visually observed, i.e., the color of the solution changed from purple for Ce^{3+} to dark brown and finally light yellow for Ce^{4+} [51]. However, it was shown from the equilibrium calculation in the Ce^{3+}–Ce^{4+}–H_{2}O–O_{2} system that hydrated CeO_{2} can be directly precipitated from the Ce^{3+} solution [52]. When (NH_{3})_{2}Ce^{4+}(NO_{3})_{6} is used as a starting material [53], the Ce^{4+} state may be stabilized in the aqueous solution due to the formation of complex ions. For such a case, it is plausible that the CeO_{2} NCs are directly precipitated from the aqueous solution. Further studies are required in order to ascertain the precipitation reaction and its mechanism. For the doped CeO_{2} NCs, such as the Gd_{2}O_{3}-doped CeO_{2} (GDC), Gd(NO_{3})_{3} as well as the cerium source is dissolved in the starting solution [38].

The valence state of the cerium ions has been discussed for the undoped ceria NCs. Upon decreasing the size to less than several tens of nanometers, an anomalous lattice expansion is observed [54]. The mechanism was based on the presence of Ce^{3+}, whose size is larger than that of Ce^{4+} in the ceria NCs. The presence of Ce^{3+} ions was supported by XRD [55], EXAFS [56] and XPS [57] data; the Ce^{3+} ion concentration was reported to be as high as 17% for the 30 nm NCs and 44% for the 3 nm NCs [57]. The driving force of the reduction was explained by the relaxation of the strain due to the extremely high surface area of the NCs. For the bulk cerium oxides, many intermediate compounds appear between the Ce^{3+}O_{3} and Ce^{4+}O_{2}, i.e., Ce_{6}O_{2n–2} phases [58–60]; the oxygen-deficient site in the bulk Ce_{6}O_{2n–2} phases is in an ordered arrangement. It is very interesting whether or not the oxygen-deficient site in the reduced ceria NCs is ordered.

3. Electrical properties

3.1. Zirconia-based NCs

According to the electrical conductivity studies of the YSZ microcrystallines, the total conductivity decreased with decreasing grain size [61,62], because the grain boundary conductivity decreased with decreasing grain size. In contrast to the microcrystalline case, the enhanced conductivity upon decreasing the grain size was observed for the YSZ NCs [63–65], whose grain size was less than ~100 nm (Fig. 3). When the space charge theory, which well explains the enhanced conductivity for the BaF_{2}/CaF_{2} multilayered films [2], is applied to the YSZ case, the Debye length \( \lambda = \left[ \varepsilon_{e}RT/2F^{2}C_{\infty} \right]^{1/2} \) was calculated to be 0.2 nm, assuming that the dielectric constant, \( \varepsilon \), and the bulk carrier concentration, \( C_{\infty} \), are 30 and 1.3 \times 10^{21} \text{cm}^{-3}, respectively. For this case, an enhanced conductivity should appear for the NCs with a grain size less than 1 nm; the space charge theory cannot explain the enhanced conductivity for the YSZ NCs. The theoretical model, which can completely describe the enhanced conductivity in the YSZ NCs, is yet to be established, but the defect segregation in the vicinity of the grain boundary is proposed as one of the possible mechanisms [66, 67]. Details of the defect segregation will be described in the next section.

Densification suppressing grain growth is an important process in order to form an electrolyte from the NC powders. High-pressure densification by applying several GPa is a possible process at this time [68,69]. It was reported that the NCs can be densified up to 92% of their theoretical density at 4.5 GPa for the YSZ NCs, and the grain growth was suppressed to less than ~20 nm. However, its electrical conductivity was two orders of magnitude lower than that of the microcrystalline samples [68]. This observation is not consistent with the other studies; therefore, further study is needed. Densification applying several GPa is not suitable for the practical production because of its low productivity. To develop the densification process without grain growth with high productivity is an important issue in order to use the NCs in the practical devices.

3.2. Ceria-based NCs

For the ceria-based NCs, the observed nano-effect on the electrical conductivity can be categorized into two groups
depending on whether the NCs are undoped or heavily doped. The conductivity increases with the decreasing grain size for both the undoped and heavily doped ceria NCs as shown in Fig. 4; however, the major conduction carriers are the electrons for the undoped and slightly doped cases \[70–75\], but the oxide ions for the heavily doped case \[76–81\].

For the undoped and slightly doped cases, the enhanced electronic conductivity has been possibly explained by the two brick-layer models consisting of (i) a grain core and grain boundary core, and (ii) a grain core, grain boundary core and space charge zone as shown in Fig. 5. Kosacki, Tuller et al. discussed the enhancement from the formation enthalpy of the oxygen vacancies, \(\Delta H\), and implicitly used

![Fig. 4. Arhenius plots of the electrical conductivity of (a) undoped and (b) doped CeO\(_2\) NCs. Data were obtained from Refs. \[76,78,80\]. The thin films of CeO\(_2\) and GDC indicated as spray in the figures were prepared by spray pyrolysis of cerium nitrate and gadolinium chloride solutions. The substrate temperature was at 310 °C. The CeO\(_2\) NC films, whose grain sizes are 10 and 20 nm, and 10 mol% GDC films, whose grain sizes are 15 and 36 nm, were prepared by spin coating a polymer precursor solution. The solution was prepared by cerium and gadolinium nitrate, ethylene glycol and nitric acid. The YDC and SDC films were prepared by fast-firing process at 700 °C for 3 min of uniaxial-pressed ultra-fine powders.](image1)

![Fig. 5. Schematic illustrations of proposed conduction path by the brick-layer model for the CeO\(_2\) NCs. (a) Model consisting of grain core (bulk) and grain boundary core (gc), and (b) model consisting of grain core, grain boundary core and the space charge zone (scz). In the former model corresponding to model (i) in the text, both electronic and ionic conductions are enhanced. In the latter model corresponding to model (ii) in the text, the space charge zone enhances the electronic conduction, but it behaves as a barrier to the ionic conduction. The latter model well explains the observation for CeO\(_2\) NCs.](image2)
model (i) [71]. \( \Delta H \) was evaluated from the oxygen pressure dependence of the conductivity and the activation energy obtained from the Arrhenius plot of the electrical conductivity. They determined a smaller \( \Delta H \) for the NCs than that for the microcrystallines. The formation of oxygen vacancies is described by the following reaction:

\[
O^+_0 \rightarrow V^-_o + 2e^- + 1/2O_2. \tag{3}
\]

Therefore, a decrease in the \( \Delta H \) of the oxygen vacancies results in an increased electron density. The increase in the electron density in the grain boundary core caused the enhanced conductivity. There is an objection to their model such that the model cannot explain the enhancement for only the electronic conduction, because a decrease in \( \Delta H \) results in an increase in the concentration of both the electrons and oxygen vacancies [75]. However, the model cannot be disregarded due to the following reason: the decrease in the \( \Delta H \) of the oxygen vacancies is consistent with the presence of many Ce\(^{3+}\) ions in the ceria NCs as described in Section 2.2 [54–57]. When the oxygen vacancies in the reduced ceria NCs are ordered as observed in the bulk Ce\(_2\)O\(_{2n-2}\) phases [58–60], the inferred mobility of the oxide ions is suppressed. Based on this assumption, only the enhancement of the electronic conduction due to the high electron density and the suppression of the ionic conduction due to the low mobility are plausible.

Tschöpe [81] discussed the enhanced conductivity of undoped ceria NCs based on the model (ii) including the space charge zone using the Gouy–Chapman theory [82], which describes the deviation of the point defect concentrations from their bulk value in the vicinity of the electrically charged grain boundaries, i.e., the space charge zone. According to the model, the electronic carrier is enriched in the space charge zone; therefore, the space charge zone becomes a highly conducting path with respect to the electronic current. On the contrary, depletion of the oxygen vacancies in the space charge zone occurs. Therefore, the space charge zone behaves as a barrier to the ionic conduction as shown in Fig. 5(b). Kim, Maier et al. also explained the electrical properties of the undoped ceria NCs using model (ii), but they employed the Mott–Schottky model in order to evaluate the charge concentration profile in the vicinity of the interfaces [73–75].

For the heavily doped ceria NCs, the enhanced ionic conductivity was explained by the defect segregation in the vicinity of the grain boundaries and decrease in the activation energy, \( E_a \), of conduction in most studies [76–79]. The enriched dopant concentration in the grain boundary with respect to the bulk was experimentally detected by several independent techniques such as electron energy-loss spectroscopy, HRTEM and nano-Auger spectroscopy [77–79]. Based on these observations, the enhanced ionic conductivity in the heavily doped ceria NCs has been described by the higher dopant concentration in the grain boundary than that in the bulk and the high grain boundary density due to the extremely small grain size. Bellino et al. [78] explained the enhanced conductivity by a decrease in \( E_a \), but they attributed the decrease in \( E_a \) to the increase in the grain boundary diffusivity.

4. Summary and feature challenges

In the present paper, the synthesis and the size-dependent electrical conductivity due to the nano-effect for zirconia- and ceria-based NCs were briefly reviewed. The advances in NC syntheses have allowed an understanding of the nano-effect in these materials possessing a grain size less than \( \sim 100\) nm. The major interest in the nano-effect on the electrical conductivity is the mechanism of the enhanced conductivity. The space charge theory provides a powerful model to describe the enhanced conductivity. However, the mechanism still remains an open question, because some experimental results, which cannot be described by the theory, remain. On the other hand, one must still elucidate the fundamental properties of the NCs as to whether or not the oxygen vacancies in the reduced ceria NCs are ordered.

In addition to these issues, the following items are very interesting challenges:

(a) **Grain size effect on electrical conductivity for grains possessing a single nanometer grain size**: Investigations with respect to the electrical conductivity of zirconia- and ceria-based NCs have been covered for grain sizes larger than \( 10\) nm. The nano-effect for the single nanometer grains is yet to be clarified.

(b) **Hetero-interfaces**: In previous studies, the target materials consisted of doped zirconia or ceria NCs; therefore, the nano-effect introduced by the homo-interfaces has been primarily addressed. The strong conductivity enhancement due to the nano-effect has been observed for the materials containing the hetero-interfaces [1,2]. For the hetero-interfaces, conductivity enhancement due to atomic defect is also expected. Recently, an enhanced conductivity for the doped zirconia/ceria multilayered films [83] and the syntheses of core/shell-type composite NCs, such as Ce\(_2\)O\(_2/ZrO_2\) [27] and ZrO\(_2/Al_2O_3\) [84], have been reported. Further advances are expected for investigating composite NCs.

(c) **Artificial assembly of NCs**: Recent developments of the artificial assembly technique of NCs are remarkable. It is expected that the artificial assembly of NCs leads a way to the high-performance solid electrolytes and electrodes.

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