Electrical Conduction and Impedance Behavior of Sr$_{0.97}$Ti$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ Electrode Containing YSZ for Various Applications

Zhong-Zhou Yi$^{a,b}$, Fengrui Zhai$^{a,b}$, Nan Li$^{a,b}$, Ke Shan$^{a,b,*}$

$^a$ College of Science, Honghe University, Yunnan Province, 661199, China

$^b$ Local Characteristic Resource Utilization and New Materials Key Laboratory of Universities in Yunnan, College of Science, Honghe University, Yunnan Province, 661199, China

Corresponding author: shankekeshan@163.com

Abstract. Sr$_{0.97}$Ti$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ (STF) and 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) composites were prepared by mixing them in different weight fractions. The composites were compacted into discs, sintered and evaluated for phase stability, microstructure and mixed ionic-electronic conductivity. Phase analysis by XRD showed no clearly detectable secondary phases. Chemical analysis by energy dispersive spectroscopy (EDS) also showed the diffusion of elements (especially Y and Zr from YSZ). The electrical conductivity measurement on the STF-YSZ composites showed a decrease in total electrical and ionic conductivities with YSZ amount increasing. And the ionic conduction mechanism was concerned by impedance behavior analysis.

1. Introduction

In the last few years, the most developed fuel electrode in solid oxide cells is based on Ni-YSZ composite. However, the limitations of these electrodes include sulfur poisoning and mechanical instability due to large volume changes associated with Ni oxidation and reduction[1,2]. Ceramic electrodes are considered as an alternative to Ni-YSZ cerments because oxides are stable upon exposure to oxidizing conditions. Oxides anodes are more stable than metals to coarsening at high temperatures. Furthermore, oxides are generally more tolerant of impurities like sulfur than metals[3]. Strontium titanate (SrTiO$_3$) with perovskite structure shows high chemical stability at high temperature under both oxidizing and reducing atmosphere, and has strong resistance to carbon deposition and poison[4]. However, its relatively low electronic and ionic conductivity are unsuitably practical anode for SOFCs. Common to most titanate perovskites, acceptor doping promotes p-typing conduction and ionic conductivity[5].

Doped SrTiO$_3$ attracted great deal of attention because of their mixed electronic and ionic conduction behaviors that make the triple-phase boundary (TPB) extend to the entirely exposed anode surface[6-12]. D.P. Fagg observed that Fe co-doped SrTiO$_3$ materials can be potentially used as electrodes in solid oxide cells with comparable electrochemical performance of Ni-YSZ cerments[13]. However, Sr(Ti,Zr)O$_3$ was found at the composites of Sr$_{0.97}$Ti$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ and YSZ, which may result from the reaction after the inter-diffusion of Zr from the YSZ and Sr or Ti from the oxide.
anode[3,13,14,15]. Therefore, the compositional stability issues in these composite electrodes should be focused.

All present works mainly focused on the effect of doping elements on the total conductivity of doped SrTiO$_3$ and scarce work concerns the oxygen ionic conductivity, although ionic conductivity is a very important factor for anode. In the present work, Fe-doped SrTiO$_3$ (STF) was chosen and composites were prepared with 8 mol% yttria doped zirconia (YSZ). The chemical compatibility between STF and 8YSZ with an increasing YSZ weight fraction was examined after the high temperature. The electrical and ionic conductivities of STF-YSZ composites were investigated because the formation of the composites between SrTiO$_3$ and YSZ has a very important effect on the triple-phase boundary for SOFCs. Finally, the ionic conduction mechanism was concerned by impedance behavior analysis.

2. Experiments

Preparation of Sr$_{0.97}$Ti$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ powders was carried out by sol-gel method from high purity Ti(OC$_4$H$_9$)$_4$, Fe$_2$O$_3$, and Sr(CH$_3$COO)$_2$·2H$_2$O. Strontium acetate was completely dissolved in a deionized water and Ti(OC$_4$H$_9$)$_4$ was dissolved in a mixed solution of isopropanol and absolute ethanol (Volume ratio is 4:1). Then, Fe$_2$O$_3$ was added to Ti(OC$_4$H$_9$)$_4$ solution, Strontium acetate solution was introduced to the mixture at room temperature with high stirring rate on magnetic stirrer. The reaction mixture was stirred for 30 min then was allowed for 24 h to settle down and dried at 60°C. Calculation of reactants at 1100°C for 12 h and preparation of pellets by uniaxial pressing were followed. Dense single-phase samples were obtained after sintering in air at 1250°C for 6 h. Then, YSZ powder was prepared by the co-precipitation method. The mixture solution of ZrOCl$_2$·8H$_2$O (AR) and Y(NO$_3$)$_3$(AR) reacted with NH$_3$·H$_2$O (AR) in aqueous solution (pH value=10) at room temperature with high stirring rate on magnetic stirrer. The reaction mixture was stirred for 12 h then was allowed for 24 h to settle down. Calculation of reactants at 600°C for 2.5 h was sintered at 1400°C for 5 h in air. The weight ratio of STF to YSZ were 97:3 and 95:5, respectively. The obtained mixed powders were ground with mortar and pestle and were uniaxially pressed into a pellet. The green pellets were densified at 1250°C for 6 h in air to achieve dense samples for the measurement of total electrical and ionic conductivities.

The phase composition of samples was identified using an X-ray diffractometer (XRD) with CuK$_\alpha$ radiation (Rigaku D/ max-B, Tokyo, Japan). The microstructure of the fracture surfaces were observed with scanning electron microscope (SEM) (Quanta FEG 650). The AC impedance spectra were obtained over the frequency range of 1 MHz to 0.01 Hz at an amplitude of 5 mV by an impedance analyzer (Chi660B). The temperature fluctuation at each temperature point was controlled to be within ± 0.1 °C. Platinum paint and Pt wires were used to fabricate the electrodes. The paint was applied to the entire areas of both sides of the pellets and fired at 800°C for 30 min.

The electrical conductivity ($\sigma$) was measured in air by impedance method in the temperature range of 400–800°C and the ionic conductivity ($\sigma_{\text{ion}}$) was determined by electron-blocking method within 600-950°C in air. STF-YSZ composite pellet was plastered onto a dense YSZ pellet with a little Pt paste which was used to overcome the interface resistance (Figure 1). In the device, the electron flux is blocked by YSZ layer because YSZ is considered to be almost a pure oxygen ion conductor. Glass seal was used to prevent oxygen leakage along the sides of the assembled sample. Because the testing sample connects with the YSZ layer in series, the total impedance should be the sum of the oxygen ionic impedance of STF sample and YSZ layer. Therefore, the ionic conductivity of sample ($\sigma_{\text{ion}}$) can be worked out by its oxygen ionic impedance. The total electrical and ionic conductivities data were taken in an interval of 100°C and 50°C respectively.

The resistance of YSZ layer was measured firstly. The XRD and electrical conductivity of the prepared cubic YSZ were shown in Figure 1. Because the testing sample and the YSZ layer connect in series, $R_{\text{total}}$ should be the sum of the oxygen ionic resistances of sample ($R_{\text{sample}}$) and YSZ ($R_{\text{YSZ}}$) layers. Therefore, the ionic conductivity of sample ($\sigma_{\text{ion}}$) can be worked out by Eqs. (1) and (2):
\[ R_{\text{sample}} = R_{\text{total}} - R_{\text{YSZ}} \quad (1) \]
\[ \sigma_{\text{ion}} = h/S \cdot R_{\text{sample}} \quad (2) \]

S and \( h \) represent the area and the thickness of the testing sample, respectively.

**Figure 1.** XRD spectra of the prepared cubic YSZ; Temperature dependence of the electrical conductivity for YSZ (inset)

**Figure 2.** XRD spectra of STF- \( x \) YSZ \((x=0, 3, 5)\) at 1250°C for 6h; SEM micrographs of fracture surfaces for the corresponding samples (inset).
3. Results and discuss

3.1. XRD and SEM results
Figure 2 shows the XRD patterns and SEM micrographs of the powders of STF-\(x\)YSZ (denoted respectively as STF, STF-3YSZ and STF-5YSZ) after sintering at 1250°C for 6h. All of the peaks are assigned to a cubic perovskite structure without detectable impurity for STF and STF-3YSZ. However, the diffraction peaks of 31° and 55° can be indexed as SrZrO\(_3\)-based solid solution for STF-5YSZ. Obviously, the results are consistent with some migration of Y and Zr of YSZ into STF to form the SrZrO\(_3\)-based solid solution. The relative density of dense STF-\(x\)YSZ samples as a function of YSZ amount is shown in Figure 3. It decreases with increasing YSZ amount, indicating that the formation of SrZrO\(_3\)-based material (migration of Y and Zr of YSZ into STF) impedes the densification process of SrTiO\(_3\) materials. The SEM micrographs of fracture surfaces of dense STF-\(x\)YSZ samples are shown in Figure 2. With the increasing YSZ amount, the porosity increases. This is consistent with the results shown in Figure 3.

![Figure 3. Relation between relative density and YSZ amount.](image)

![Figure 4. Results from EDS analysis on the micrographs for STF-\(x\) YSZ samples: (a) STF-3YSZ and (b) STF-5YSZ.](image)
In order to get a better understanding of elements diffusion in the STF-x YSZ composites, the compositional analysis of the STF-3YSZ and STF-5YSZ was carried out using EDS analysis. Figure 4 shows the elemental distribution of the two materials. In addition, the analyzing areas were spot 1 for Figure 4 (a) and (b). Averaged cation elemental concentration in the respective material is presented in Table 1. From the concentration in Table 1, it was clearly evident that there is an inter-diffusion of the Zr and Y elements. However, no secondary phases involving these elements were detected for STF-3YSZ, which may be attributed to the less addition of YSZ.

| Cation at.% | Sr  | Ti  | Fe  | Zr  | Y   |
|------------|-----|-----|-----|-----|-----|
| STF-3YSZ   | 17.7| 18  | 6.5 | 1.9 | 1.2 |
| STF-5YSZ   | 20.1| 13.5| 7.8 | 3.3 | 1.76|

Figure 5. Temperature dependences of the total electrical conductivities in 400-900 °C in air of STF-x YSZ (x=0, 3, 5).

3.2. Effects of YSZ on the total electrical and ionic conductivities of STF

Figure 5 presents the temperature dependencies of the total electrical conductivity of STF-x YSZ composites with varying weight fractions of YSZ. The increase in the electrical conductivity as a function of temperature confirms the p-type conductivity behavior of these composites. As is evident in Figure 5, there was a steep decrease in the electrical conductivity for samples with a YSZ weight fraction greater than 3 wt%, which was attributed to the decreasing relative density. The total electrical conductivity of STF increases as the temperature increased in the low temperature range and thereafter became saturated, which was attributed to offsetting contributions from intrinsic electron-hole generation. This conduction behavior tends to increase the conductivity as the temperature increases, and the reduction reaction which decreases the (p-type) conductivity at relatively high oxygen pressures [5]. The electrical conductivities were 0.065 S/cm for STF-3YSZ and 0.052 S/cm for STF-5YSZ at 800 °C, respectively.

Figure 6 (a) indicates that the oxygen ionic conductivity increases with temperature increasing. As shown in Figure 6 (a), the ionic conductivity decreases with the YSZ addition increasing. The ionic conductivity were 0.0073 S/cm for STF-3YSZ and 0.0051 S/cm for STF-5YSZ at 700 °C, respectively. The values of the most common perovskite-type mixed conductors vary from $10^{-3}$ to $10^{-2}$ S/cm at
700°C [4]. Figure 6 (b) shows that the activation energy for conduction increases with YSZ amount increasing, which indicates YSZ is unfavorable for the ionic conduction of STF-x YSZ.

Figure 6. Temperature dependences of the ionic conductivities of STF-x YSZ (x=0, 3, 5).

Figure 7 shows that the ion transference number increases with temperature increasing. The ion transference number is 0.02-0.23 for the three samples in 600-900 °C, which is close to the D.P. Fagg’s STF system [13]. Figure 7 demonstrates that the electronic conductivity contribution is more than that of ionic conductivity for all samples and the electronic contribution decreases gradually with YSZ amount increasing.

The change in the conductivity behavior could be due to the inter-diffusion of the elements, as observed from the EDS analysis. EDS analysis shows STF-5YSZ contain more migration of Zr of YSZ into STF than that of STF-3YSZ in relatively atomic amounts, with traces of Y, Ti and Fe, thus confirming the formation of SrZrO₃-based solid solution. The formation of SrZrO₃-based solid
solution in terms of diffusion elements could change the conduction behavior of the STF, which result in the decreasing electrical and ionic conductivities. A further detailed conduction mechanism needs to be investigated to explain these observed changes.

3.3. Effect of YSZ on impedance characteristics of ionic conduction

The complex impedance plots and the corresponding equivalent circuits are illustrated in Figure 8 for STF and STF-5YSZ specimens. As shown in Figure 8, there is only one depressed semicircle following with a section of arc for all samples. The behavior of dense samples is described by the intercept in horizontal axis in the high frequency, a simple RC term in the medium and a small contribution in the low frequency range can be ascribed to the external material/electrode interface. Therefore, for a bulk crystal containing interfacial boundary layers, the equivalent circuit may be considered as a R, two parallel RC and RQ elements connected in serial: one for the bulk crystal (grain) and the other two for grain-boundary and material/electrode interface response respectively. As is evident in Figure 8, as temperature increased, the resistances of grain and grain boundary decrease for both samples, which observed by the shrunken intercept and semicircle, respectively. It notices that grain boundary resistance decreased considerably faster than grain resistance with temperature increasing.

Figure 9 shows frequency dependence of $-Z''$ relation at different temperatures. As shown in Figure 9, the relaxation effects are clearly represented by the peaks. The single peak in medium frequency range corresponding to the grain boundary contribution indicates a single relaxation process. The peak intensity is weaken gradually with temperature increasing, which is observed for the samples [16]. Also, the peak is shifting towards a higher frequency with rise in the temperature. The relaxation time can be deduced from the equation $\tau = 1/(2\pi f_{\text{max}})$, where $f_{\text{max}}$ is the frequency of the peak $Z''_{\text{max}}$ [18-19]. For STF, the $f_{\text{max}}$ value is 0.55, 0.81 and 1.184 Hz at 600, 650 and 700 °C, respectively and remains unchanged from 700 to 950 °C. The relaxation time lies in the range from 134 to 290 ms. In the case of STF-5YSZ, the value is 2.55, 5.486 and 11.91 Hz at 600, 650 and 700 °C, respectively and remains unchanged from 700 to 950 °C. The relaxation time lies in the range from 13 to 62 ms. Thus, the relaxation time of space charge polarization decreases with rise in temperature.

In order to describe the characteristics of relaxation in STF-x YSZ, the relaxation frequency in Figure 10 obeys the Arrhenius relation given by
Figure 8. AC impedance spectra of (a) STF and (b) STF-5YSZ as a function of temperature; The Equivalent circuit for STF and STF-5YSZ (inset).

\[ \omega_{\text{max}} = \omega_0 \exp \left[ -\frac{E_{\text{rel}}}{k_B T} \right] \]  \hspace{1cm} (3)

\[ \omega_{\text{max}} = 2\pi f_{\text{max}} \]  \hspace{1cm} (4)

The activation energy \( E_{\text{rel}} \) calculated from the \( \lg f_{\text{max}} \) — 1/T data. The calculated activation energy of STF-\( x \) YSZ is 0.56, 1.43 and 1.13 eV, respectively. It is observed that the activation energy for relaxation frequency of charge carriers is more than for the activation energy for conduction (Figure 6 (b)). It is known that the activation energy for conduction \( (E_{\text{con}}) \) is the sum of both the creation of charge carriers and migration or hopping free energy of charge carriers over a long distance while the activation energy for relaxation frequency of charge carriers \( (E_{\text{rel}}) \) is equal to the migration free energy of charge carriers and hopping of these charge carriers between the adjacent lattice sites[20]. Therefore, YSZ results in the increasing activation energy for relaxation and conduction of STF-\( x \) YSZ.
Figure 9. Variation of impedance $-Z''$ as function of frequency at (a) STF, (b) STF-3YSZ and (c) STF-5YSZ.

Figure 10. Temperature dependence of the maximum relaxation frequency obtained from the normalized imaginary part of impedance plots for STF $-x$ YSZ ($x = 0, 3, 5$).
4. Conclusions
Doping SrTiO$_3$ materials have been widely used as the electrodes of solid oxide cells and the formation of the composites between SrTiO$_3$ (as electrode) and YSZ (as electrolyte) has a very important effect on the triple-phase boundary for SOFCs. However, scarce work concerns the electrical properties and chemical compatibility about the composites. Therefore, Fe-doped SrTiO$_3$-YSZ composites were prepared with varying weight fractions of YSZ. Phase analysis of the composites by XRD after sintering at 1250 $^\circ$C did not show any clearly detectable secondary phases. EDS analysis showed the migration of Y and Zr of YSZ into STF to form the SrZrO$_3$-based solid solution. The electrical conductivity and ionic conductivity of STF-YSZ composites decrease with YSZ amount increasing. The decreasing electrical conductivity ($\sigma_T$ and $\sigma_{ion}$) results from the increasing activation energy for conduction ($E_{con}$) and relaxation ($E_{rel}$) with YSZ increasing. The electrical conductivity was 0.065 S/cm for STF-3YSZ and 0.052 S/cm for STF-5YSZ at 800$^\circ$C, respectively. The ionic conductivity was 0.0073 S/cm for STF-3YSZ and 0.0051 S/cm for STF-5YSZ at 700$^\circ$C, respectively.

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References
[1] Minh N Q 1993 J.Am. Ceram.Soc. 76 563
[2] Toebes M L, Bitter J H, Van Dillen A J and De Jong K P 2002 Catal. Today 76 33
[3] He H P, Huang Y Y, Vohs J M, Gorte R J 2004 Solid State Ionics 175 171
[4] Li X, Zhao H, Gao F, Chen N and Xu N 2008 Electrochem. Commun 10 1567
[5] Rothschild A, Litzelman S J, Tuller H L, Meneskhou W, Schneider T and Ivers-Tiffee E, 2005 Sens. Actuators B 108 223
[6] Moos R, Hardtl K H 1996 J. Appl. Phys 80 393
[7] Hui S and Petric A 2002 J. Eur. Ceram. Soc. 22 1673
[8] Fu Q X, Mi S B, Wessel E and Tietz F 2008 J. Eur. Ceram. Soc. 28 811
[9] Kurokawa H, Yang L, Jacobson C P, Lutgard C, De Jonghe S J and Visco 2007 J. Power. Sources 164 510
[10] Hiroaki M, Kurosaki K, Shinsuke Y 2003 J. Alloys. Compd. 350 292
[11] Litzelman S J, Rothschild A and Tuller H L 2005 Sens. Actuators B 108 231
[12] Khartov V V, Kovalovsky A V, Viskup A P, Jurado J R, Figueiredo F M, Naumovich E N and Frade J R 2001 J. Solid State Chem 156 437
[13] Fagg D P, Khartov V V, Frade J R and Ferreira A A L 2003 Solid State Ionics 156 45
[14] Sudireddy B R, Blennow P and Nielsen K A 2012 Solid State Ionics 216 44
[15] Ma Q L, Tietz F, Sebold D and Stover D 2010 J. Power. Sources 195 1920
[16] Jaiswal S K and Kumar J 2011 J. Alloys. Compd. 509 3859
[17] Subbarao E C, New York: Plenum Press, 1980
[18] Abrantes J C C, Labrincha J A and Frade J R 2002 J. Eur. Ceram. Soc 22 1683
[19] Dong M, Reau JM and Ravez J 1996 Solid State Ionics 91 183
[20] Molak A, Ksepko E, Gruszka I, Ratuszna A, Paluch M and Uja Z 2005 Solid State Ionics 176 1439.