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Authors

Zhao, L

Brouwer, J

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Electrical Properties of Sr$_{0.86}$Y$_{0.08}$TiO$_3$ Under Redox and Full Cell Fabrication Conditions

Li Zhao

Jacob Brouwer[1]
e-mail: jb@apep.uci.edu

Advanced Power and Energy Program,
University of California,
Irvine, CA 92697-3550

The effects of manufacturing and preparation conditions on the structural and electrical properties of Sr$_{0.86}$Y$_{0.08}$TiO$_3$ (SYT) reduced in 5% NH$_3$ (95% N$_2$) are discussed. The realization of an SYT-based SOFC anode is challenging because the conductivity of SYT is highly dependent upon the thermal history combined with heat treatment atmosphere used in manufacturing. To obtain highly conductive SYT as a candidate for an SOFC anode material, all samples in this study were prereduced to 1400 °C under reducing conditions (ammonia) for 8 h. After prereduction, three samples were oxidized in air at 850 °C, 950 °C, and 1050 °C, respectively, for 4 h to evaluate the impact of oxidizing conditions in practical cell fabrication processes on the SYT conductivity. XRD analyses showed that the lattice parameter of SYT sintered in ammonia was slightly different than the sample sintered in air. Measured at 800 °C in reducing atmosphere (dry N$_2$/4% H$_2$), the maximum electrical conductivity of 36.3 S/cm was observed in SYT reduced in ammonia at 1400 °C. However, the observed conductivities were not preserved after oxidation-reduction cycles. Various SYT samples prereduced in ammonia at 1400 °C and then oxidized in air at 850 °C, 950 °C, and 1050 °C showed an irreversible drop on conductivity measured in a reducing atmosphere, and the higher the oxidation temperature, the lower the conductivity became. The conductivity results indicate a strong dependence upon the SYT manufacturing and processing conditions. Despite the irreversible drop due to the oxidation cycle, the conductivity of SYT sintered in ammonia at 1400 °C is still reasonable as a candidate for SOFC anodes, with careful management of cell fabrication conditions to avoid any oxidation processes at temperatures above 1050 °C. [DOI: 10.1115/1.4007117]

Keywords: strontium titanate, anode material, SOFC, planar, electric conductivity

Introduction

Current state-of-the-art SOFC systems most frequently use Ni/YSZ cermet anode materials, which possess excellent catalytic activity and conductivity. However, Ni/YSZ has many disadvantages, including nickel coarsening, sulfur poisoning, carbon deposition, which can hinder the direct use of practical hydrocarbon fuels, and volume instability during redox cycles, which may cause fracture. What is more, nickel and nickel oxide may lead to allergies or cancer, adding difficulties in handling the material during manufacture [1].

Recently yttrium-doped strontium titanate (SYT) has been considered to be a promising alternative SOFC anode material [1–6]. Several groups demonstrated that SrTiO$_3$-based materials satisfied the anode requirements well, being thermodynamically stable in anodic conditions, electronically and ionically conductive, chemically compatible with the electrolyte and interconnect, and has a similar thermal expansion coefficient as other cell components (the thermal expansion coefficient of yttrium doped SrTiO$_3$ and YSZ are $(11–12) \times 10^{-6}$ K^{-1} and $(10.6–10.9) \times 10^{-6}$ K^{-1}, respectively) [7–10]. One of the most attractive properties of SYT compared to the nickel-based anode is the intrinsic sulfur tolerance and coking resistance, which indicate that practical fuels such as natural gas could be directly applied in SOFC without the addition of steam and extra balance of plant (BOP). These properties further enable SOFC use in stationary power generation to utilize fuels that are currently used such as natural gas and coal

syngas. However, SYT still needs to be further improved to compete with Ni/YSZ in terms of conductivity and catalytic activity. Yttrium doped SrTiO$_3$ exhibits very poor electro catalytic activity for fuel oxidation, especially for the oxidation of methane, possibly due to the lack of significant ionic conductivity in the materials [7]. Catalytic infiltration or impregnation has been demonstrated to solve the problem. The catalytic activity issue could be addressed by Ni or Pd infiltration as demonstrated by Gorte's group [8,11,12].

The conductivity issue of donor doped SrTiO$_3$ has been reported extensively in the literature showing that to possess a high conductivity, the SYT must be prereduced in a reducing environment at an elevated temperature and that the extent of reduction might not be preserved during other cell fabrication processes. In recent studies, the exact influence of the oxidizing heat treatment that might be inevitable in the cell fabrication process was not clearly reported. In the present work, A-site deficient yttrium-doped SrTiO$_3$ Sr$_{0.86}$Y$_{0.08}$TiO$_3$ was prepared, characterized, and the conductivities under various preparation conditions and redox cycles were tested.

Experimental

SYT Powder Synthesis. Sr$_{0.86}$Y$_{0.08}$TiO$_3$ powders were prepared by a modified Pechini method. A flow chart of the synthesis process is shown in Fig. 1. The SYT powder was synthesized using Sr(NO$_3$)$_2$ ($\geq$99.0% Fluka), Y(NO$_3$)$_3$·6H$_2$O (99.9%, Sigma-Aldrich), and Ti(OC$_3$H$_7$)$_4$ (98%, Sigma-Aldrich) as precursors. Ethylene glycol was first added into a flask, and the stoichiometric amount of Ti(OC$_3$H$_7$)$_4$ and absolute ethanol were then added into the ethylene glycol. The mixture was heated in a water bath held at a temperature between 70 and 80 °C. Nitrate solution made of

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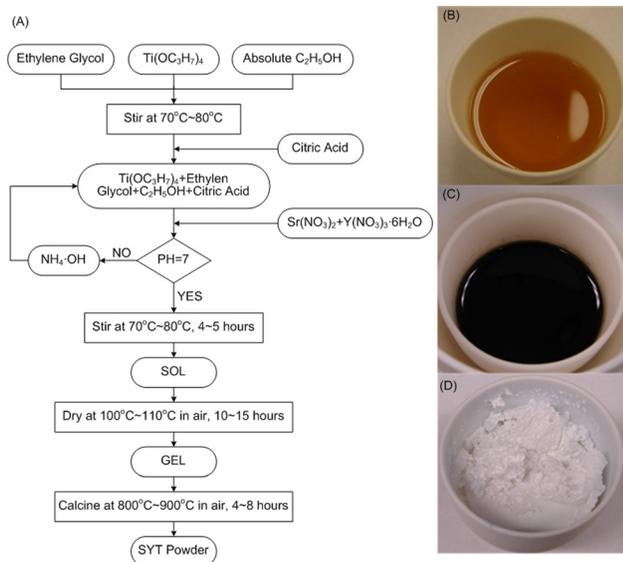
Fig. 1 SYT synthesis via modified Pechini method, (*a*) flow chart, (*b*) SYT SOL, (*c*) SYT gel, (*d*) SYT powder

Sample	Open porosity	Density (g/cm^3)	Relative density
A1	0.9%	4.56	90.8%
A2	1.1%	4.32	86.1%
A3	0.9%	4.60	91.7%
A4	2.3%	4.33	86.2%

stoichiometric amounts of $Sr(NO_3)_2$, $Y(NO_3)_3 \cdot 6H_2O$ and deionized water, and quantities of citric acid (99.5 +%, Sigma-Aldrich) were then gradually added into the mixture. The *p*H of the resulting solution was measured and adjusted to 6-7 by adding appropriate quantities of NH_4OH. After the solution was held at 70–80 °C for 4–5 h, a viscous clear solution of metal-citrate complexes was yielded. After drying the resulting solution at 100–110 °C for 10–15 h, the solution was transformed into a thick purple-brown gel. The resulting gel was then calcined at 900 °C in air for 8 h to generate a foam-like SYT powder. The stages of the solution, the gel, and the powder are also shown in Fig. 1. The detailed description of the synthesis is published elsewhere [13].

Preparation and Measurement. After the synthesized SYT powder was first calcined to 900 °C in air for 8 h, selected powders were sintered to 1400 °C for 4 h in 5% Ammonia/N_2. After ball milling for 24 h, the sintered powders were pressed into pellets (13 mm in diameter and 1 mm in thickness) at 180 MPa using a manual uniaxial hydraulic press. The as-pressed pellets were sintered at 1400 °C for 4 h in 5% Ammonia/N_2. Selected pellets were then oxidized in air for 4 h at 850 °C, 950 °C, or 1050 °C. The preparation of various samples investigated in the present work is listed in Table 1. The density of the as-sintered samples was measured using Archimedes method, and the relative densities were calculated. The crystalline structures of series of SYT pellets with various thermal histories were examined using an X-ray diffractometer (XRD, *Bruker* D5000), and XRD patterns were taken using a Ni-filtered Cu-K$_\alpha$ radiation source (operating at 40 V/30 mA), with a 2θ step of 0.02 deg.

For the conductivity measurements, platinum gauze (Alfa Aesar, 99.9%) and platinum paste (Engelhard, A3788A) were used as current collector. The SYT samples with platinum current collectors were fired at 950 °C in N_2 for 1 h to establish good bonding between the pellets and platinum paste. N_2 was also expected not to facilitate the oxidation of SYT. Four-probe electrical conductivity measurements were carried out in forming gas (4% H_2/N_2) at temperatures ranging between 500 °C and 800 °C with a temperature increment of 50 °C. *AC* impedance spectra were collected to measure ohmic resistance using a Solartron 1260 A/1480 A system operating in the frequency range of 100 kHz to 0.1 Hz with an excitation voltage amplitude of 5 mV.

Results and Discussion

The relative density and the open porosity of samples are presented in Table 2. The relative densities of the pellets after heat treatment were all larger than 85% (density of SYT powder was taken as 5.02 g/cm^3). With the increasing relative density of the sample, the effective contact area between grains will be increased, which is favorable to both the electron and ion mobility.

As shown in the X-ray diffraction patterns of Fig. 2, all as-sintered pellets showed a clear cubic perovskite structure regardless of their thermal history. Small traces of secondary phase $Ti_2Y_2O_7$ also presented in some of the samples (denoted with *). In a closer view, the XRD peaks of the A2-A4 samples were shifted to smaller angles compared to the peaks of the A1 sample. The shift indicates that the lattice constant varied slightly with various postreduction oxidizing conditions. The change of lattice constant of SYT samples due to different heat treatment atmosphere is estimated to be less than 1%, and the induced variation in residual stress should be negligible. The small change upon reduction/oxidation also suggests that the structural integrity of SYT is tolerant to oxidation/reduction cycling or to the

Table 1 Various thermal histories of the samples investigated

| Sample	Thermal history		
	Powder heat treatment	Reduction and oxidation	Current collector heat treatment
A1	900 °C in air, 8 h	1400 °C in 5% NH_3, 4 h powder 1400 °C in 5% NH_3, 4 h pellet	950 °C in N_2, 1 h
A2	900 °C in air, 8 h	1400 °C in 5% NH_3, 4 h powder 1400 °C in 5% NH_3, 4 h pellet 850 °C in air, 4 h	950 °C in N_2, 1 h
A3	900 °C in air, 8 h	1400 °C in 5% NH_3, 4 h powder 1400 °C in 5% NH_3, 4 h pellet 950 °C in air, 4 h	950 °C in N_2, 1 h
A4	900 °C in air, 8 h	1400 °C in 5% NH_3, 4 h powder 1400 °C in 5% NH_3, 4 h pellet 1050 °C in air, 4 h	950 °C in N_2, 1 h
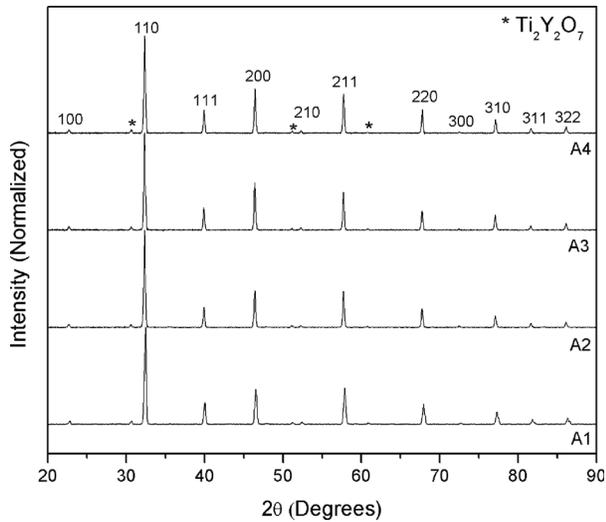
Fig. 2 XRD patterns for samples prepared in different conditions

variation of oxygen partial pressure between fuel inlet and outlet during cell operation [10].

The results of conductivity are shown in Fig. 3. For all samples investigated, at a temperature range of 500–800 °C the conductivity increases with the increase of temperature after being reduced in dry N_2/4%H_2 at 800 °C for 36 h, indicating a negative temperature coefficient of resistance and a nonmetallic type conductive behavior. The results suggest that the electronic conduction is not the predominant conduction mechanism in the material. Consequently, SYT samples exhibit mixed electron-ion conductivity under the current preparation conditions. The Arrhenius plots were not perfectly linear for some of the samples, and the relation between conductivity and temperature suggests a fairly clear Arrhenius dependence. Averaged activation energy is derived from the slope of the Arrhenius plot in the range 500–800 °C and lies in the range of 0.31 eV to 0.95 eV. The activation energy of conductivity is an important parameter to evaluate the electrical conductivity of materials. In our study, it is clear that conductivity and activation energy decrease with increasing oxidization tem-

perature exposure during processing. The electrical conductivity at 800 °C in forming gas was found to be 12.1, 9.9, and 6.1 S/cm for the samples with oxidation at 850 °C, 950 °C, and 1050 °C in air, respectively. The A1 sample, which had not been sintered in air, has the highest conductivity of 36.3 S/cm at 800 °C. The conductivity of SYT ($Sr_{0.86}Y_{0.08}TiO_{3-\delta}$) with similar heat treatment process reported was 22 S/cm [13] and 82 S/cm [10] at a temperature of 800 °C.

The defect chemistry and its effect on conductivity in yttrium-doped $SrTiO_3$ has been widely reported in the literature. The extra positive charge of the donor (Y^{3+}) can be compensated either by strontium vacancies (ionically) in an oxidizing atmosphere or conduction electrons (electronically) provided by the Ti^{4+} reduction to Ti^{3+} in reducing atmospheres [14]. The more dominant the electronic compensation mechanism, the higher the conductivity of SYT has been observed. The temperature and atmosphere of the final heat treatment steps determine the compensation mechanism, which, therefore, affect the conductivity. The results show that the A1 sample possesses the highest degree of reduction, which suggests that the electronic compensation mechanism accounts for a larger portion of the conductivity than for the A2-A4 samples. The degree of reduction of A2-A4 are lowered with increasing oxidation temperature, and the conductivities showed a decreasing trend. It indicates that part of the electronic compensation mechanism is converted to ionic compensation, and the conversion tends to be proportional to the increasing oxidation temperature.

The rate of reduction of SYT with various thermal histories had been studied by measuring the change in the electrical conductivity as a function of time, as all samples were tested in 4% H_2 for 36 h at 800 °C (shown in Fig. 4). The conductivity increased rapidly with the exposure to the reducing atmosphere and tended to reach a plateau after some time. The changes of conductivities show noticeable parabolic time dependence features, which were also reported in the study of Hui and Petric [9]. Two processes in series have been proposed for the reduction reactions, the gas solid interface reaction and bulk diffusion [9,15]. The behavior shown in Fig. 5 indicates a diffusion controlled process as the rate of the reduction decreases with time. After the samples are exposed to the reducing atmosphere, fast surface reactions occurred and triggered the composition change, followed by mass transport via diffusion from the gas/solid interface into the bulk, and formed a reduced/oxidized interface. With the extent of reduction increased, the reduced/oxidized interface moved further from the gas/solid interface into the bulk (increased diffusion
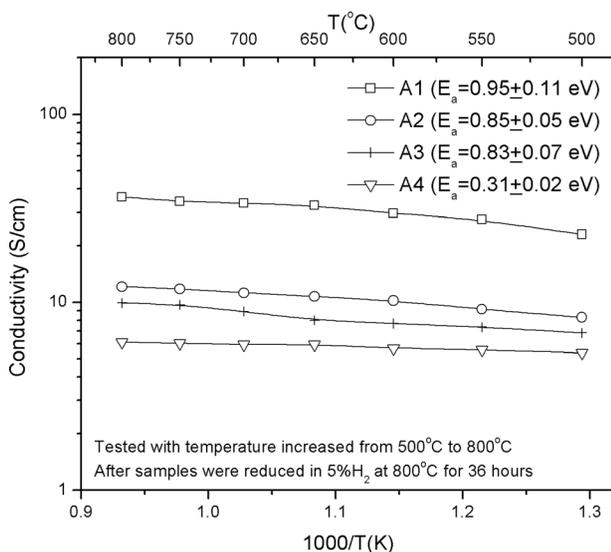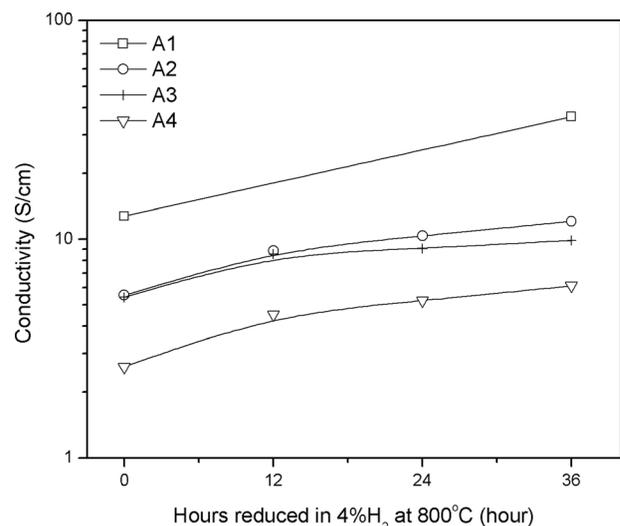

Fig. 3 Temperature dependence of the electrical conductivity measured in dry N_2/4% H_2 for samples with different preparation conditions. All samples prereduced in dry N_2/4% H_2 at 800 °C for 36 h.

Fig. 4 Time dependence of the electrical conductivity measured in dry N_2/4% H_2 for samples with different preparation conditions, measured at 800 °C
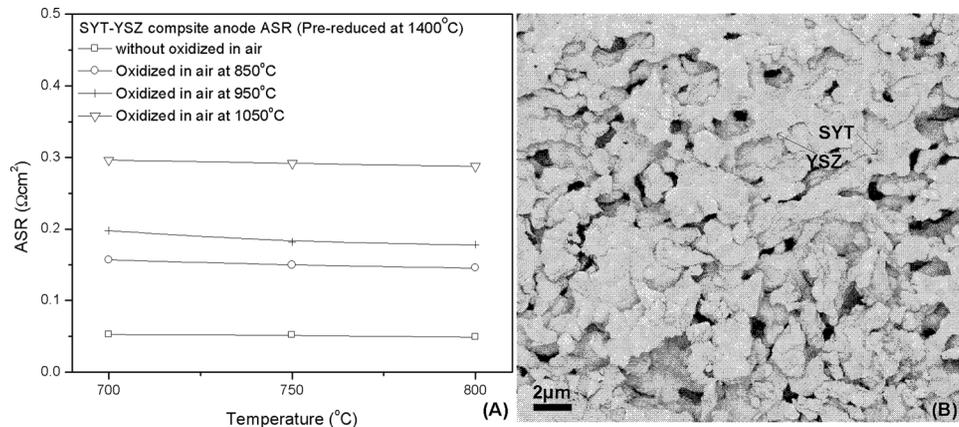
Fig. 5 (*a*) Calculated ASR of 1 mm thick composite anode with various thermal histories, (*b*) microstructure of STY-YSZ composite after sintered to 1400 °C

length); therefore, the rate of reduction decreases with time. It has been reported that the rate of oxidation is much faster than that of reduction. The reason for a much slower rate of reduction is due to the fact that the incorporation of oxygen into lattice is much easier than the release of oxygen from lattice. The results also suggest that to fabricate a SYT-based single cell, any cosintering processes in air will cause a relatively long reduction period to restore the extent of reduction and fulfill the conductivity requirement. However, if the degree of reduction of SYT was partly preserved during cell fabrication processes, one can expect increasing performance of an SYT anode in time since the diffusion controlled reduction processes will continuously occur under an anode atmosphere at the SOFC operating temperature.

The electrical conductivity of an SYT-YSZ composite anode (SYT: YSZ: Pores = 30:30:40 in vol. %) at various temperatures was calculated, and the ASR of a 1 mm thick anode (assuming an anode-supported cell) is plotted in Fig. 5(*a*). The results show that an SYT-YSZ composite anode that has been prereduced in ammonia at 1400 °C (same thermal history as A1) has the lowest ASR (~ 0.05 Ωcm^2) compared to the other composite anodes oxidized in air at various temperatures. The model is based on the percolation theory developed by McLachlan et al. [16], which is in general employed to calculate the electrical conductivity of a composite. The equation is presented in Eq. (1).

$$\sigma_{comp} = \sigma_{SYT} \left(\frac{V_{SYT} - V_c}{1 - V_c} \right)^t \qquad (1)$$

where t is a system specific parameter, and typical values of the parameter t fall in the range of 1.2–1.6 [17]. In this study $t = 1.6$. V_c is the critical (percolation) volume fraction of SYT, and V_{SYT} is the volume fraction of SYT phase in the composite. σ_{comp} and σ_{SYT} are the electrical conductivities of the composite and SYT phase, respectively. In our model, it is assumed that SYT is a discontinuous conductive particle embedded in a YSZ (and pore) insulating matrix, and the SYT loading is above the percolation threshold. The critical volume fraction of SYT (V_c) is estimated by the microstructure of STY-YSZ composite shown in Fig. 5(*b*). The microstructure of the composite suggested that the particle size of SYT (dark color) and the YSZ (light color) were approximately identical; as a result, V_c tends to be in the range of 0.16 according to McLachlan et al. [16]. As the particle size of SYT decreases below the particle size of YSZ, the value of the critical volume fraction will drop, and as a result, the conductivity of the composite will be increased with a more effective conducting network. Based on McLachlan's percolation model, the critical volume fraction will drop and reach about 0.05 when the SYT particle is 30 times smaller than that of the YSZ particle [16], and the predicted ASR will be halved for all cases discussed.

The ASR of a 1 mm thick composite anode predicted using the composite conductivity model is also compared to experimental results as shown in Fig. 6. The results show that the ASRs predicated by the model agree well with an SYT-YSZ composite anode that has been prereduced in ammonia at 1400 °C. It is argued that the ASR of a 1 mm thick anode lower than 0.1 Ωcm^2 is required in order to achieve high performance with alternative ceramic anode materials [18,19]. The results, therefore, show that the porous SYT-YSZ composite anode that is reduced at 1400 °C without any oxidative manufacturing processes in air meets the minimum conductivity requirements. Whereas, any additional heat treatments processed in air at elevated temperature will result in the increase of ASR and reduce the current composite anode from being a viable candidate anode materials set, in proportion to the oxidation temperature. The results also suggest that to fabricate an SYT-based single cell, any cosintering processes in air should be avoided or should be accomplished in Ar or N_2 atmosphere (as an alternative) to fulfill the anode conductivity requirements. Under some circumstances, cosintering processes in air at the temperature range of 850–1100 °C is inevitable. An alternative way to lower the anode ASR is to optimize the percolation of SYT particles in YSZ and optimize the microstructure of the composite.
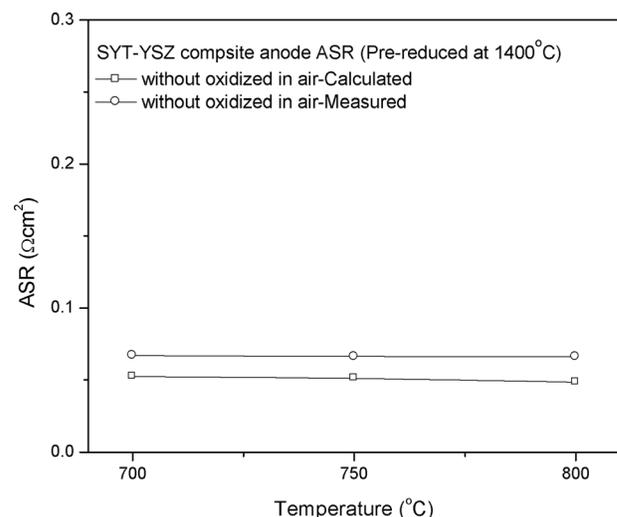

Fig. 6 ASR of porous SYT-YSZ composite anode that is reduced at 1400 °C without any oxidative manufacturing processes in air, calculated and measured

Conclusions

The XRD results indicate that all as-sintered in ammonia SYT pellets showed a perovskite structure regardless of the thermal history, and the lattice constant varied slightly due to the various preparation conditions.

The conductivity results suggest that the SYT reduced at a high temperature (1400 °C) in ammonia has sufficient conductivity for use as an SOFC anode material. In addition, to fabricate an SYT-based single cell, any cosintering processes in air should be avoided, or one should use Ar or N_2 atmosphere as an alternative to preserve the degree of SYT reduction. Although the conductivity value of SYT is still orders of magnitude lower than the Ni-based anode materials, it was demonstrated that SYT or SYT composite materials can be used as an anode or anode current collector through careful morphological design and controlled fabrication processes.

Acknowledgment

References

[1] Goodenough, J. B., and Huang, Y. H., 2007, "Alternative Anode Materials for Solid Oxide Fuel Cells," J. Power Sources, **173**(1), pp. 1–10.

[2] Sun, X. F., Wang, S. R., Wang, Z. R., Qian, J. Q., Wen, T. L., and Huang, F. Q., 2009, "Evaluation of $Sr_{0.88}Y_{0.08}TiO_3$-CeO_2 as Composite Anode for Solid Oxide Fuel Cells Running on CH4 Fuel," J. Power Sources, **187**(1), pp. 85–89.

[3] Savaniu, C. D., and Irvine, J. T. S., 2009, "Reduction Studies and Evaluation of Surface Modified A-Site Deficient La-Doped $SrTiO_3$ as Anode Material for IT-SOFCs," J. Mater. Chem., **19**(43), pp. 8119–8128.

[4] Lu, X. C., Zhu, J. H., Yang, Z. G., Xia, G. G., and Stevenson, J. W., 2009, "Pd-Impregnated SYT/LDC Composite as Sulfur-Tolerant Anode for Solid Oxide Fuel Cells," J. Power Sources, **192**(2), pp. 381–384.

[5] Pine, T. S., Lu, X. Y., Do, A. T. V., Mumm, D. R., and Brouwer, J., 2007, "Operation of an LSGMC Electrolyte-Supported SOFC With Composite Ceramic Anode and Cathode," Electrochem. Solid-State Lett., **10**(10), pp. B183–B185.

[6] Li, X., Zhao, H. L., Shen, W., Gao, F., Huang, X. L., Li, Y., and Zhu, Z. M., 2007, "Synthesis and Properties of Y-Doped $SrTiO_3$ as an Anode Material for SOFCS," J. Power Sources, **166**(1), pp. 47–52.

[7] Fu, Q. X. Tietz, F. Sebold, D. Tao, S. W. and Irvine, J. T. S., 2007, "An Efficient Ceramic-Based Anode for Solid Oxide Fuel Cells," Journal of Power Sources, 171(2), pp. 663–669.

[8] He, H. P., Huang, Y. Y., Vohs, J. M., and Gorte, R. J., 2004, "Characterization of YSZ-YST Composites for SOFC Anodes," Solid State Ionics, **175**(1–4), pp. 171–176.

[9] Hui, S. Q., and Petric, A., 2002, "Evaluation of Yttrium-Doped $SrTiO_3$ as an Anode for Solid Oxide Fuel Cells," J. Eur. Ceram. Soc., **22**(9–10), pp. 1673–1681.

[10] Hui, S. Q., and Petric, A., 2002, "Electrical Properties of Yttrium-Doped Strontium Titanate Under Reducing Conditions," J. Electrochem. Soc., **149**(1), pp. J1–J10.

[11] Lee, S., Kim, G., Vohs, J. M., and Gorte, R. J., 2008, "SOFC Anodes Based on Infiltration of $La_{0.3}Sr_{0.7}TiO_3$," J. Electrochem. Soc., **155**(11), pp. B1179–B1183.

[12] Ahn, K., Jung, S., Vohs, J. M., and Gorte, R. J., 2007, "A Support Layer for Solid Oxide Fuel Cells," Ceram. Int., **33**(6), pp. 1065–1070.

[13] Lu, X. Y., Pine, T. S., Mumm, D. R., and Brouwer, J., 2007, "Modified Pechini Synthesis and Characterization of Y-Doped Strontium Titanate Perovskite," Solid State Ionics, **178**(19–20), pp. 1195–1199.

[14] Fu, Q. X., Mi, S. B., Wessel, E., and Tietz, F., 2008, "Influence of Sintering Conditions on Microstructure and Electrical Conductivity of Yttrium-Substituted $SrTiO_3$," J. Eur. Ceram. Soc., **28**(4), pp. 811–820.

[15] Fu, Q. X., and Tietz, F., 2008, "Ceramic-Based Anode Materials for Improved Redox Cycling of Solid Oxide Fuel Cells," Fuel Cells, **8**(5), pp. 283–293.

[16] Mclachlan, D. S., Blaszkiewicz, M., and Newnham, R. E., 1990, "Electrical-Resistivity of Composites," J. Am. Ceram. Soc., **73**(8), pp. 2187–2203.

[17] Marinsek, M., Pejovnik, S., and Macek, J., 2007, "Modelling of Electrical Properties of Ni-YSZ Composites," J. Eur. Ceram. Soc., **27**(2–3), pp. 959–964.

[18] Gross, M. D., Vohs, J. M., and Gorte, R. J., 2007, "Recent Progress in SOFC Anodes for Direct Utilization of Hydrocarbons," J. Mater. Chem., **17**(30), pp. 3071–3077.

[19] Gross, M. D., Vohs, J. M., and Gorte, R. J., 2007, "A Strategy for Achieving High Performance With SOFC Ceramic Anodes," Electrochem. Solid-State Lett., **10**(4), pp. B65–B69.