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Electrical conductivities of translucent $BaZr_xCe_{0.8-x}Y_{0.2}O_{3-\delta}$ (x = 0.5, 0.6, 0.7) ceramics

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A B S T R A C T

The electrical conductivities of translucent $BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-\delta}$ (x = 0.5, BZCY532), $BaZr_{0.6}Ce_{0.2}Y_{0.2}O_{3-\delta}$ (x = 0.6, BZCY622) and $BaZr_{0.7}Ce_{0.1}Y_{0.2}O_{3-\delta}$ (x = 0.7, BZCY712) proton conductors were investigated systematically in different atmospheres and also at different oxygen partial pressures. The obtained results indicate that translucent BZCY532, BZCY622 and BZCY712 ceramics are pure oxygen-ion and proton conductors without unfavorable electronic conduction. In addition, they represent promising proton conductors to be used as intermediate temperature solid oxide fuel cell electrolytes.

Proton-conducting ceramic materials have attracted more and more interests in the development of intermediate temperature solid oxide fuel cells (ITSOFCs). This is due to their higher proton conductivities (10^{-3}–10^{-2} S cm^{-1} at 600 °C) and lower activation energies (0.3–0.7 eV) during the transport process compared to 8YSZ-based electrolytes [1,2]. In addition, many lanthanides (Ln) doped perovskite-type cerates and zirconates as well as their solid solution mixture materials have been investigated in order to obtain higher proton conductivity combined with improved chemical and mechanical stability [2–10].

Despite that these Ln-doped $BaZrO_3$-$BaCeO_3$ ($BaZr_xCe_yLn_{1-x-y}O_{3-\delta}$) materials have a relative higher conductivity than 8YSZ-based electrolytes, their sintering temperatures are always high up to 1500 °C or even higher. This is also accompanied by a long sintering time for obtaining densified ceramics [11]. However, unfavorable Ba loss will occur when the sintering temperature is higher than 1500 °C and this Ba loss always leads to a reduced conductivity [12–14]. Therefore, various efforts, including the addition of sintering aids and the introduction of wet-chemical synthesis methods to prepare ultra-fine powder, have been done during the recent years to reduce the sintering temperatures and to increase their relative densities as well as to improve the desired proton conductivities [2,11,15]. Besides of these, the recent sintering method improvement, especially spark plasma sintering (SPS), points out another route to prepare high quality ceramics with a lowered sintering temperature and a shortened sintering time compared to conventional sintering methods. Moreover, this SPS method has been used for preparation of various ceramic materials with improved properties [16].

Though there are many kinds of ceramics that have been prepared successfully by SPS method, there is few study on the preparation of dense Ce-containing $BaZrO_3$-$BaCeO_3$ ceramics by using the SPS method. This is due to the unfavorable Ce reduction. However, this Ce reduction should be controllable if proper sintering parameters are applied. In our latest study, dense and translucent $BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-\delta}$ (x = 0.5, BZCY532), $BaZr_{0.6}Ce_{0.2}Y_{0.2}O_{3-\delta}$ (x = 0.6, BZCY622) and $BaZr_{0.7}Ce_{0.1}Y_{0.2}O_{3-\delta}$ (x = 0.7, BZCY712) proton conductors were prepared successfully by SPS method at 1350 °C and using a holding time of 5 min. As this kind of Ce-containing $BaZrO_3$-$BaCeO_3$ ceramics were prepared by SPS for the first time, how their conductivities are and do these materials can be used for final SOFC applications become urgent issues to be answered. Just because of this, the electric conductivities of translucent BZCY532, BZCY622 and BZCY712 ceramics were determined in atmospheres of dry air, wet N_2 and wet H_2, respectively. Furthermore, their total conductivities were also tested at different oxygen partial pressures (P_{O2}), in order to identify whether some electronic conduction existed in these ceramics.

The BZCY532, BZCY622 and BZCY712 powders were synthesized by the solid-state reaction method using water-based milling combined with a freeze drying process. The operating details can be found in our previous study [17]. The prepared powders were sintered through a 3rd generation SPS furnace (SPS-20T-10, Chenhua Furnace Company, Shanghai, China). The BZCY532, BZCY622 and BZCY712 powders were sintered at 1350 °C with a sintering pressure of 50 MPa and using a

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holding time of 5 min [18]. After SPS sintering, the prepared pellets were placed in a furnace and were heated to 1350 °C for 2 h to remove the needless defect. Then, dense and translucent BZCY532, BZCY622 and BZCY712 ceramics were obtained.

The micro-structure characterizations of these prepared ceramics with respect to their crystal structures, cross-sectional morphologies and elemental analysis had been determined by XRD, SEM and EDS, respectively [18]. In this work, their electrical conductivities were determined by using a MinisTest6000S platform (Toyo Corporation, Japan). Their conductivities in the atmospheres of dry air, wet N_2 and H_2 were tested at 200–600 °C. A frequency range of 0.1–100 kHz and an excitation voltage of 100 mV were employed. In addition, their total conductivities at different P_{O2} conditions ($1–10^{-24}$ atm) were tested at 600–800 °C.

Fig. 1 shows the typical electrochemical impedance spectra (EIS) of BZCY532, BZCY622 and BZCY712 ceramics, when they were tested in dry air, wet N_2 and wet H_2 atmospheres at 600 °C. From Fig. 1, it can be seen that the spectra of BZCY532, BZCY622 and BZCY712 in wet H_2 and wet N_2 always show a reduced resistance compared to the spectra in dry air. Moreover, the resistance in wet H_2 is a little bit smaller than in wet N_2. This is a solid evidence to support that the prepared ceramics have a relative higher electrical conductivities when they were tested in the water-containing atmospheres, and proton conductivities domain of the majorities. Their conductivities were calculated and summarized in a form of Arrhenius plot in Fig. 2 (a)–(c). In addition, these data are also summarized and compared at the same atmosphere in order to make a better comparison between different samples, see Fig. 2 (d)–(f). Moreover, their detailed conductivities at 600 °C are summarized and listed in Table 1 in order to enable a better comparison with previously reported data.

For the BZCY532, BZCY622 and BZCY712 ceramics, the changes of their conductivity are very similar when they were tested in different atmospheres. Take BZCY532 ceramic for example (Fig. 2(a)), its conductivity in wet H_2 is always higher than in wet N_2. The lowest conductivity was obtained in dry air. These phenomena indicate that proton conductivities exist in wet N_2 and H_2. Hydroxyl groups will be formed when they are exposed to a hydrogen/water-rich atmosphere. This newly generated hydroxyl groups can provide proton conductivities (Eq. (1)). According to Grotthuss mechanism [19], the actual conducting charge carriers are protons (H^+). And, these protons will provide a faster transmission compared to an oxygen-ion conduction, which was provided by oxygen vacancies ($V_o^{\cdot\cdot}$). This can be explained by Eq. (2) and have been confirmed by previous data from isotope experiments tested for similar materials [20].

$$H_2O\ (gas) + V_o^{\cdot\cdot} + O_O^X \leftrightarrow 2OH_O^{\cdot} \tag{1}$$

$$\sigma = \frac{A}{T}\exp\left(-\frac{E_a}{kT}\right) \propto \frac{1}{\sqrt{m}}\exp\left(-\frac{E_a}{kT}\right) \tag{2}$$

where E_a is the activation energy, A is the pre-exponential factor, T is the Kelvin temperature, k is the Boltzmann constant and m is the mass of effective particle, respectively. As for the comparison in the same testing atmosphere (Fig. 2(d)–(f)), the total conductivities of BZCY532 is always higher than BZCY622, followed by BZCY712. The reasons for this should be contributed to the differences of Ce content and grain size [21].

From Table 1, it can be seen that these dense BZCY532, BZCY622 and BZCY712 ceramics have equivalent or even higher conductivities compared to the reported data in literatures [1,3,22–26]. These results further confirm that dense BZCY532, BZCY622 and BZCY712 proton conductors are good electrolyte candidates, which have the potential to be used for ITSOFC applications.

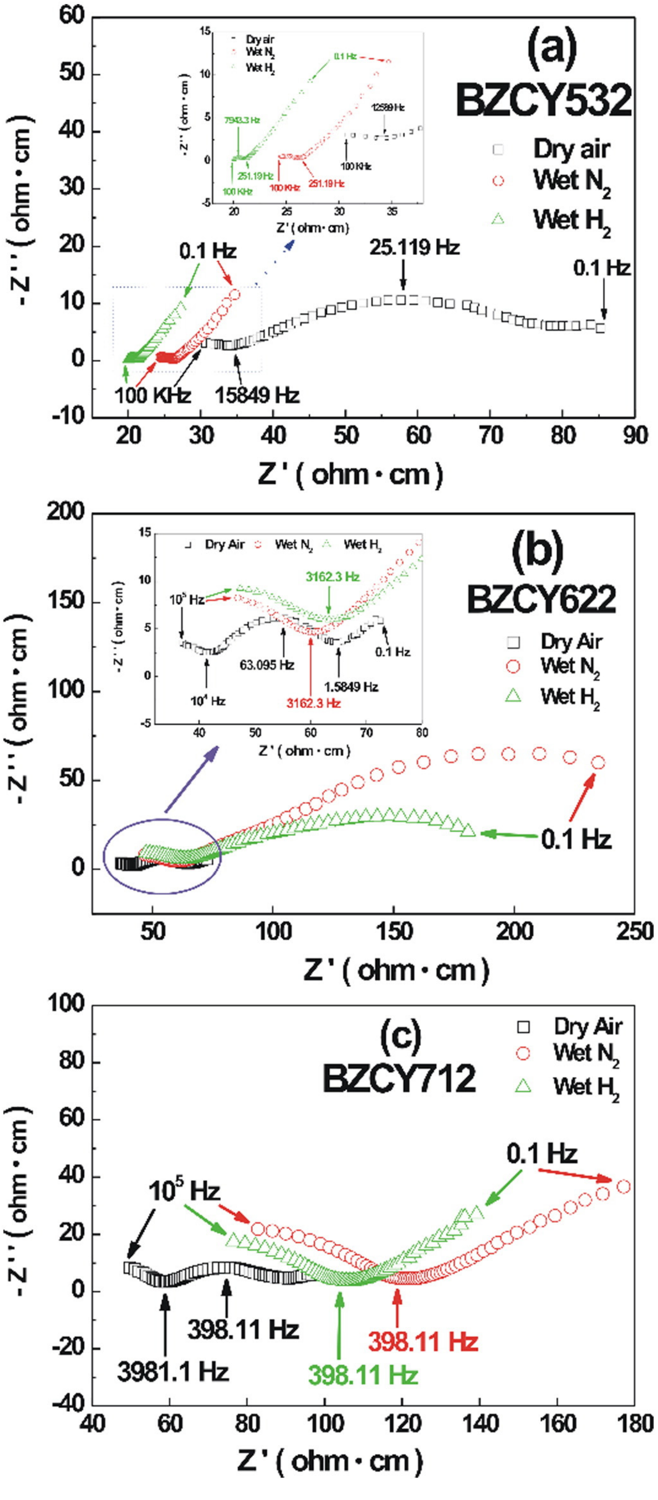

Fig. 1. Typical impedance spectra of sintered (a) BZCY532, (b) BZCY622 and (c) BZCY712 ceramics, which were tested at 600 °C.

In consideration of the severe reducing condition during the sintering process, there is an urgent question that should be answered: *is there some unfavorable electronic conduction exist in these SPS method prepared ceramics*? This is due to that electronic conduction will lead to a reduced cell performance, which was caused by the partial short-circuit occurrence. Therefore, their total conductivities were determined at temperature of 600–800 °C in a broad P_{O2} range ($1–10^{-24}$ atm), as shown in Fig. 3. The total conductivities of BZCY532, BZCY622 and BZCY712 ceramics showed a decreasing tendency when the P_{O2} dropped continually. The reason for this decreasing tendency is that a lowered P_{O2} leads to a lowered content of active oxygen ions and a lowered hole conduction (Eq. (3)). Normally, the total conductivities will have a huge increase if there were electronic conduction in prepared samples and the P_{O2} was lower than 10^{-15} atm or even