Structure and impedance of ZrO₂ doped with Sc₂O₃ and CeO₂

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Abstract

Scandia and ceria doped zirconia samples, with 10 mol% Sc₂O₃ and different content of CeO₂, were synthesized and characterized. The XRD results depict that the sintered samples have a cubic phase structure. However, Raman spectra show that besides the main cubic phase, a secondary phase is also present in the sintered samples. The addition of CeO₂ can raise the content of the cubic phase, but the minor metastable tetragonal phase (t'-phase) exists even at the CeO₂ content as high as 10 mol%. The near-UV Raman spectra indicate that the deformed tetragonal structure predominates at the grain boundary. The addition of CeO₂ can reduce the impurity at grain boundary, and no impurity can be found by near-UV Raman spectroscopy at the grain boundary of the samples with high CeO₂ content. The impedance measurements show that with the increase of CeO₂ content, the impedance of grain boundary decreases and the bulk impedance increases. The low impedance of grain boundary can be attributed to the formation of a clean grain boundary upon CeO₂ doping, and the increase of the bulk impedance is due to the blocking effect of the large Ce(IV) ions.

Keywords: Doped ZrO₂; Ac impedance; Raman spectra; Grain boundary

1. Introduction

The development of intermediate temperature solid oxide fuel cells (IT-SOFCs, operating between 600 and 800 °C) requests electrolytes with higher oxide ionic conductivity than that of 8 mol% Y₂O₃ stabilized ZrO₂ (YSZ). Because of the ionic radii closeness between Sc³⁺ (101 pm, 8 facefold coordination) and Zr⁴⁺ (98 pm, 8 facefold coordination), 10 mol% scandia stabilized zirconia (10ScSZ) shows the highest conductivity in doped zirconia electrolytes. The similar chemical properties at SOFC operating environments, especially the similar thermal expansion coefficient of ScSZ and YSZ, make ScSZ match excellently with conventional electrode materials. So, ScSZ is regarded as a promising alternate electrolyte for IT-SOFCs.

Notwithstanding the attracting ionic conductivity and compatibility with electrode materials, some key issues remain to be solved for the application of ScSZ as an electrolyte in IT-SOFCs. Firstly, the doped Sc₂O₃ concentration generally ranges from 5 to 15 mol%, in which ScSZ gives a relatively high oxide ionic conductivity, but in this range, the phase assembly of ScSZ is quite complex [1,2]. It is very difficult to obtain a pure phase ScSZ, and the true equilibrium phase diagram is still left as a question. Recently, Zhang et al. [3–5] reported the synthesis of nano-crystalline of 8 mol% Sc₂O₃ doped ZrO₂ by different methods, but it is difficult to obtain a pure and stable cubic phase after sintering [4]. Secondly, because the driving force for homogenous distribution of cations is very weak in ScSZ materials, the ScSZ electrolyte exhibits a poor sintering property and cation inhomogeneity, even after high temperature annealing [6,7]. The direct use of ScSZ as electrolyte seems prohibited.

X-ray diffraction (XRD) is generally adopted for phase structure study, and up to the present, most results about ScSZ phase assembly are based on XRD investigation. But for ScSZ materials, it is difficult to discriminate t-ZrO₂ and...
c-ZrO$_2$ by XRD because of the analogical diffraction patterns. Further, it is impossible to analyze the structure and species at ceramic grain boundary by XRD. Some new techniques are required for the deep understanding of the phase structure of ScSZ electrolyte. Raman spectroscopy is a sensitive method to differentiate the vibrations of various ZrO$_2$. Especially, Raman scattering exited by ultra-violet laser is quite sensitive to various structures at ZrO$_2$ surfaces [8]. In this paper, by Raman spectroscopy and AC impedance spectroscopy, the effects of CeO$_2$ doping on the structure and impedance property of ScSZ bulk and grain boundary will be examined.

2. Experimental

10ScSZ powders doped with CeO$_2$ were synthesized by co-precipitation–azeotropic distillation method. ZrOCl$_2$·8H$_2$O (36.18% ZrO$_2$), Sc$_2$O$_3$ (99.99%) and Ce(NO$_3$)$_3$·6H$_2$O (99.5%), were used as starting materials without further pretreatment. Sc$_2$O$_3$ was firstly dissolved into a hot concentrated hydrochloric acid solution, and then Zr$^{4+}$ and Ce$^{3+}$ were introduced and mixed. The uniform salt solution was dropped into an ammonia solution with a PH value of 9~10 and then aged under stirring for several hours to let the metal ions precipitate entirely. The precipitate was filtered and washed with de-ionized water repeatedly until Cl$^-$ cannot be detected by AgNO$_3$ solution (0.1 M). To abbreviate the agglomeration of particles, the precipitate was dehydrated by azeotropically distilling in n-butanol [9]. After the powders were pressed uniaxially under 153 MPa, ScSZ ceramic discs were sintered at 1600 °C.

XRD and Raman spectroscopy were used to identify the various possible phases in the bulk and at the grain boundary. X-ray patterns were taken on X-ray diffractometer (Rigaku D/max-yb) using Cu K$\alpha$ radiation. Visible Raman scatterings were carried out with an Argon ion laser source (532 nm) with wave number ranging from 1000 to 100 cm$^{-1}$, and near-UV Raman spectra were recorded from 800 to 100 cm$^{-1}$ with a 325 nm laser source.

For the AC impedance measurements, the Pt electrodes were applied on the samples by painting with platinum slurry and a calcination at 1000 °C for 1 h. AC impedance spectra were measured in air with a frequency response analyzer (FRA, Solartron-1260) over a frequency ranging from 0.1 Hz to 10 MHz with an applied potential of 10 mV.

3. Results and discussion

Fig. 1 gives the XRD patterns of the sintered ScSZ samples with different content of CeO$_2$. All the diffractions can be designated to the cubic structure. But the splitting of some diffraction peaks is observed, which may indicate a complicated phase composition. Because t-ZrO$_2$ and c-ZrO$_2$ have similar diffraction patterns, it is difficult to determine the phase assembly by the XRD results.

Fig. 2 shows visible Raman spectra of the sample. The strongest peak in Raman spectra, centered at 613 cm$^{-1}$, indicates the abundant presence of the cubic phase [10]. The peaks centered at 157, 256 and 485 cm$^{-1}$ suggest that trace meta-stable t'-phase also exists [8,10]. The intensities of these peaks turn weaker gradually with increasing CeO$_2$ content. Especially the band at 256 cm$^{-1}$, usually referred as the fingerprint of t-ZrO$_2$, dies down step by step. Nevertheless, other characteristic peaks of t'-ZrO$_2$ remain. Thus, the addition of CeO$_2$ raises the content of the major cubic phase and suppresses the minor t'-phase, but the minor t'-phase cannot be eliminated even at the CeO$_2$ content as high as 10 mol%.

Near-UV Raman spectra were recorded from the freshly fractured surfaces of the sintered samples, as displayed in Fig. 3. Both the spectra (a) and (b) are obtained from the sample doped with 1 mol% CeO$_2$ at different spots, (d) and (e) from the sample with 10 mol% CeO$_2$ similarly, and (c) 5 mol%. Little difference is observed in the near-UV Raman spectra from different spots. A strongest peak at 635 cm$^{-1}$ appears in all spectra. This mode could be designated to either t-ZrO$_2$ or monoclinic ZrO$_2$ (m-ZrO$_2$). Since the strong characteristic peak at 472 cm$^{-1}$ for m-ZrO$_2$ is absent, the peak at 635 cm$^{-1}$ can only be ascribed to t-ZrO$_2$. Regarding the absence of other characteristic peaks of t-ZrO$_2$, such as 157, 256, 485 cm$^{-1}$ and so on, the mode at 635 cm$^{-1}$ should be designated to a deformed tetragonal structure, which predominates at the grain boundary.

A unique weak vibration mode, centered at 170 cm$^{-1}$, appears in the near-UV Raman spectra of the sample doped with 1 mol% CeO$_2$ but disappears with increasing CeO$_2$ content. This peak cannot be attributed to any structure of doped ZrO$_2$. With CeO$_2$ content increasing to 5 and 10 mol%, the peak disappears. So the peak at 170 cm$^{-1}$...
cm$^{-1}$ might be aroused from some impurity at the grain boundary. The absence of this peak may suggest a clean grain boundary.

**Fig. 4** displays the ionic conductivity as a function of temperature. The electric conductivities of the three samples reach 0.084, 0.060 and 0.049 S/cm at 800°C, respectively. Similar conductivity activation energy of ca. 35 kJ/mol is observed on the three samples show. For 10 mol% Sc$_2$O$_3$ doped ZrO$_2$, a conductivity jump is observed around 600°C, and the conductivity activation energy is also changed in a different temperature range. This jump corresponds to the transformation from the rhombohedral phase to the cubic one [1]. The electric conductivities decrease with increasing the content of dopant CeO$_2$. The variation of conductivity upon ceria addition can be interpreted by the steric blocking effect, that is, a larger dopant cation than the host cation can block the oxygen ion migration through vacancy. It is noted that, with 8 facefold coordination, the ionic radii of Zr$^{4+}$, Sc$^{3+}$ and Ce$^{4+}$, is 98, 101 and 111 pm, respectively.

The Ac impedance spectra of solid electrolyte measured at 300~400°C can generally be divided into three arcs, corresponding to the contribution of the bulk, grain boundary and electrode/electrolyte interface, respectively [11]. **Fig. 5** gives the Ac impedance spectra of ZrO$_2$ doped with 10 mol% Sc$_2$O$_3$ and different content of CeO$_2$. It is shown that the bulk impedance occupies the main part of the whole spectra and increases with CeO$_2$ content. This phenomenon is usually interpreted by the blocking effect of large Ce (IV) ions embedded in ZrO$_2$ lattice. In addition, the notable distortion of the first arc, exhibited in **Fig. 4**, can be ascribed to the complex structure in the bulk of these samples. In contrast, the second arc from grain boundary decreases remarkably with increasing CeO$_2$ content. Obviously, the composition and structure of grain boundary are remodeled step by step with increasing CeO$_2$.
4. Conclusions

XRD patterns indicate that ZrO$_2$ doped with 10 mol% Sc$_2$O$_3$ and different content of CeO$_2$ have a cubic phase structure. Raman spectra reveal that a minor secondary phase is also present in the bulk. The addition of CeO$_2$ can raise the content of the cubic phase, but the minor metastable tetragonal phase (t’-phase) still exists even at the CeO$_2$ content as high as 10 mol%. On all samples, a deformed tetragonal structure predominates at the grain boundary. The impurity is detected at the grain boundary of 1 mol% CeO$_2$ doped sample. By increasing CeO$_2$ content, the impurity at the grain boundary can be suppressed effectively and result in a clean grain boundary with low impedance.

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References