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Fabrication of $SrZrO_3$-based Proton Conductors and Their Characterization

Douck-Young Byun and Kwang Soo Yoo[†]

Department of Materials Science and Engineering, University of Seoul, Seoul 130-743, Korea

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The Y- or Yb-doped $SrZrO_3$ proton conductors were fabricated using the powders prepared by the self-propagating high-temperature synthesis (SHS). The electrical conductivity was evaluated from an a.c. impedance measurements. The conductivity of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ was 1.8×10^{-3} Scm^{-1} at 900°C in dry air atmosphere and its activation energy was 0.50 eV. The conductivity in wet air was larger, compared with the dry air, and the activaton energy of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ in wet air was 0.40 eV.

Key words: $SrZrO_3$, Proton conductor, Self-propagating high-temperature synthesis, Electrical conductivity

I. Introduction

Solid state proton conductors have attracted considerable interest because of their applications such as fuel cells, hydrogen sensors, humidity sensors, and so on.[1-3)] It is known that the proton migrates in the interstitial sites around oxygen ions by hopping in these proton conductors.[4)] Conventional proton conductors are unstable at elevated temperatures higher than 300°C, since they are dehydrated, eading to a decrease in conductivity.[5)] However, many proton conducting ceramics of the perovskite-type (ABO_3) structure based on $SrCeO_3$, $BaCeO_3$, $CaZrO_3$, or $SrZrO_3$ exhibit high proton conduction under hydrogen-containing atmospheres at high temperature.[4-6)]

Among the oxides described above, $BaCeO_3$-based ceramcs show the highest conductivity. However, the contribution of the oxygen-ions in total conduction grows markedly with increasing temperature. On the other hand, the conductivity of $SrCeO_3$-based ceramics is rather low, but the transport number of protons is higher than that of $BaCeO_3$-based ceramics. The zirconate-based ceramics show lower than those of the cerates, but they are superior with respect to their chemical and mechanical strength.[7)]

In perovskite-type ceramics, B-site cations are partially substituted by aliovalent cations such as Y, Yb, Sc, and so on. This substitution results in the formation of oxygen vacancies or holes, which play an important role in the ntroduction of proton into the proton conductor according to following reactions:[8)]

$$H_2+2h^{\bullet}=2H^{+} \qquad (1)$$

$$H_2O+2h^{\bullet}=2H^{+}+1/2O_2 \qquad (2)$$

$$H_2O+V_o^{\bullet\bullet}=2H^{+}+O_o^{x} \qquad (3)$$

In general, $SrZrO_3$-based proton conductors are sintered at high temperatures above 1600°C by a solid state reaction. Self-propagating high-temperature synthesis (SHS) is an economical method of manufacturing many inorganic materials and has also been successfully used to synthesize complex oxide materials.[9-11)] SHS is a process in which initial reagents, when ignited, spontaneously transform into products, due to the exothermic heat of reaction. SHS reactions occur by propagation of a combustion wave (layer-wise) with a definite velocity through a reactant pellet converting it into products.

Accordingly, the purpose of the present paper is to fabricate Y- or Yb-doped $SrZrO_3$ proton conductors at the temperature below 1600°C using powders synthesized by the SHS method, and characterize their electrical properties in dry and wet air atmospheres using an a.c. impedance analyzer.

II. Experimental

1. Specimen Fabrication

The powders of $SrZrO_3$ doped with Y_2O_3 or Yb_2O_3 were prepared by SHS process from the mixtures of $SrCO_3$ (Cerac, 99.5%), Zr (Sejong Materials, 99.9%), Y_2O_3 (Cerac, 99.9%), or Yb_2O_3 (Cerac, 99.9%). The compositions of $SrZrO_3$-based proton conductors are $SrZr_{0.92}Y_{0.08}O_{3-\delta}$, $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$, $Sr_{0.95}Zr_{0.92}Y_{0.08}O_{3-\delta}$, and $Sr_{0.95}Zr_{0.92}Yb_{0.08}O_{3-\delta}$. According to a prievious report,[12)] the sinterability and conductivity was improved by A-site deficiency. Therefore, in this study, A-site deficient proton conductors were also fabricated. The powders were then pressed to form pellets with a diameter of 25.4 mm and thickness of 20 mm. Each pellet was supported on a Pt foil on the hot plate at 250°C and ignited in air using a match.

The powders obtained by SHS process were calcined at

Corresponding author : ksyoo@uos.ac.kr

1400°C for 4 hours in air. The calcined powders were uniaxially pressed with a pressure of 2000 kg/cm^2 to form pellets with a diameter of 10 mm and thickness of 3 mm and sintered at 1600°C for 4 hours in air.

2. Characterization

The X-ray diffraction patterns for $20° \leq 2\theta \leq 90°$ were taken using a powder x-ray diffractometer (Siemens, D5000) with a Cu K_α target and a Ni filter. For a.c. impedance measurements, the pellets were polished and painted with Pt paste. The porous Pt electrodes were fired at 1400°C for 10 minutes for good electrical contact. The sintered samples were treated in dry air atmosphere at 900°C for 4 hours and after measurements in dry air those were kept in wet air atmosphere at 500°C overnight. The flow rate of compressed air was 15 cc/min and the wet air atmosphere was made of bubbling compressed air through water at room temperature. Before impedance measurements, the samples were kept for at least 1 hour at each measuring temperature. Measurements were carried out at temperatures ranging from 350°C to 900°C in dry and wet air atmospheres, respectively, by using a computer-interfaced impedance/gain phase analyzer (Solatron, 1260A) in the frequency range of 1 Hz to 30 MHz. The collected data were analyzed using a ZView software.[13]

III. Results and Discussion

The SHS process was used to synthesize the proton conductors $Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-\delta}$(x=0, 0.05, M=Y, Yb) by the following reactions, respectively:

$$SrCO_3+0.92\ Zr+0.08\ Y_2O_3 \rightarrow SrZr_{0.92}Y_{0.08}O_{3-\delta}+CO_2(g)+\Delta Hr \qquad (4)$$

$$SrCO_3+0.92\ Zr+0.08\ Yb_2O_3 \rightarrow SrZr_{0.92}Yb_{0.08}O_{3-\delta}+CO_2(g)+\Delta Hr \qquad (5)$$

$$0.95SrCO_3+0.92\ Zr+0.08\ Y_2O_3 \rightarrow Sr_{0.95}Zr_{0.92}Y_{0.08}O_{3-\delta}+0.95CO_2(g)+\Delta Hr \qquad (6)$$

$$0.95SrCO_3+0.92\ Zr+0.08\ Yb_2O_3 \rightarrow Sr_{0.95}Zr_{0.92}Yb_{0.08}O_{3-\delta}+0.95CO_2(g)+\Delta Hr \qquad (7)$$

The average relative densities of the sintered specimens $Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-\delta}$(x=0, 0.05, M=Y, Yb) were approximately 67% for x=0 and 78% for x=0.05, respectively. It was reported that the sinterability of these materials is very poor.[12] The sintered density of $SrZr_{0.92}M_{0.08}O_{3-\delta}$ is similar to the results of other investigaters[14] and the sinterability of A-site deficient $Sr_{0.95}Zr_{0.92}M_{0.08}O_{3-\delta}$ was improved.

Fig. 1 shows the X-ray diffraction (XRD) patterns of the specimen prepared by the SHS method. These XRD patterns are in good agreement with an XRD pattern of $SrZrO_3$ shown in JCPDS 44-0161 and no impurity phase was found.

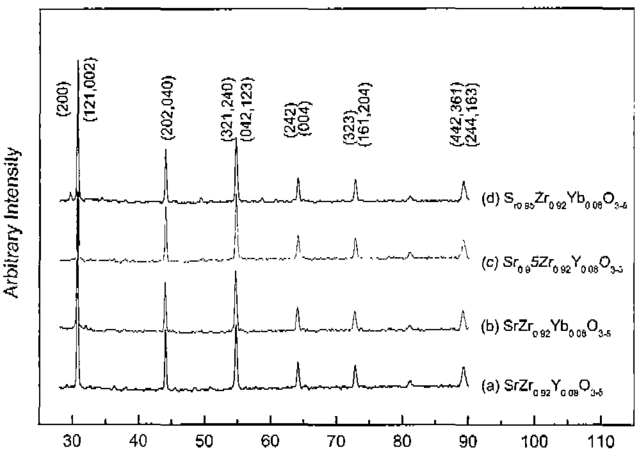

Fig. 1. X-ray diffraction patterns of $Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-\delta}$(x=0 0.05, M=Y, Yb) prepared by SHS.

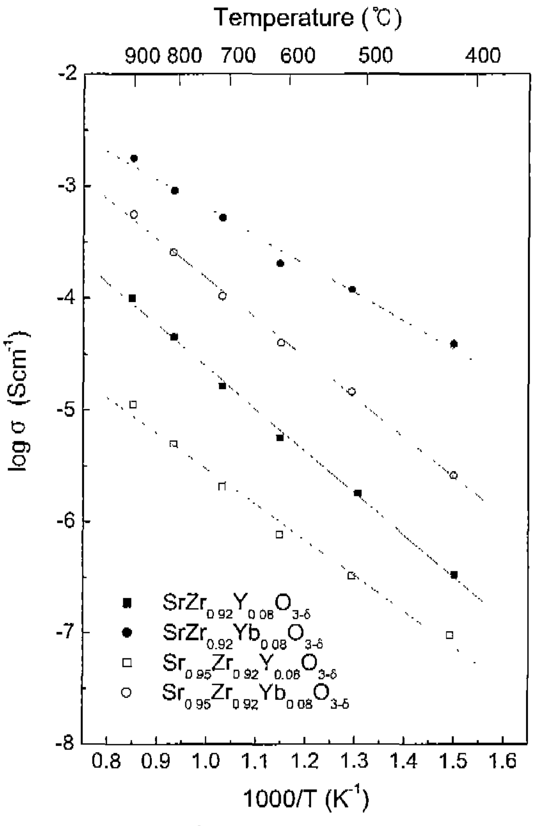

Fig. 2. Arrhenius plot of the conductivity of $Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-}$ (x=0, 0.05, M=Y, Yb) measured in dry air atmosphere.

The Arrhenius plot for the electrical conductivity of the specimens obtained from impedance measurements in dry air is represented in Fig. 2. Among four compositions of $Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-\delta}$(x=0, 0.05, M=Y, Yb), the conductivity of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ specimen is the highest value (1.8×10^{-3} S cm^{-1} at 900°C). This value is a little bit higher than those already reported for the same compositional materials.[8] In

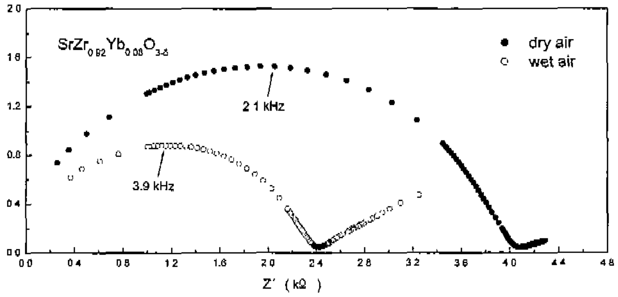

Fig. 3. Typical complex impedance spectra of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ measured at 500°C in dry and wet air atmospheres.

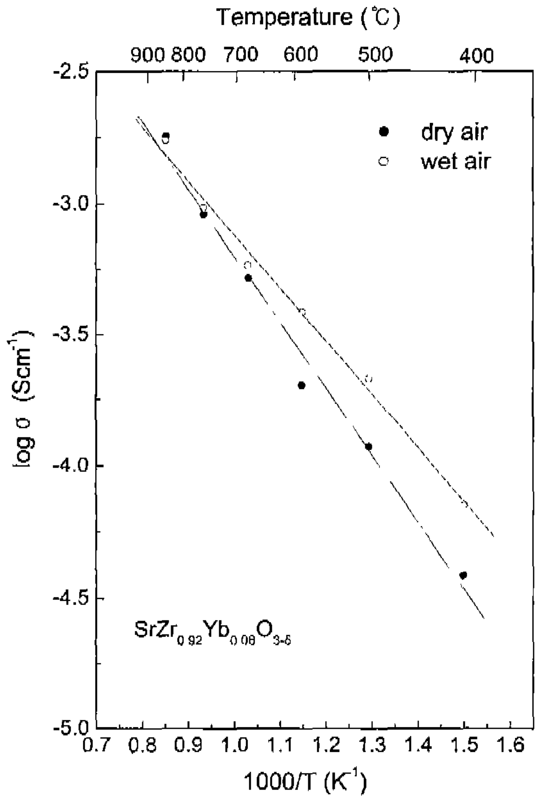

Fig. 4. Arrhenius plot of the conductivity of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ measured at 500°C in dry and wet air atmospheres.

the present experiment, A-site deficiency did not affect the conductivity.

Typical complex impedance spectra of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ measured at 500°C in dry and wet air atmospheres are shown in Fig. 3. These spectra usually show relatively well defined grain boundary semicircles for both dry and wet air atmospheres. Relaxation frequencies at the peak of the semicircles in Fig. 3 are in a few kHz at 500°C, which is much lower than those reported for bulk (grain interior) behavior of $SrZr_{0.95}Y_{0.05}O_{3-\delta}$ single crystal (a few hundred kHz to a few MHz).[15] This large grain boundary resistance may be due to the pores existing in the specimen (the sintered relative density is about 67%). At 500°C, the resistance of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ is about 4 kΩ in dry air but 2.3 kΩ in wet air. Therefore, the electrical conductivity in wet air increased due to the proton conduction. In the lower frequency range, the linear impedance variation in wet air represents behavior occuring at the proton conductor-electrode interface.[16] The complex impedances were also measured at various temperatures from 350°C to 900°C; these results were similar to those obtained at 500°C.

Figure 4 shows the Arrhenius plot for the electrical conductivity of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ in dry and wet air atmospheres. At 500°C, the conductivity was 1.2×10^{-4} S cm^{-1} in dry air and 2.2×10^{-4} Scm^{-1} in wet air. The solid lines in Fig. 4 are obtained by the linear regression from experimental data. The activation energies in wet air and dry air were 0.40 eV and 0.50 eV, respectively, and these are lower than the results of other investigators.[8]

IV. Summary

$Sr_{1-x}Zr_{0.92}M_{0.08}O_{3-\delta}$(x=0, 0.05, M=Y, Yb) proton conductors were fabricated using the powders prepared by the SHS process. The electrical conductivity of these materials obtained from impedance measurements were characterized. The electrical conductivity of $SrZr_{0.92}Yb_{0.08}O_{3-\delta}$ at 900°C in dry air atmosphere was 1.8×10^{-3} Scm^{-1} which is the highest value. It was confirmed that A-site deficiency affects the sinteribility but does not affect the conductivity. The conductivity in wet air atmosphere was higher than that in dry air.

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