

Modified Pechini synthesis and characterization of Y-doped strontium titanate perovskite

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Abstract

This work reports the modified Pechini preparation and properties of an A-site deficient perovskite $\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (SYT). Good chemical homogeneity and electrical conductivity were determined, making SYT a potential conductive component material in a composite anode for solid oxide fuel cells. As an oxide with inherent resistance to oxidation and hydroxylation, SYT could be a substitute for the metallic Ni component in composite anodes for solid oxide fuel cells, particularly for reversible solid oxide fuel cells with attendant high steam concentrations.

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1. Introduction

Solid oxide fuel cell (SOFC) technology based on the yttria-stabilized zirconia (YSZ) materials set is being advanced for a variety of applications. This technology typically employs a composite nickel-YSZ anode, which limits the electrochemical reaction zone to the region very near the triple-phase-boundary (TPB). At typical SOFC operating temperatures (700–1000 °C), Ni particles tend to coarsen over time, which results in greater polarization losses. Some intermediate temperature SOFC technologies, such as that based on strontium and magnesium-doped lanthanum gallate (LSGM) electrolyte, cannot use a composite Ni-LSGM anode because sintering produces undesirable insulating phases, such as lanthanum nickelate [1].

Replacing the metallic Ni-containing anode with a ceramic mixed-conducting anode that possesses similar electrical and electrocatalytic properties could significantly improve the long-term stability of SOFC technology. In addition, use of a mixed ionic- and electronic-conductor (MIEC) in the place of nickel

may reduce the tendency of carbon formation and deposition when operating an SOFC on a hydrocarbon fuel.

In addition, reversible SOFC (R-SOFC) technology could also benefit from an MIEC composite anode. Several investigators have studied the YSZ materials set in R-SOFC stacks using a Ni-YSZ anode and a strontium-doped lanthanum manganite (LSM) cathode [2–4]. These studies have advanced understanding of R-SOFC technology and provided useful insights into electrode performance optimization. These studies generally confirm the robust performance of the YSZ materials set in fuel cell mode, but, suggest high rates of degradation in electrolyzer mode.

The observed degraded electrolyzer mode performance is believed to be due to Ni oxidation or hydroxylation in the Ni-YSZ anode. Oxidation or hydroxylation can readily occur at high temperatures in the presence of high steam concentration. When pure steam is used for electrolysis, the thermodynamic equilibrium oxygen partial pressure (P_{O_2}) is 7.0×10^{-8} atm at 700 °C and 4.7×10^{-7} atm at 800 °C. Thermodynamic calculations indicate that the Ni/NiO equilibrium P_{O_2} is 10^{-14} atm at 800 °C for unit activities of condensed phases. Therefore, NiO will be readily formed from surface oxidation of metallic Ni particles in the electrolysis environment, even at intermediate operating temperatures of 700–800 °C. This oxidation results in severe electrode polarization and deactivation.

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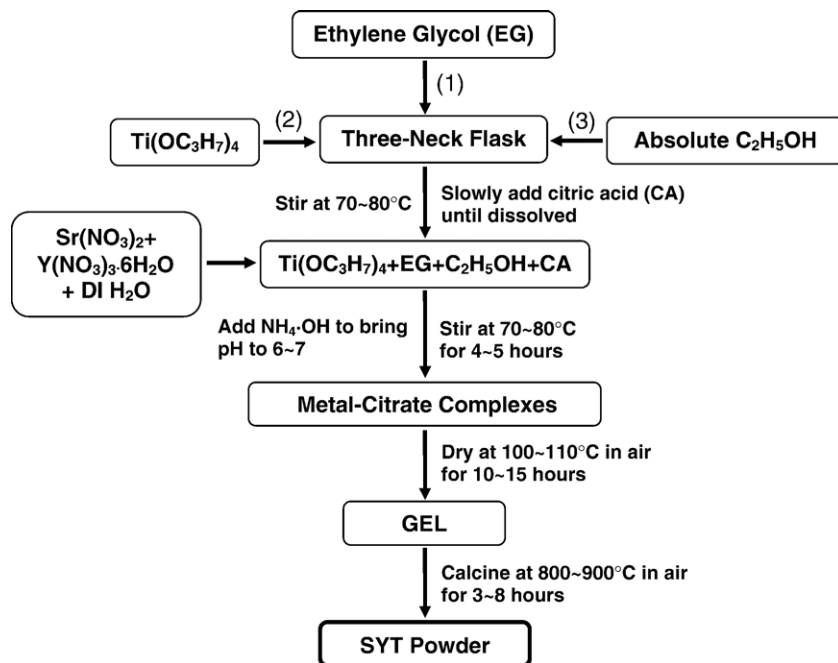


Fig. 1. Flow chart of a modified Pechini process to synthesize $\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (SYT) powder.

Yttrium-doped strontium titanate ($\text{Sr}_{1-1.5x}\text{Y}_x\text{TiO}_{3-\delta}$) displays relatively high electrical conductivity and good chemical stability under reducing conditions [5,6]. An optimized composition with A-site deficient $\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (SYT) shows electrical conductivity as high as 82 S/cm at 800 °C with oxygen partial pressure of 10^{-19} atm. This material has been demonstrated to have high structural stability over a broad range of temperatures (up to 1400 °C) and oxygen partial pressures ($1-10^{-20}$ atm). No phase change was found to occur for mixtures of SYT and LSGM sintered at 1400 °C for 10 h. Finally, the thermal expansion of SYT was determined to be compatible with those of LSGM and YSZ [7,8]. All these features suggest that SYT could be used as an active ceramic oxide component in the hydrogen-side electrode for SOFCs as well as R-SOFCs.

However, to-date the synthesis of SYT material has predominantly relied upon conventional solid-state reaction processes. Synthesis begins with mixtures of precursor oxides and carbonates, which are subjected to prolonged heating at elevated temperatures (1500–1700 °C) to obtain the desired perovskite phase. This process is straightforward, but it is energy intensive and the materials produced are often substandard, exhibiting non-homogeneous phase distribution, large grain sizes, strongly bonded agglomerates, and chemical contamination from repetitive grinding and milling processes. In order to avoid such undesirable aspects of SYT synthesis, a low-cost modified Pechini process, based on the original work of Pechini [9], has been developed to synthesize ultra fine SYT powder with desired chemical homogeneity. In this work, we describe the synthesis approach, and subsequently characterize SOFC-relevant properties of the as-synthesized SYT.

2. Experimental

2.1. Modified Pechini Process

The SYT powder was synthesized using the following precursors: $\text{Sr}(\text{NO}_3)_2$ ($\geq 99.0\%$ Fluka), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich), and $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (98%, Sigma-Aldrich). Stoichiometric amounts of $\text{Sr}(\text{NO}_3)_2$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved into deionized water to make a nitrate solution. The minimum amount of water necessary to fully dissolve the nitrates was utilized (e.g. 25 ml of H_2O for 3.640 g of Sr nitrate and 0.613 grams of Y-nitrate). Quantities of citric acid (99.5+%, Sigma-Aldrich), in a 3:1 molar ratio with respect to the total amount of cations, and ethylene glycol (99+%, Alfa Aesar), in a 4:1 molar ratio with respect to the citric acid were prepared. Ethylene glycol was first added into a three-neck flask. The stoichiometric amount of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was then carefully added into the ethylene glycol. The flask containing this mixture was then placed in a water bath, held at a temperature between 70 and 80 °C, and stirred with a magnetic stir bar. An amount of absolute ethanol representing a 2:1 molar ratio with the deionized water used in making the nitrate solution was then added to the three-neck flask. The previously measured citric acid was gradually added, continuing to stir the solution. Upon complete mixing of the citric acid, the nitrate solution was gradually added. The pH of the resulting solution was adjusted to 6–7 by adding appropriate quantities of NH_4OH . With the flask left open (one or two necks unsealed), the solution was held at the bath temperature (70–80 °C) and continuously stirred for 4–5 h, yielding a viscous clear solution of metal-citrate complexes. The resulting solution was then transferred to an alumina crucible to be dried in a convection oven at 100–

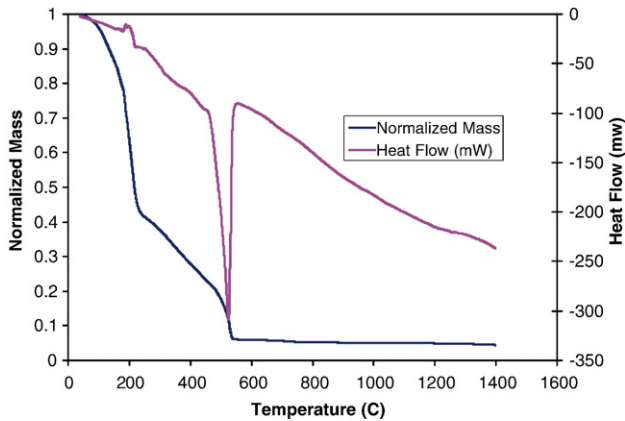


Fig. 2. Simultaneous TG/DTA curves of SYT gel precursor at a heating rate of 10 °C/min in air.

110 °C for 10–15 h. After drying, the solution was transformed into a thick purple-brown gel. Finally, the resulting gel was further calcined at 900 °C in air for 8 h to generate a foam-like power. This modified Pechini synthesis procedure is summarized in the flow chart illustrated in Fig. 1.

2.2. Physicochemical and Structural Characterization

Thermal analysis of the conversion of SYT gel precursor (from the above modified Pechini process) to ceramic powder was conducted on a thermogravimetric/differential thermal analysis system (TG/DTA, PerkinElmer Diamond) running PYRIS software. The gel was heated in an open-topped platinum crucible, from 40 °C to 1400 °C at a heating rate of 10 °C/min in air. The Brunauer–Emmett–Teller (BET) specific surface area of the as-calcined SYT powder was measured with an automated volumetric sorption analyzer (Quantachrome, Autosorb-1) using high surface area sample cells and nitrogen as the adsorbate at –196 °C.

The crystalline structure of a series of SYT powders fired for 3 h at temperatures ranging from 800 to 1400 °C was examined using an X-ray diffractometer (XRD, Bruker D5000). XRD patterns were taken using a Ni-filtered Cu-K α radiation source

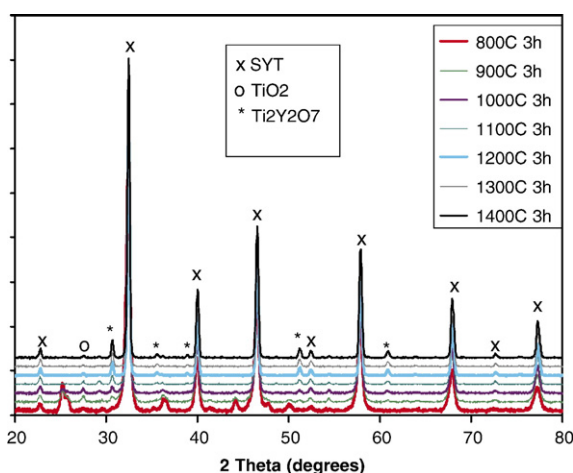


Fig. 3. XRD patterns of the SYT powders fired in a temperature range of 800 to 1400 °C in air for 3 h.

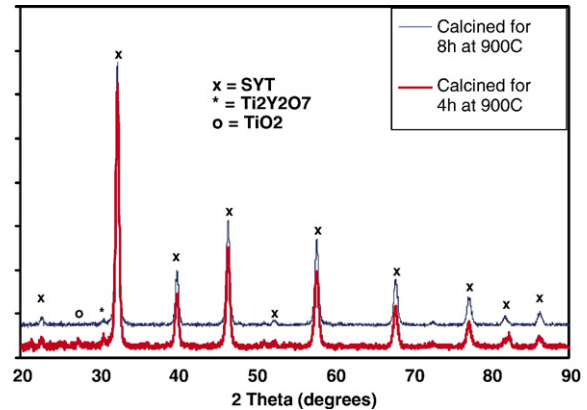


Fig. 4. XRD patterns of the SYT powders fired at 900 °C in air for 4 h and 8 h.

(operating at 40 V/30 mA), with a 2 θ step of 0.02°. The nano-scale structure of the 900 °C-calcined SYT powder was observed using transmission electron microscopy (TEM, Philips CM20). The microstructure of sintered SYT pellet samples was examined by using scanning electron microscopy (SEM, Zeiss Ultra 55).

2.3. Electrical Conductivity Measurement

For the electrical characterization, the 900 °C-calcined SYT powder was first ground in an agate mortar and pestle. The powder then was pressed into a pellet (33 mm in diameter and 2 mm in thickness) at 180 MPa using a manual uniaxial hydraulic press. The as-pressed pellet was sintered at 1400 °C for 6 h in an environment of forming gas (10% CO+90% N $_2$) maintaining that environment during the entire firing cycle. The sintered pellet was subsequently machined to a bar geometry with dimensions of 1.0 mm \times 2.5 mm \times 6.6 mm. Platinum paste (Engelhard, A3788A) was brush-painted onto the two ends of the SYT bar as current collectors, and platinum gauze (Alfa Aesar, 52 mesh woven from 0.1 mm dia wire, 99.9%) with spot-welded platinum lead wires (two wires on each end) were buried in the platinum paste to further improve the current-collecting efficiency. The SYT bar samples with platinum current collectors were fired at 1000 °C in air for 1 h to establish good bonding between the SYT and platinum paste. Four-probe electrical conductivity measurements were carried out in a mixed reducing gas atmosphere (50% H $_2$ + 50% N $_2$) at temperatures ranging between 600 °C and 1000 °C

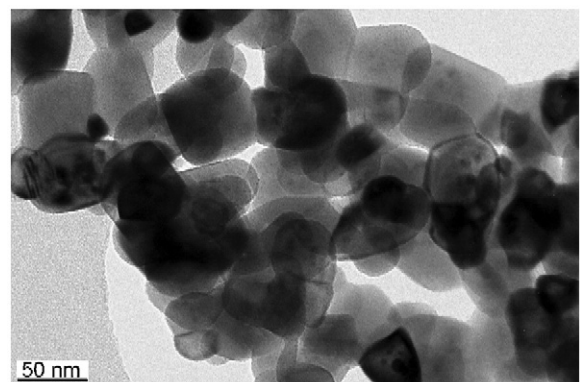


Fig. 5. TEM micrograph of the SYT powder calcined at 900 °C in air for 8 h.

with a temperature increment of 50 °C. AC impedance spectra were collected using a Solartron 1260A/1480A system operating in the frequency range of 100 kHz to 0.1 Hz with an excitation voltage amplitude of 5 mV.

3. Results and discussion

3.1. Thermal Properties of SYT Gel Precursor

The simultaneous TG/DTA curves of SYT gel precursor in Fig. 2 reveal rapid mass loss upon reaching a temperature of 170 °C, attributed to the removal of superficial and structural water in the gel precursor. The mass loss around 200 °C, attributed to the combustion of nitrates and ethylene glycol, occurs with exothermic peaks in the DTA curve. Further mass loss between 200 °C and 460 °C is due to the removal of different forms of chemisorbed hydroxyl groups and further combustion of the remaining organic groups. Alkoxide groups bonded to metal cations can be removed by heating to 460 °C in air, accompanied by a significant endothermic peak in the DTA curve. After this endothermic process, there are no further major thermal events. The TG curve gradually levels off to a normalized mass of 0.044 at 1400 °C. This profile is typical of a modified Pechini process and confirms that there are no unexpected phase transformations in the temperature range of 550 to 1400 °C. It also confirms that the majority of the mass loss occurs under 550 °C and allows for optimization of the heat treatment program.

3.2. Characterization of SYT powder and sintered pellet

The XRD patterns of the SYT powders fired in air over a temperature range of 800 to 1400 °C (Fig. 3) indicate that increasing the firing temperature serves to increase the fraction of the pyrochlore phase $\text{Ti}_2\text{Y}_2\text{O}_7$. The undesirable TiO_2 rutile phase that is observed at low firing temperatures can be eliminated by lengthening the firing time in air from 4 h to 8 h at 900 °C (Fig. 4). This treatment was found to eliminate the rutile

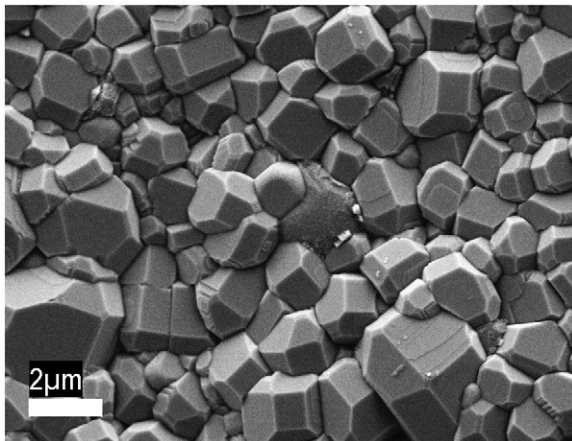


Fig. 6. SEM micrograph of a top-view of the SYT pellet sintered at 1400 °C for 6 h in an environment of forming gas (10% CO+90% N_2). The same forming gas environment was maintained during the entire firing cycle.

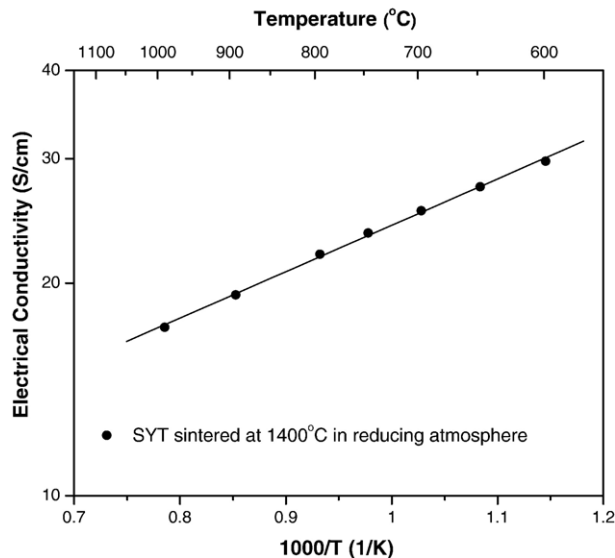


Fig. 7. Electrical conductivity of the SYT sintered at 1400 °C in forming gas (10% CO+90% N_2). Measurements were carried out in a mixed gas atmosphere (50% H_2 +50% N_2) in a temperature range of 600 to 1000 °C.

phase while simultaneously minimizing the formation of the pyrochlore phase, leading to the final SYT powder in perovskite phase and with fine grain size and high phase purity. Rietveld refinement of the lattice parameter using the General Structure Analysis System (GSAS) software suite establishes that the cubic lattice parameter of the reduced SYT is $a=3.905$ Å.

The specific surface area of the 900 °C-calcined SYT powder was measured to be 21.3 m^2/g with a standard deviation of 0.9 m^2/g , indicating that a highly refined powder with nanoscale grain size is obtained.

ATEM micrograph of the SYT powder calcined at 900 °C in air for 8 h (Fig. 5) shows that the average particle size is 50 nm. The SYT particles are equiaxed with a narrow size distribution. The nanoscale dimensions of the particles and the apparent homogeneity make the modified Pechini process-derived SYT powder a good candidate material for the SOFC anode application.

The density of the sintered SYT pellet was determined to be 4.75 g/cm^3 using the Archimedes principle and associated attachments to an analytical balance. This density value is 94.5% of the theoretical density calculated based on the lattice parameters measured by using XRD.

A SEM micrograph of the SYT pellet sintered in a reducing atmosphere (Fig. 6) shows a highly densified microstructure composed of polyhedral grains on a micron scale. The high degree of control over grain size in the final SYT pellet that results from the highly refined grain size in the initial powder synthesis process is vital to the practical processing of SYT as an SOFC anode component.

3.3. Electrical Conductivity

The electrical conductivity of the sintered SYT – the principal characteristic of interest for use as an SOFC anode component – was measured in a mixed gas atmosphere (50%

H₂+50% N₂) in a temperature range of 600 to 1000 °C. The mixed gas atmosphere is used to ensure full equilibrium with the low partial pressure of oxygen found in a typical SOFC anode compartment. As illustrated in Fig. 7, the temperature dependence of electrical conductivity for the sintered SYT exhibits a metallic behavior over the temperature range investigated, rather than the typical semiconductor behavior for a perovskite oxide. The metallic behavior can be primarily attributed to Ti⁴⁺ reduction to Ti³⁺ that is facilitated by the very high sintering temperature of 1400 °C and reducing atmosphere.

4. Conclusions

The synthesis of SYT using a modified Pechini process has resulted in high phase purity perovskite oxide powder with mono-dispersed nanoscale grain size. An extended calcining period at 900 °C in air was found to eliminate the formation of TiO₂ rutile phase while minimizing the formation of pyrochlore. The electrical conductivity of the SYT sintered at 1400 °C in a reducing atmosphere was measured, and found to exhibit a metallic behavior under reducing conditions in the tested temperature range of 600 to 1000 °C. The high electrical conductivity of the modified Pechini process-derived SYT makes it a promising candidate for use as a conductive component in composite SOFC anodes.

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References

- [1] K. Huang, R.S. Tichy, J.B. Goodenough, C. Milliken, *J. Am. Ceram. Soc.* 81 (1998) 2581.
- [2] D. Kusunoki, Y. Kikuoka, V. Yanagi, *Int. J. Hydrogen Energy* 20 (1995) 831.
- [3] K. Eguchi, T. Hatagishi, H. Arai, *Solid State Ion.* 86–88 (1996) 1245.
- [4] J.S. Herring, J. O'Brien, C. Stoots, P. Lessing, R. Anderson, INEEL, Hydrogen, Fuel Cells, Infrastructure Technologies, U.S. DOE FY2003 Progress Report, 2003.
- [5] S. Hui, A. Petric, *J. Electrochem. Soc.* 149 (2002) J1.
- [6] O.A. Marina, N.L. Canfield, J.W. Stevenson, *Solid State Ion.* 149 (2002) 21.
- [7] S. Hui, A. Petric, *J. Eur. Ceram. Soc.* 22 (2002) 1673.
- [8] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. Mcevoy, M. Mogensen, S.C. Singhal, J. Vohs, *Nat Matters* 3 (2004) 17.
- [9] M. Pechini, Sprague Electric Co., U.S. Pat., 1967, #3,330,697.