THE ELECTROCHEMICAL PROPERTIES OF $Sr(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-\delta}$ PROTON-CONDUCTING OXIDES UNDER VARIOUS WATER VAPOR PRESSURES

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Abstract— In this study, the $Sr(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-\delta}$(SCZY) perovskite structure proton-conducting ceramics are successful prepared by Ethylenediaminetetraacetic acid (EDTA)-Citric acid complex method. The effect of water vapor pressure on the electrochemical properties of the SCZY in hydrogen atmosphere is investigated.The conductivity of the SCZY in dry condition is higher than that of SCZY in wet condition.From the result of AC impedance analysis, it is found that the main resistance of the SCZY both in dry or wet conditions is charge transform resistance. Thecharge transform resistance of the SCZYunder high water vapor pressure is apparently higher than that of the SZCY in dry and low vapor pressure conditions.The hydrogen permeation flux of the SCZY increases from to mmol $min^{-1}\cdot cm^{-2}$ as the temperature increases from 500 ^oC to 800^oC.

Keywords— Proton Conductor, Hydrogen, Ceramic, Water Vapor Pressure.

I. INTRODUCTION

Proton-conducting oxides recently have attracted considerable attention, because of their potential applications in proton-type solid oxide fuel cells (p-SOFCs) [1]-[4], hydrogen pumps [5], membrane separators [6]-[8] and steam electrolyzes [9]. Iwahara[10] first revealed that the perovskite $SrZrO_3$ and $LaYO_3$ had the proton-conducting conductivity. Recently, perovskite-type oxides, such as $BaCeO_3$, $SrCeO_3$, $BaZrO_3$, $SrZrO_3$doped with rare-earth elements, were widely investigated due to their high proton conductivity [11]-[14]. However, they always have the poor chemical stability in CO_2 and water containing atmosphere [15-16].

Comparing to the $BaCeO_3$-based oxides, $SrCeO_3$-based oxides have higher proton conductivity and structure stability especially in humid atmosphere [13-14]. However, the structure of $SrCeO_3$-based oxides easily decomposed into CeO_2 and $Sr(OH)_2\cdot H_2O$. The $SrZrO_3$ has a good structure stability both in CO_2 and water-containing atmosphere, even its proton conductivity is much lower than that of the $SrCeO_3$-based oxides. Therefore, $SrCe_{1-x}Zr_xO_3$-based oxides were investigated and they show high proton conductivity and good structure stability. In addition, the partial substitution of trivalent elements, such as Y^{3+}, Yb^{3+}, and Tm^{3+}, for Ce^{4+} improved the electrical conductivity and hydrogen permeation of $SrCe_{1-x}Zr_xO_3$-based oxides[8, 17,18].

The proton-conducting oxides powders are typically prepared by the solid-state reaction method, which requires a high temperaturecalcination and long dwell time. Comparing to the traditional solid-state reaction method, the powder prepared by the ethylenediaminetetraacetic acid (EDTA)-citrate acid complex method exhibits small particle size, high specific surface area, and uniform particle size distribution.

The electrochemical performance of the proton-conducting oxides depends on various factors, such as the composition, operating temperature, atmosphere and humidity, thickness and microstructure of membrane. In this study, the electrical/proton conductivity, electrochemical performance of the$Sr(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-\delta}$ (SCZY) under various water vapor pressures in hydrogen atmosphere are investigated in detail.

II. EXPERIMENTAL

$Sr(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-\delta}$ (SCZY) powder was synthesizedby the Ethylenediaminetetraacetic acid (EDTA)-Citric acid complex method [19]. The$Sr(NO_3)_2$ (Alfa Aesar, 99.0%), $Ce(NO_3)_3\cdot 6H_2O$, and $Zr(NO_3)_2\cdot 2H_2O$ (Alfa Aesar, 99.0%), and $Y(NO_3)_3\cdot 6H_2O$ (J. T. Baker, 99.8%) were dissolved in NH_3-EDTA solution, which contains 6 M NH_4OH and EDTA (Riedel-de Haën, 98%). The molar ratio of EDTA: citric acid: total metal ions was 1:1.5:1. The pH of solution was adjusted to6 with 6 M NH_4OH solution. The solution was heated to 180 ^oC on a hotplate to evaporate the water into a sticky gel. This gel was heated at 250 ^oC for 3 h, and calcined at 1100 ^oC for 12 h. The calcined powders were pressed into 10-mm-wide × 0.5-mm-thick discs at 89.63 MPa and sintered at 1450^oC for 6 h.

The structures of the SCZYpowder were analyzedbya powder diffractometer (Bruker, D2 PHASER), which emits Ni-filtered Cu Kα radiation that scans diffraction angles of 10^o to 80^o in 0.01^o steps at a rate of $1^o \cdot min^{-1}$.The microstructure of sintered SCZY disks is observed by a Field-Emission Scanning Electron Microscopy (JOEL JSM-6701F). The Archimedes method was used to measure the open porosity of the sintered ceramic pellet in distilled water. The electrical conductivity of the SCZY was measured inhydrogen atmospheres under 0, 2.46×10^{-2} and 4.93×10^{-2} atm partial pressures of waterby a DC two-terminal method. An Agilent Technologies 34970A, which comprise Pt metal electrode and wire, was used. The electrochemical impedance spectra (EIS) of the SCZYwas performed using a Solartron (1255B & SI1287) in a frequency range of 0.1 Hz to 10MHz and an AC amplitude of 30 mVat 500°C, 700°C and 900°C.

The hydrogen permeation membrane was prepared using tape casting. The SCZY powders were mixed with NiO in a weight ratio of 55 : 45, and an excess 15 wt.% of carbon powder (as the pore former) was added by ball milling the samples in ethanol for 12 h, followed by drying at 100 °C. The weight ratio of powder to ZrO_2 ball is 1: 10, and the ZrO_2 ball size is 3 mm. In order to produce the slurry, the powder and binder (B-73305, Ferro-MSI) were mixed in a weight ratio of 5:2. Ten layers of NiO/SCZY tape and one layer of SCZY tape were pressed at 90 MPa of pressure to a 35-mm diameter and 1-mm in thickness. The hydrogen permeation membrane was sintered at 1450 °C for 2 h. The hydrogen permeation measurement was conducted using a custom-made device. The membrane was sealed on an Al_2O_3 tube, using a glass ring. The Ni-SCZY side was exposed to pure hydrogen gas, and the dense SCZY side was exposed to pure argon. The gas flow rate was 150 mL/min on both sides. A gas chromatograph (GC, China Chromatography 9800) with packed columns was used to analyze the effluent. The hydrogen permeation tests were performed in a temperature range of 500-800 °C.

III. RESULTS AND DISCUSSION

A. Structure

The X-ray diffraction (XRD) pattern of the SCZYsintered at 1450 °C for 6 h was shown in Fig. 1.The all diffraction peaks match the characteristic reflections of the ABO_3 orthorhombic perovskite structure of $SrCeO_3$ (JCPDS 82-2370).A small amount of the SrY_2O_4 second phase was observed.The lattice parameters of the SCZY determined using the XRD pattern are a = 8.4458 Å, b = 5.9354 Å, c = 6.0154Å, and cell volume = 301.55 $Å^3$, which are in agreement with the results of Zhang [18]. The lattice parameters of the SCZY are smaller than those of $SrCeO_3$ (a = 6.000 Å, b = 6.145 Å, c = 8.575 Å, and cell volume = 316.2 $Å^3$, JCPDS 82-2370), due to the substitution of Zr^{4+} (0.72 Å) and Y^{3+} (0.90 Å) for Ce^{4+} (0.87 Å). In this study, the Ce^{4+} was replaced by 36 % of Zr^{4+} and 10 % of Y^{3+}. Even the radius of Y^{3+} is slightly larger than that of Ce^{4+}, but the amount of Zr^{4+} is much higher that of Y^{3+}. Therefore, the lattice parameters of SCZY is apparently smaller than that of $SrCeO_3$. This XRDresult confirms the dissolution of Zr and Y in the $SrCeO_3$-based perovskite structure.

B. Morphology

Fig. 2 shows the SEM micrograph of the SCZY disk sintered at 1450°C for 6h. It is observed that the microstructure of the sintered SCZY disk is dense with a few closed pores in the SCZY. The relative density of the sintered SCZY diskis 99.32 %, which was measured by Archimedes method. In addition, it was found that the SrY_2O_4 second phase is observed on the grain boundary of the SCZY.The average grain size of the sintered SCZY is 3.87μm.

C. Electrical conductivity

Fig. 3 shows the electrical conductivity of the SCZY as a function of temperature in hydrogen atmosphere under various partial pressures of water. The conductivity of the SCZY both in dry and wet hydrogen atmospheresincreases as the temperature increases, which prove the carrier is proton. The conductivity of the SCZY in dry hydrogen atmosphere ismuch higher than that in wet hydrogen atmosphere at various temperatures. The electrical conductivity of SCZY in dry hydrogen atmosphereis 0.012 $S \cdot cm^{-1}$at 800 °C, which ismuch higher than that in wet hydrogen atmosphere. However, there is not apparent difference in conductivity for the SCZY under P_{H2O}=2.46□10^{-2} atm and P_{H2O}=4.93□10^{-2} atm, respectively.

Fig. 4 shows the Arrhenius plot of conductivity of SCZY under various water vapor pressures. In the Arrhenius plot, it shows one conductivity mechanism for SCZY in dry and P_{H2O}=2.46□10^{-2} atm atmospheres, there are two conductivity mechanism under high water vapor pressure of P_{H2O}=4.93□10^{-2} atm. In a steam hydrogen-containing atmosphere, the hydrogen in the gas steam and oxide ions in the perovskite materials are directly incorporated as protons and electrons. In addition, the interaction of oxygen vacancies with water produces proton charge carriers ($OH_o^{\cdot}$). A proton jumps from one oxygen ion to another and each jump is followed by a rotation around the oxygen ion to position for the next jump [20]. The water vapor pressure and the concentration of the oxygen vacancies in perovskite materials are the major factors that affect the conductivity and hydrogen permeation flux of the material. In this study, the concentration of oxygen vacancy is fixed, which is generated by the doped Y^{3+} cations. Therefore, the conductivity of the SCZY only depends on the water vapor pressure. In dry hydrogen atmosphere, the hydrogen reacts with oxide ions in the lattice to produce the hydroxide species and electrons, resulting in increasing the electron conductivity. In dry air, the

SCZY perovskite is a mixed conductor of oxygen-ion, proton and electron [21]. However, it is only a mixed conductor of proton and electron in hydrogen steam atmospheres because the oxygen partial pressure is low. The oxygen partial pressure depends on water vapor pressures. The oxygen partial pressure of P_{H2O} = 2.46 x 10^{-2} and P_{H2O} =4.93 x 10^{-2} atm respectively is 3.43 x 10^{-22} and 1.45 x 10^{-21}atm at 800 °C. Higher steam concentration and higher temperature results in higher oxygen partial pressure. Therefore, it was found that the conductivity of SCZY in humid H_2 atmosphere is lower than that in dry hydrogen atmosphere, which was shown in Fig. 3. This result is consist to the results reported by Zhang [18].

D. Electrochemical impedance spectroscopy

Fig.5 shows the impedance spectra of SCZYsample at different temperatures in hydrogen atmosphere under various water vapor pressure.The symbols of Z_c,R_b, R_{gb}, R_{ct} and $R_t$respectivelyis the ohm resistance, bulk resistance,grain boundaryresistance, charge-transfer resistanceand total resistance.The Z_c,R_b, R_{gb},R_{ct} and $R_t$of SCZYtypically decrease with the temperature increases. The main resistance comes from the charge-transfer phenomenon, which is apparently higher than Z_c,R_b and R_{gb}. At low temperature (500°C), the R_t of the SCZY under dry hydrogen is higher than that in the wet hydrogen; however,at high temperatures (700°C and 900°C), the R_t of the SCZY under wet hydrogen is higher than that in the dry hydrogen. From the result of EIS, it was found that ohm resistance(Z_c), bulk resistance(R_b),grain boundaryresistance(R_{gb})andcharge-transfer resistance(R_{ct})are allaffected bythe water vapor pressure, especially for the charge-transfer resistance(R_{ct}). The charge-transfer resistance of SCZY under high water vapor pressure increases due to the lower electrical conductivity at higher oxygen partial pressure.

E. Hydrogen flux

The cross-sectional SEM micrograph of the Ni-SCZY/SCZY hydrogen transport membrane is shown in Fig. 6. The thickness of the SCZY membrane is approximately 60μm. This microstructure shows that SCZY membrane is dense and bondedwell with the Ni-SCZY porous supporter. There is no crack between SCZY membrane and porous Ni-SCZY supporter. The pores in Ni-SCZY supporter are formed when carbon powders (the pore former)are removed during sintering process and NiO is reduced to Ni in hydrogen atmosphere.

Fig.7 shows the hydrogen permeation flux of the Ni-SCZY/SCZY hydrogen transport membrane as a function of temperature. The hydrogen permeation flux ofthe SCZY membrane respectively is 0.94, 1.22, 1.37 and 1.47 ml·min^{-1}·cm^{-2} at 500, 600, 700 and 800°C. Apparently, the hydrogen permeation flux increases as the temperature increases.

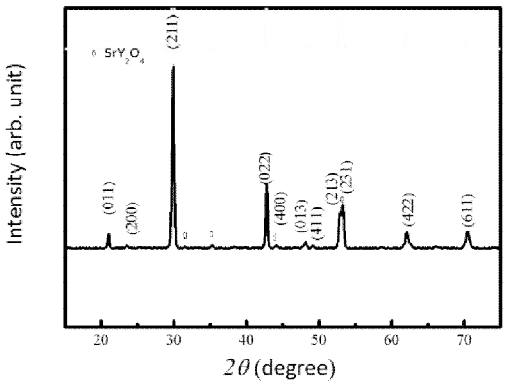


Fig 1. XRD pattern of the SCZYsintered at 1450 °C for 6 h.

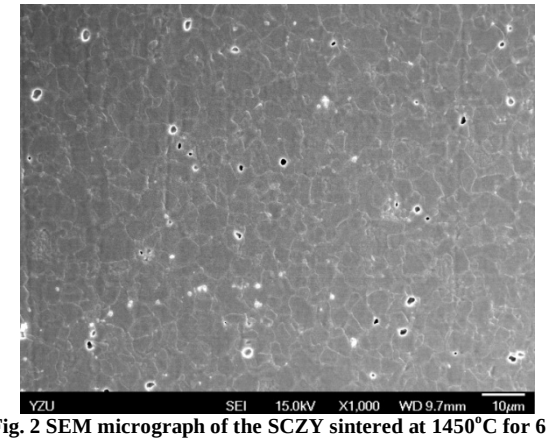


Fig. 2 SEM micrograph of the SCZY sintered at 1450°C for 6 h

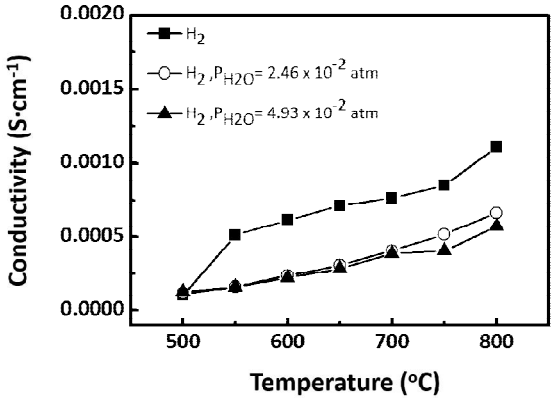


Fig 3. Conductivity of the SCZYat various temperatures under different atmospheres.

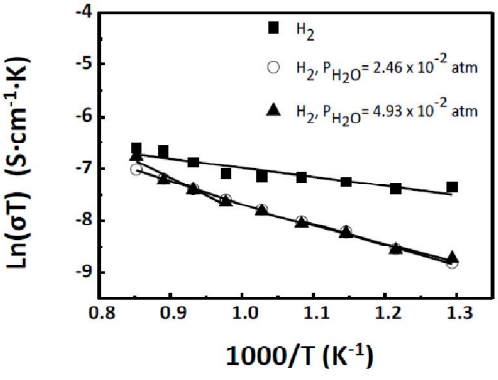


Fig. 4 Arrhenius plot of conductivity of SCZY under various

water vapor pressures.

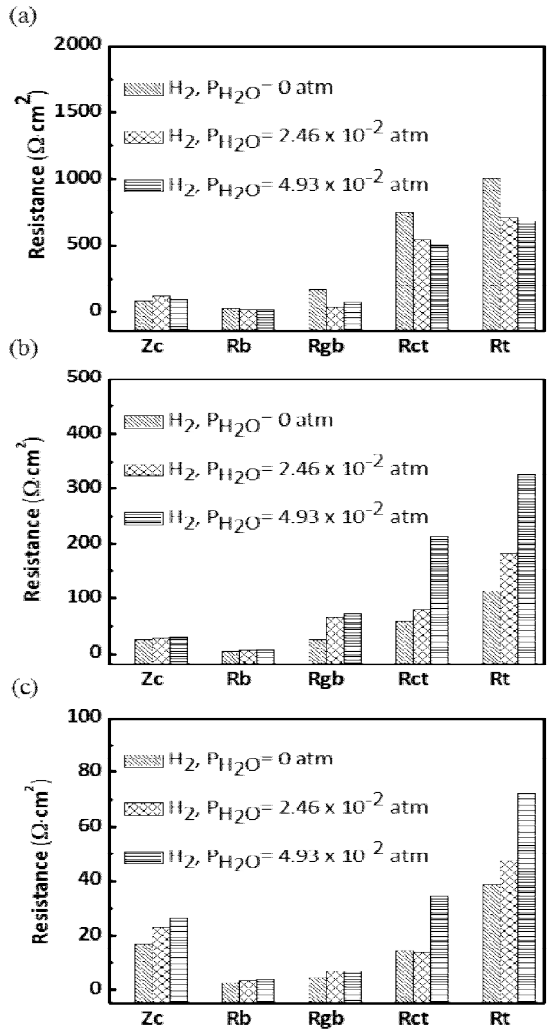


Fig. 5Resistance values of SCZY at (a)500, (b)700, and (c)900 °C under different atmospheres.

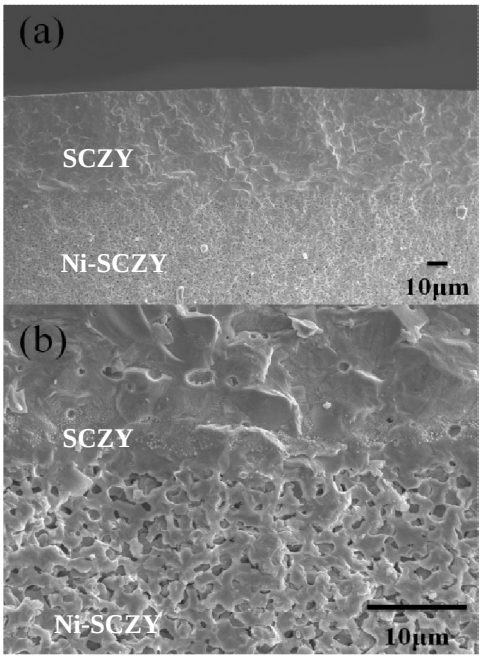


Fig. 6 The cross-section micrographs of the Ni-SCZY/SCZY hydrogen transport membrane at (a) low magnification and (b) high magnification.

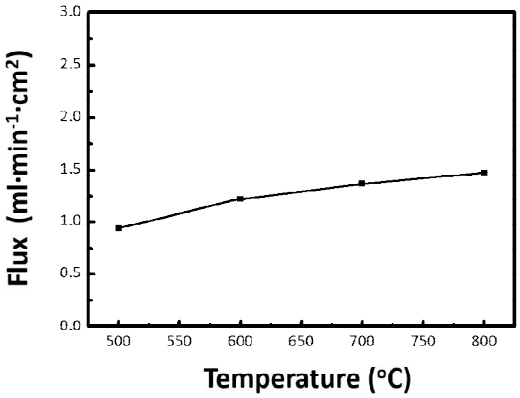


Fig. 7Hydrogen flux of Ni-SCZY/SCZY hydrogen transport membrane at various temperatures under dryhydrogen atmosphere.

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