



# Electrical properties of yttrium doped strontium titanate with A-site deficiency as potential anode materials for solid oxide fuel cells

Hailei Zhao <sup>a,c,\*</sup>, Feng Gao <sup>a,b</sup>, Xue Li <sup>a</sup>, Cuijuan Zhang <sup>a</sup>, Yueqing Zhao <sup>a</sup>

<sup>a</sup> Department of Inorganic Nonmetallic Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

<sup>b</sup> Chinese Academy of Agricultural Mechanization Sciences, China

<sup>c</sup> Beijing Key Lab of New Energy Materials and Technology, Beijing 100083, China

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## ABSTRACT

Yttrium doped strontium titanate with A-site deficiency ((Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub>) was synthesized by conventional solid state reaction. The deficiency limit of A-site in (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> is below 6 mol% in Ar/H<sub>2</sub> (5%) at 1500 °C. The sinterability of (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> samples decreases slightly with increasing A-site deficiency level (x). The ionic conductivity of (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> samples increases while the electronic conductivity decreases with increasing A-site deficient amount. The defect chemistry analysis indicates that the introduction of A-site deficiency results in not only the increase of oxygen vacancy concentration but also the decrease of Ti<sup>3+</sup>-ion concentration. The latter plays the main role in the electrical conduction. (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> shows good thermal-cyclic performance in electrical conductivity and has an excellent chemical compatibility with YSZ electrolyte below 1500 °C.

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## 1. Introduction

Solid oxide fuel cell (SOFC) is an all-ceramic electrochemical device that operates in temperature range of 500–1000 °C. It has been studied as a promising energy conversion and generation system due to its high efficiency, fuel adaptability, low emissions and pollution [1–3], and its potential for co-generation. Anode is one of the most important components of SOFC. Nickel/YSZ cermet is the usual anode material. However, this type of anode suffers from the disadvantage of resistance losses due to nickel grain sintering at high operating temperature [4], sulfur poisoning, volume instability upon redox cycling, and carbon deposition when utilizing natural gas as fuel [5–7]. Therefore, new anode materials are in demands for further development of SOFCs.

Several authors have demonstrated that anodes based on perovskite structure are promising candidates for future fuel cell anodes [8–12]. Strontium titanate, SrTiO<sub>3</sub>, which has a perovskite structure, is highly attractive because of its desired thermal and chemical stability, and semiconducting behavior [13]. However, it shows a low electrical conductivity, which is one of the main problems that prevent SrTiO<sub>3</sub> as a practical anode for SOFC. Doping with aliovalent elements on A or/and B sites has the possibility to improve the electronic and/or ionic conductivity of SrTiO<sub>3</sub> via the introduction of various ionic and electronic defects [14,15]. Doping donors such as La<sup>3+</sup> on the Sr<sup>2+</sup> site and Nb<sup>5+</sup> on

the Ti<sup>4+</sup> site convert SrTiO<sub>3</sub> into a highly semiconducting *n*-type material [16,17], while doping acceptors such as Fe<sup>3+</sup>, Co<sup>3+</sup> and Al<sup>3+</sup> on the Ti<sup>4+</sup> site obtain a *p*-type material [18–21]. The fuel cell tests with La<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> anodes demonstrated the potential ability of doped SrTiO<sub>3</sub> to be used as SOFC anodes [15]. Hui and Petric [22] reported Y<sub>x</sub>Sr<sub>1-1.5x</sub>TiO<sub>3</sub> for its unusual high electrical conductivity and good compatibility with YSZ which make it a probable candidate as an anode for SOFC. Huang et al. and Li et al. [23,24] reported the electrical conduction behavior and the chemical compatibility with YSZ of Y<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>, and Y<sub>0.08</sub>Sr<sub>0.92</sub>TiO<sub>3</sub> was found to give the maximum electrical conductivity, 71 S cm<sup>-1</sup> at 800 °C in pure hydrogen. Nevertheless, the single cell with Y-doped SrTiO<sub>3</sub> as anode showed an unsatisfactory power density of 54 mW cm<sup>-2</sup> at 900 °C. More effort, undoubtedly, should be made on the optimization of yttrium-doped SrTiO<sub>3</sub>. Introducing deficiency to the A-site of perovskite structure can also enhance the electrical and ionic conductivity and control the thermal expansion coefficient [25–28]. In this work, some deficiency was introduced into the A-site of Y<sub>0.08</sub>Sr<sub>0.92</sub>TiO<sub>3</sub> to improve the ionic conductivity. The electrical conduction behavior of (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> samples was investigated, where a certain amount of oxygen vacancies is supposed to be produced as charge compensation and accordingly the ionic conductivity should be enhanced. The effects of A-site deficiency level on the properties of (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> in terms of sinterability and electronic and ionic conductivities as a function of temperature were investigated. The possible charge compensation mechanism was discussed. The thermal-cyclic performance of electrical conductivity of (Y<sub>0.08</sub>Sr<sub>0.92</sub>)<sub>1-x</sub>TiO<sub>3-δ</sub> and the chemical compatibility with YSZ electrolyte were also examined.

\* Corresponding author. Tel.: +86 10 82376837; fax: +86 10 82376837.

E-mail address: hlzhao@mater.ustb.edu.cn (H. Zhao).

## 2. Experimental

Yttrium doped strontium titanate with A-site deficiency powders ( $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$ ,  $x=0, 0.01, 0.02, 0.03, 0.04, 0.05$ ) were prepared by conventional solid-state reaction from  $Y_2O_3$ ,  $TiO_2$  and  $SrCO_3$ . After ball-milling for 10 h, the mixture of raw materials was calcined at 1300 °C for 10 h under reducing condition (5% hydrogen in argon with oxygen partial pressure of  $10^{-7}$  atm). The so-obtained powders were ground slightly to destroy agglomerates and then pressed into bars (40 mm–7 mm–3 mm) by uniaxial pressing (ca. 115 MPa). The green bars were sintered in  $Ar/H_2$  (5%) at 1500 °C for 10 h and then cooled with a cooling rate of 3–5 °C  $min^{-1}$  in different stages to get dense samples. Sintered bars were polished for density, microstructure, electrical and ionic conductivity measurements. The phase identification was attained by X-ray powder diffraction (XRD) using a Rigaku D/max-A X-ray diffractometer. The densities of all samples were determined by Archimedes' method using water as the liquid medium.

The total electrical conductivity of all samples were measured in  $Ar/H_2$  (5%) by the standard four-terminal dc method [29,30] in the temperature range of 50–1000 °C, while the ionic conductivity were determined by blocking electrodes method [31] in the temperature range of 500–1000 °C in  $Ar/H_2$  (5%). All measurements were taken after holding at each temperature to equilibrate for at least 15 min when no significant change in conductivity was observed. Each conductivity was the average of four values from different samples. To examine the compatibility of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  with YSZ, the 1300 °C-fired  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  was mixed with YSZ in the weight ratio of 1:1, followed by uniaxial pressing and sintering at different temperatures. The sintered pellet was crushed and examined by XRD to identify the phase compositions.

## 3. Results and discussion

$(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  ( $x=0, 0.04, 0.05, 0.06, 0.07, 0.10$ ) powders fired at 1500 °C for 10 h in  $Ar/H_2$  (5%) were examined by XRD to identify the phases. The results are shown in Fig. 1. Samples with  $x=0, 0.04, 0.05, 0.06$  show a single cubic perovskite structure and no impurity peaks were detected, while for samples with  $x=0.07, 0.1$ , a brookite-phase  $TiO_2$  was observed. Thus, the deficiency limit of A-site in  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  at 1500 °C in  $Ar/H_2$  (5%) is ca. 6 mol%.

SEM observation (Fig. 2) and density measurement reveal that the relative density of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  sintered at 1500 °C for 10 h in  $Ar/H_2$  (5%) decreases with increasing deficiency level of A-site elements. Usually, A-site deficiency is favorable for the densification process of

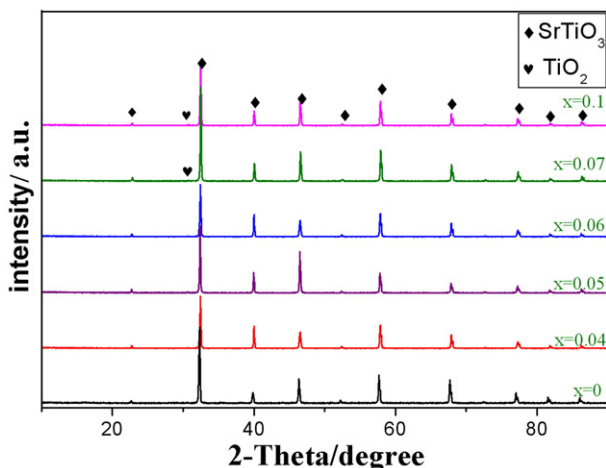


Fig. 1. XRD patterns of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  fired at 1500 °C in  $Ar/H_2$  (5%).

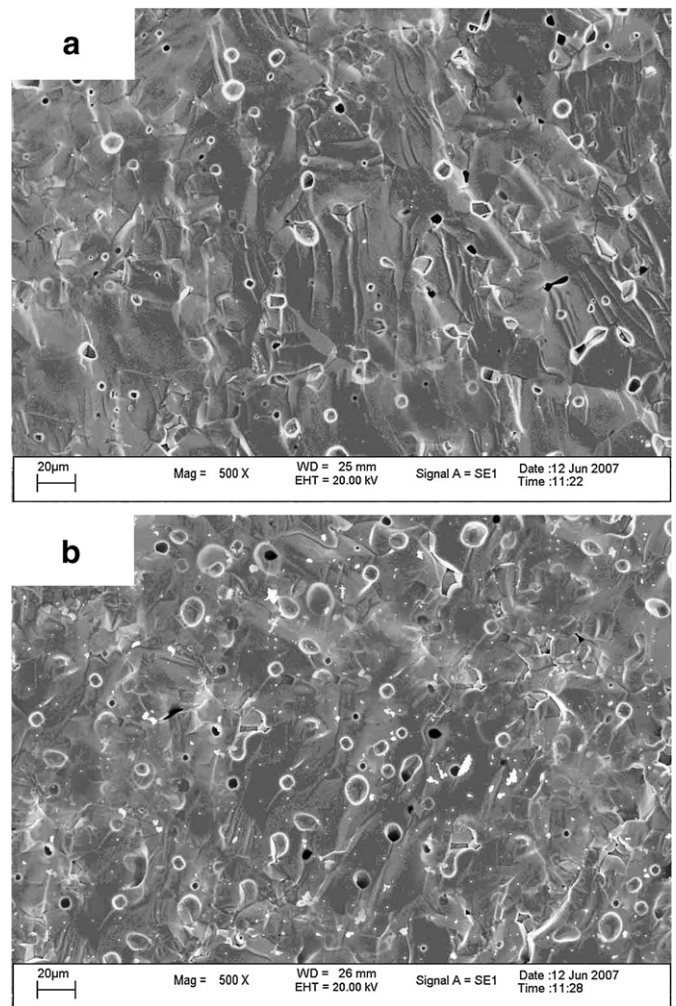


Fig. 2. SEM fractographs of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  sintered at 1500 °C for 10 h: a:  $x=0.01$  and b:  $x=0.05$ .

perovskite-type oxides due to the formation of A-site vacancy [32,33]. The decreased relative density of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  with A-site deficiency amount is attributable to the decreased Y-content in the compound. Previous studies showed that Y-doping could promote the densification process of  $SrTiO_3$  [24]. With the increase of  $x$  value, the content of Y in  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  decreases, thus the densification process of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  was impeded. Nevertheless, the relative density of all investigated samples is higher than 90%. No interconnected pore is observed in these samples.

The electrical conductivity of samples  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  ( $x=0.01, 0.02, 0.03, 0.04, 0.05$ ) was measured in  $Ar/H_2$  (5%) in the temperature range of 50–1000 °C. The results are shown in Fig. 3. The electrical conductivity of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  is much higher than the reported value [22], even higher than that we reported previously [24]. This is considered to be ascribed to the features of  $Y_2O_3$  raw material, including the purity and particle size. With increasing temperature, the electrical conductivity of yttrium doped strontium titanate with A-site deficiency increases through a maximum and then decreases, demonstrating a polaron conduction behavior of  $(Y_{0.08}Sr_{0.92})_{1-x}TiO_{3-\delta}$  materials [34–36]. The electrical conductivity decreases gradually with increasing deficiency level of A-site elements. On the other hand, the ionic conductivity increases remarkably with the deficiency level of A-site elements, as illustrated in Fig. 4. Due to the low mobility of oxygen vacancies compared to electrons, oxygen vacancies will make little contribution to the total

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