Effect of SiO$_2$ content on the ionic conductivity of Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ ceramics

T. S. ZHANG,* J. MA, L. B. KONG
School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798
E-mail: tszhang@ntu.edu.sg

S. H. CHAN
School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798

Ceria-based solid solutions, for example, 20% GdO$_{1.5}$-doped ceria (Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$), have been considered as most promising candidate electrolytes for intermediate-temperature (500 to 700 °C) fuel cells [1–3]. However, it should be noted that the grain boundary (GB) conduction becomes important, especially in the intermediate-temperature range in Gd-doped ceria. Although the deleterious GB behavior which arises from SiO$_2$ impurity has been recognized for over ten years in ceria-based solid solution, there is still a lack of clarity as to how the level of SiO$_2$ affects ionic conductivity, especially in Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ ceramics [4, 5]. In this short communication, we report the electrical properties of the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ ceramics with 30, 200, and 3000 ppm SiO$_2$.

High-purity CeO$_2$ and Gd$_2$O$_3$ powders (Yew Tree House, Tilley, Wem Shropshire SY4 5HE, England) were used as the starting materials. The levels of the main impurities, SiO$_2$, CaO, and other rare earth oxides, in the commercial CeO$_2$ and Gd$_2$O$_3$ powders are listed in Table I. (1) The Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ powder with ~30 ppm SiO$_2$ was first prepared by merely mixing the two raw oxides for over 24 hr in ethanol medium, using a ball milling process, with polypropylene jars and yttria-stabilized zirconia balls. (2) To obtain the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ powders with 200 and 3000 ppm SiO$_2$, 170 and 2970 ppm SiO$_2$, were added into the above mixed powder via a wet chemical method using tetraethyl orthosilicate (TEOS) as the starting material. The powder and TEOS were thoroughly mixed. The slurries obtained were then dried and thermally decomposed at 700 °C for 1 hr in air. The powders were pressed into pellets of 10 mm diameter, at ~100 MPa. The green densities of the pellets were ~58% of theoretical density. The pellets were finally sintered at 1600 °C for 5 hr in air, at a heating and cooling rate of 10 °C/min. To prevent any contamination during sintering, the pellets were all supported by platinum plates.

Phase composition was examined by X-ray diffraction (XRD) (Rigaku, Dmax-2200, Tokyo, Japan). After thermally etching, well-polished surfaces of the sintered samples were observed by scanning electron microscopy (SEM) (JSM-5410, Jeol, Japan). The densities of the sintered pellets were measured, via the Archimedes method, in a water bath. After being polished with emery paper, the sintered pellets were coated on both sides by silver pastes that were fired at 850 °C. At the same time, silver wires were fixed on to the silver paste serving as lead wires. The ionic conductivities of the sintered samples were measured using a two-probe impedance spectroscopy (Solartron 1260, UK), over 250 to 750 °C and from 1 to 10^7 Hz.

XRD results indicate that the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ ceramics with different levels of SiO$_2$, sintered at 1600 °C for 5 hr, are of single phase with fluorite structure like pure CeO$_2$. No other phases are observed even in the sample with 3000 ppm SiO$_2$. SEM observation suggests that the samples with 30 and 200 ppm SiO$_2$ exhibit a very similar microstructure, with ~96.4% relative density and a mean grain size of ~2.3 μm. However, the addition of more SiO$_2$ (e.g., 3000 ppm) leads to a slight decrease in both grain size (~1.7 μm) and sintered density (~94.8% relative density), which may be attributed to the pinning effect of the second phase (i.e., SiO$_2$).

The impedance characteristics of the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ ceramics, with different levels of SiO$_2$, are similar to those of other polycrystalline materials such as yttria-stabilized zirconia, as well-documented in the literature [6, 7]. Fig. 1 shows the typical impedance spectra of the Si-containing Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$, measured at 350 °C in air. The contributions of the grain interior (GI), grain boundary, and electrode polarization behavior, can be clearly identified from this figure. It is found that the GB impedance increases as the SiO$_2$ content increases. Specifically, the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ with 3000 ppm SiO$_2$ has a very large GB arc, indicating that SiO$_2$ impurity is extremely detrimental to the GB conduction of ceria-based electrolytes. Besides the effect on the GB conductivity, SiO$_2$ also has a slight influence on the GI conductivity. It is found that the GI conductivity decreases consistently as SiO$_2$ content increases, as clearly shown in the inset of this figure. The dissolution of SiO$_2$ in Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ crystallites can be considered to be responsible for this decreased GI conductivity. At high temperatures, a small quantity of SiO$_2$ can enter into the Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ crystallites at either substitutional

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*Author to whom all correspondence should be addressed.

TABLE I Main impurities in raw CeO_2 and Gd_2O_3 powders

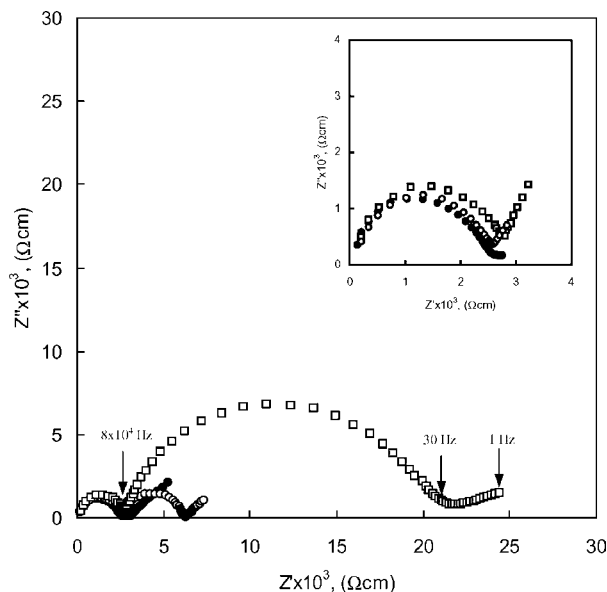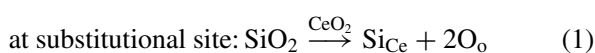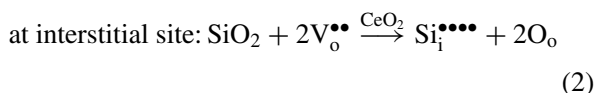| Compound	Level (wt%)
CeO_2	>99.98
Other rare earth oxides	<0.0135
CaO	<0.005
SiO_2	<0.0025 (25 ppm)
Gd_2O_3	>99.99
Other rare earth oxides	<0.0059
CaO	<0.005
SiO_2	<0.0032 (32 ppm)

Figure 1 Impedance spectra of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics with 30 ppm (●), 200 ppm (○), and 3000 ppm SiO_2 (□), measured at 350 °C in air. The GB and GI, respectively stand for the grain-boundary and grain-interior effects. Inset is the GI conductivity at high frequencies, showing the effect of SiO_2 content on the GI conductivity.

or interstitial sites:

at substitutional site: $SiO_2 \xrightarrow{CeO_2} Si_{Ce} + 2O_o$ (1)

and

at interstitial site: $SiO_2 + 2V_o^{\bullet\bullet} \xrightarrow{CeO_2} Si_i^{\bullet\bullet\bullet\bullet} + 2O_o$ (2)

Although the substitutional dissolution of SiO_2 into $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ produces no charge carriers as described in Equation 1, a large lattice distortion usually leads to a slow mobility of oxygen vacancies, as well as a high association enthalpy of complex defects. Similar results have been reported in Zr-doped $Ce_{0.75}Gd_{0.15}O_{2-\delta}$[8] and in SiO_2-doped YSZ [9]. By referring to the sizes of Si^{4+} ion (0.4 Å) and Ce^{4+} ion (0.97 Å), it is likely, however, that the interstitial dissolution by filling some oxygen vacancies is more favorable. This results in a decrease in concentration of oxygen vacancies, thus leading to a reduced GI conductivity.

Fig. 2 shows the effect of SiO_2 content on the contribution of the GB resistance to the GI value. As expected, for each sample, the GB resistance decreases
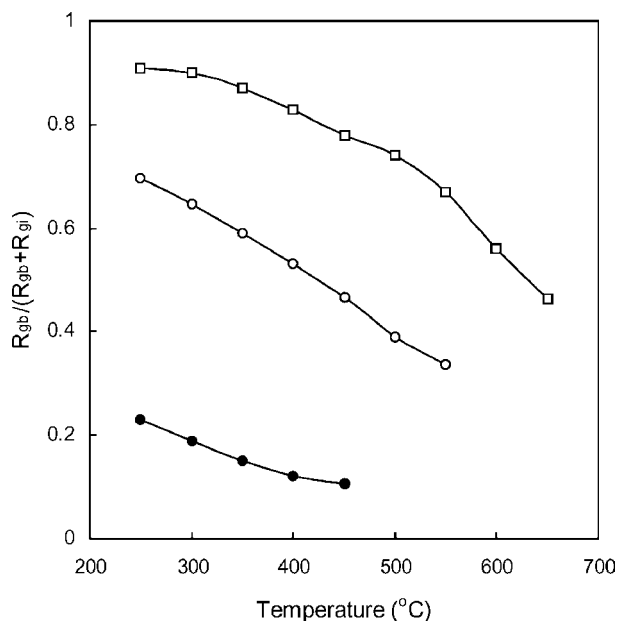

Figure 2 The relative contribution of the GB resistance to the total value of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics with 30 ppm (●), 200 ppm (○), and 3000 ppm SiO_2 (□).

as temperature increases. At a particular temperature, the contribution of the GB resistance to the total value relies on the levels of SiO_2. For instance, at 400 °C, the GB resistance accounts for 12.0, 53.2, and 83.4% of the total value in the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with SiO_2 contents of 30, 200, and 3000 ppm, respectively. It is also noted that in the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with 30 ppm SiO_2, the GB resistance plays a minor role in the total conduction even at low measurement temperatures. In materials of high purity (<50 ppm SiO_2), the GB behavior is usually attributed to intrinsic effect—space-charge layer, since the blocking effect of the siliceous phase is negligible [10, 11]. During sintering, effectively negatively charged Gd'_{Ce} species segregate to the grain boundaries, in which positively charged $V_o^{\bullet\bullet}$ are depleted.

However, the blocking effect of the grain boundaries due to the thin siliceous films should be of great concern in high-impurity materials (≫50 ppm SiO_2), although space-charge layer may still take action. During sintering a thin amorphous Si-containing film would be formed at the grain boundaries, through which the movement of oxygen ions is blocked, thus leading to a low GB conductivity. However, it remains unclear whether the siliceous films are continuous or enclose the grains. In this respect, two models (i.e., blocking model and constriction model) have been established to explain the GB effect [12, 13]. Although both models have found experimental supports, more and more evidence supports the "constriction model". Our preliminary results have revealed that no continuous GB phase is observed even in the sample with 3000 ppm SiO_2, and the Si-containing phase usually concentrates in the three-grain junctions. This suggests that oxygen ions cross the grain boundaries only through some "clean" grain to grain contacts, whose fraction is determined by the amount of the siliceous phase.

TABLE II Ionic conductivity[a] and activation energy[b] of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics with different levels of SiO_2

Composition	E_t (eV)	E_{gb} (eV)	E_{gi} (eV)	σ_t $(\Omega m)^{-1}$	σ_{gb} $(\Omega m)^{-1}$	σ_{gi} $(\Omega m)^{-1}$
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ + 30 ppm	0.826	0.920	0.768	1.65	0.201	4.14×10^{-2}
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ + 200 ppm	0.891	0.992	0.781	1.28	0.029	4.10×10^{-2}
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ + 3000 ppm	0.945	0.989	0.790	0.652	6.66×10^{-3}	3.96×10^{-2}

[a]The GI (σ_{gi}) and GB (σ_{gb}) conductivities, and the total (σ_t) conductivity were measured at 350 and 600 °C, respectively.
[b]The activation energies for the GI (E_{gi}) and GB (E_{gb}) conductivities, and the total (E_t) conductivity were measured in the temperature range of 250 to 450 °C and 250 to 700 °C, respectively.
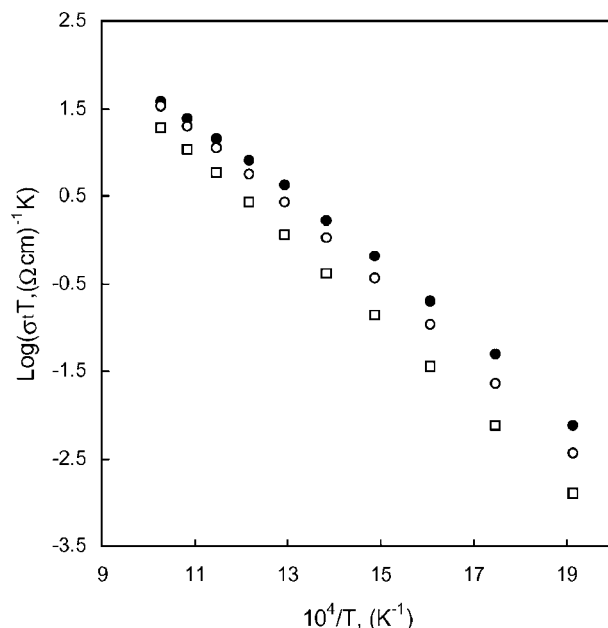

Figure 3 Arrhenius plot of the total conductivity of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics with 30 ppm (●), 200 ppm (○), and 3000 ppm SiO_2 (□), measured at 250 to 700 °C in air.

activation energy of the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with different levels of SiO_2. The values regarding the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with 200 ppm SiO_2 should be of great interest since the SiO_2 content of 200 ppm is a common impurity level in the commercial raw powders [14]. Moreover, due to the high-purity sample (~30 ppm SiO_2) used in the present study, some of the electrical properties measured may be taken as the ultimate or intrinsic values for the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics [15].

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The Arrhenius plot of the total conductivity of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with different levels of SiO_2 is shown in Fig. 3. It can be seen that the sample with 30 ppm SiO_2 has a much higher total conductivity in the temperature range of 250 to 750 °C. By examining the results in Figs 1 and 2, we see that a lower total conductivity of the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ with 200 ppm or 3000 ppm SiO_2 results mainly from the the deteriorated GB conduction since SiO_2 content has a slight effect on the GI conductivity. Table II summarizesionic conductivity and