



Regular Article

Electrical conduction behavior of mixed ionic–electronic conductor

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ABSTRACT

$Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ was synthesized via sol–gel method. With the Sc-doping amount increasing, the electrical conductivity of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ increased in 400–900 °C and the ionic conductivity increased between 600 and 900 °C. The optimized $Y_{0.08}Sr_{0.92}Ti_{0.93}Sc_{0.07}O_{3-\delta}$ sample exhibits an electrical conductivity in the order of 0.058–0.085 S·cm⁻¹ at 400–900 °C. The ionic conductivity for $Y_{0.08}Sr_{0.92}Ti_{0.93}Sc_{0.07}O_{3-\delta}$ was 0.027 S·cm⁻¹ and increased about 140% compared with $Y_{0.08}Sr_{0.92}Ti_{0.97}Sc_{0.03}O_{3-\delta}$ at 800 °C. Sc-doping increased the oxygen vacancy concentration and decreased the oxygen migration energy, therefore enhancing the conduction process of oxygen ions in $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$. The possible charge compensation mechanism of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ can be described as $Y_{0.08}Sr_{0.92}Sc_x^{3+}Ti_{0.92-2\delta-x_1}^{4+}Ti_{0.08+2\delta-x_2}^{3+}O_{3-(\delta+x_1/2)}(x=x_1+x_2)$.

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1. Introduction

Perovskite oxides (ABO₃) are particularly attractive for high-temperature applications, because of the microstructural stability to improve reliability and long-term performance and mixed electronic–ionic conductivity that make the triple-phase boundary extend to the entirely exposed anode surface as anode materials for solid oxide fuel cells, in addition to having high melting and decomposition temperatures [1,2]. Strontium titanate (SrTiO₃) with perovskite structure shows high chemical stability at high temperature under both oxidizing and reducing atmospheres and has strong resistance to suffer poison [3]. In addition, the perovskite structure of strontium titanate has two differently-sized cations, which makes it favorable to a variety of dopants. This doping flexibility can control the electron and ion transport properties to optimize performance for different applications. Generally, electronic conduction can be enhanced in SrTiO₃ by replacing A- or B-site cations with n-type dopants such as La³⁺, Y³⁺ or Nb⁵⁺ [4–8]. It is well known that n-doping generates a defect with an effective positive charge in the host lattice. Ionic conduction can be improved by doping with Fe³⁺, Cr³⁺, Sc³⁺ or Ni²⁺ [9–19], in place of the B site, results in a p-type semiconductor by generating oxygen vacancy.

The relevant studies indicated that donor-doping on A-site of SrTiO₃ mainly affected the electronic conductivity rather than ionic conductivity [20]. In addition, the study by Li X and Zhao H [3] demonstrated that the tendency of oxygen ion migration energy increases in the order B = Sc < Co < Ni < Ti for SrBO₃, implying Sc was a good choice

of all the present elements to improve the ionic conductivity of SrTiO₃-based materials. Therefore, the effects of Sc-doping amount on the electrical and ionic conductivities of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ with temperature were investigated. The charge compensation mechanism in $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ was discussed.

2. Experimental

2.1. Sample preparation

$Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ ($x = 0.03, 0.05, 0.07$) powders were synthesized by using sol–gel method. The raw materials were high purity Sr(CH₃COO)₂·2H₂O, Ti(CH₃CH₂CH₂CH₂O)₄, Sc₂O₃ and Y₂O₃. Appropriate amounts of the starting materials (Ti(CH₃CH₂CH₂CH₂O)₄, Sc₂O₃ and Y₂O₃) were dissolved into the mixed solution with the molar ratio of isopropanol to ethanol at 4:1 under magnetic stirring followed by the addition of strontium acetate. The resultant solution was heated in a water bath of 60 °C until a viscous gel was formed. The gel was heated in an evaporating dish on an electric furnace until self-igniting, yielding white and porous powders. The ground powders were calcined at 1100 °C for 10 h. The calcined powders were uniaxially pressed into pellets under the pressure of 50 MPa. The sintering step was carried out at 1450 °C for 5 h with the green pellets being into the platinum crucible for the measurement of total electrical and ionic conductivities.

2.2. Characterization

X-ray diffraction (XRD, Rigaku D/max-A) with Ni filtered Cu K α radiation was employed to identify the phase composition for the sintered samples $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ ($x = 0.03, 0.05, 0.07$) with a 0.02°

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stepwise at room temperature. The relative density of all the samples was around 95%, which was estimated from the weight and dimensions measurement. The cross-section morphology was observed by scanning electron microscopy (SEM, Quanta FEG 650).

The total electrical conductivity was measured by AC impedance spectroscopy with the CHI660B electrochemical workstation over the frequency range of 1 MHz to 0.01 Hz with a perturbation amplitude of 5 mV. The data analysis was carried out with appropriate equivalent circuit by Zsimpwin software. The well-polished samples (~7.2 mm in diameter and ~1.6 mm in thickness) were painted with platinum paint on both sides and Pt wires were used to fabricate the electrodes and baked at 800 °C for 0.5 h. The total electrical conductivity calculation was performed with overall area and thickness of the samples.

The ionic conductivity was measured by electron-blocking method within 600–900 °C. The sample was plastered onto dense YSZ tablet with a little Pt paste, overcoming the interface resistance. Platinum paint was painted to the side of sample and YSZ tablet. The electron is blocked by YSZ layer because YSZ is almost a pure oxygen ion conductor. Glass seal can prevent oxygen leakage along the sides of the assembled samples. The impedance spectra of double layer materials can be observed at designated temperatures. Therefore, the ionic conductivity calculation of sample (σ_i) was performed as following equation:

$$\sigma_i = \frac{d_{YSTS}}{(R_T - R_{YSZ}) \times A_{YSTS}} (\text{Ohm} \cdot \text{cm})^{-1} \quad (1)$$

Where d_{YSTS} is the thickness of sample (in cm), R_T is the total resistance, R_{YSZ} is the resistance of YSZ and A_{YSTS} is the area (in sq. cm) of the sample.

3. Results and discussion

3.1. XRD patterns and SEM micrographs

XRD patterns of the sintered samples were collected at room temperature and the results were displayed in Fig. 1. The sample $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ with $x = 0.07$ shows a single cubic perovskite structure (inset PDF79-174), whereas a secondary phase of $Y_2Ti_2O_7$ was observed the doping level decreased to 0.05 and 0.03. The content of the secondary phase decreases with Sc-doping amount increasing as indicated by the strengthening diffraction intensity of $Y_2Ti_2O_7$, indicating that Sc-doping facilitates the formation of single cubic perovskite phase.

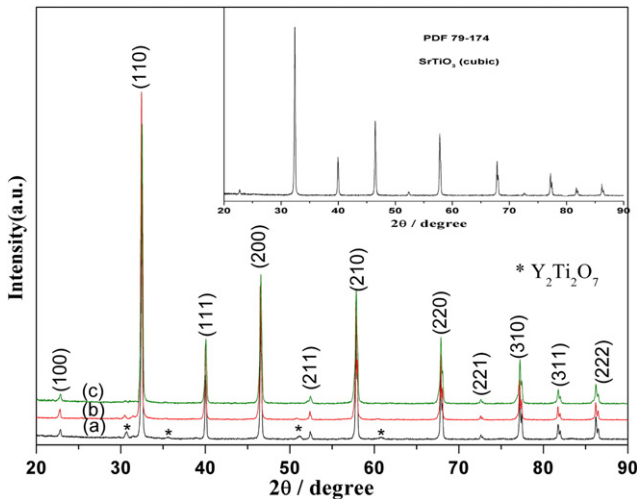


Fig. 1. XRD patterns of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ after sintering at 1450 °C for 5 h: (a) $x = 0.03$; (b) $x = 0.05$; (c) $x = 0.07$.

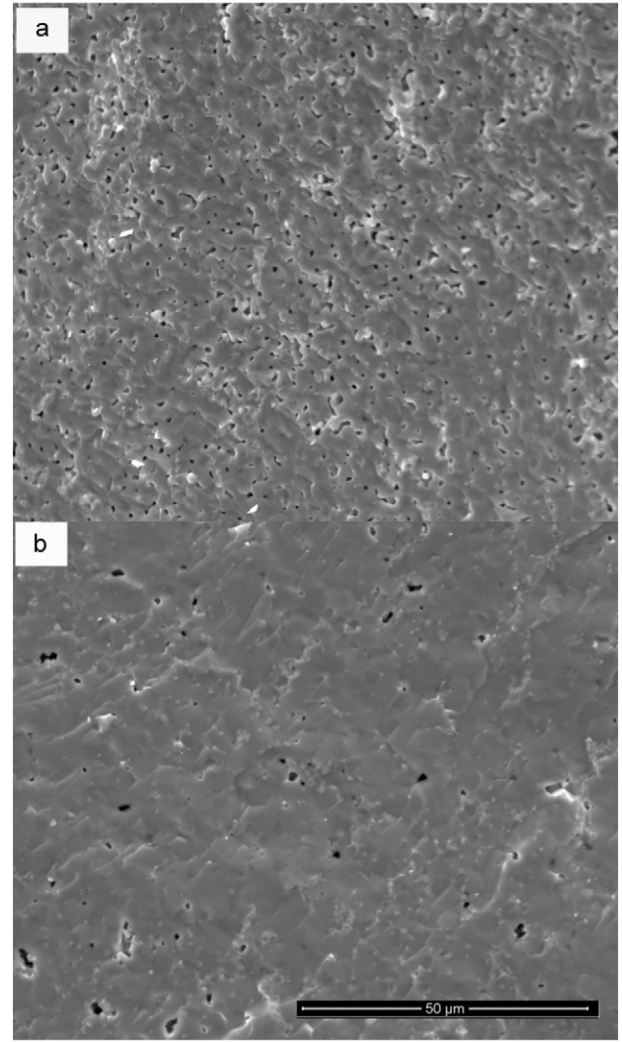


Fig. 2. SEM micrographs of fracture surfaces of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$: (a) $x = 0.03$ and (b) $x = 0.07$.

The microstructure of a couple of selected samples was observed by SEM on fracture surfaces and representative micrographs are reported in Fig. 2. As shown in Fig. 2, the densities of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ samples increase with Sc-doping amount increasing, indicating that Sc-doping is favorable to the densification process of the materials synthesized by the sol-gel route in the present work.

3.2. The electronic and ionic conductivities of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$

The temperature dependence of total electrical conductivities of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ ($x = 0.03, 0.05, 0.07$) is shown in Fig. 3. Sc-doping enhances the electrical conductivity of $SrTiO_3$ significantly. The optimized $Y_{0.08}Sr_{0.92}Ti_{0.93}Sc_{0.07}O_{3-\delta}$ sample exhibits an electrical conductivity in the order of $0.058\text{--}0.085 \text{ S} \cdot \text{cm}^{-1}$ at 400–900 °C. The total electrical conductivity is the sum of electronic conductivity and ionic conductivity and its value is directly related with the type and concentration of point defects existing in the materials. In addition, the total electrical conductivity increased through a maximum then decreased with the temperature increasing, indicating a polaron conduction behavior of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$, corresponding to the high electron concentration. On the other hand, the ionic conductivity of $Y_{0.08}Sr_{0.92}Ti_{1-x}Sc_xO_{3-\delta}$ increased with Sc-doping amount increasing remarkably (Fig. 4). The ionic conductivity of $Y_{0.08}Sr_{0.92}Ti_{0.97}Sc_{0.03}O_{3-\delta}$ was $0.02 \text{ S} \cdot \text{cm}^{-1}$ at 850 °C, while it increased to $0.029 \text{ S} \cdot \text{cm}^{-1}$ for $Y_{0.08}Sr_{0.92}Ti_{0.95}Sc_{0.05}O_{3-\delta}$ and $0.033 \text{ S} \cdot \text{cm}^{-1}$ for

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