ELECTRICAL CONDUCTIVITY AND REDOX BEHAVIOUR OF YTTRIUM-SUBSTITUTED SrTiO₃: DEPENDENCE ON PREPARATION AND PROCESSING PROCEDURES

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ABSTRACT

The electrical conductivity and redox behaviour of 10 mol% yttrium-substituted SrTiO₃ (with and without 5 mol% Co co-substitute at Ti site) were studied in relation to their potential use as alternative redox-stable anode materials. The Pₒ₂ at which the samples experience a high temperature process (e.g., sintering) determines the initial electrical conductivity, and the conductivity under the proposed application conditions is then determined by the re-equilibration kinetics. Due to the slow ionic transports on both anion and cation sublattices during the re-equilibration, it is practically difficult to obtain the true equilibrium conductivity values. Therefore the property of a sample depends to a very large extent on its particular history. Porous and fine-grained samples indeed show much faster re-equilibration kinetics than dense and coarse-grained samples. While the initial electrical conductivities of high-temperature reduced samples are quite high, some extent of degradation is observed upon redox cycling, which is worth further investigation.

INTRODUCTION

In the current anode-supported planar SOFC, the state-of-the-art anode, Ni/YSZ, has a number of disadvantages including Ni agglomeration, sulphur poisoning and carbon deposition when the SOFC is fuelled by natural gas without sufficient steam being added. Moreover, to ensure sufficient current collection, the Ni content is usually over 35 vol%, resulting in large dimensional change upon redox cycling, which may cause cracking on either itself or the thin electrolyte layer in case of a failure in fuel supply. The use of a protective gas to flush the anode chamber during the breakdown would be costly and impractical, especially for small-scale residential CHP (combined heat and power) systems. Therefore, new redox-stable anode materials are required to overcome these problems. In recent years, ceramic oxides with mixed ionic and electronic conduction are attracting more and more attention. This type of material is expected to offer considerable improvement over Ni/YSZ with respect to most of these problems.

Strontium titanate is a chemically stable perovskite oxide that exhibits n-type electronic conduction upon reduction due to the presence of Ti³⁺ (1). Its electrical conductivity can be remarkably improved by donor (e.g., La³⁺ (2-4), Y³⁺ (5-6), or Nb⁵⁺ (7-8)) substitution. Due to their good chemical stability and relatively high electronic conductivity in reducing atmosphere, these materials have been considered as possible SOFC anode.
materials. Recently, Hui and Petrie (5) found that yttrium-substituted SrTiO$_3$ showed unusually high conductivity (64 S/cm at 800°C and 10$^{19}$ atm P$_{O_2}$) compared to those with rare earth substitutes. On the other hand, acceptor substitution is generally used to improve the ionic conductivity of this material (9-10). Based on the assumption that these two types of substitution would function independently, Hui and Petrie (6) further investigated the effect of some acceptor substitutes (Fe, Co, Ni, Cr) at Ti site on the electrical property. Of these the 5 mol% Co-substituted sample (Sr$_{0.85}$Y$_{0.10}$Ti$_{0.95}$Co$_{0.05}$O$_3$) showed the highest conductivity and also higher resistance to re-oxidation than Sr$_{0.85}$Y$_{0.10}$TiO$_3$. However, it is difficult to understand that acceptor substitution, by means of which oxygen diffusion rate is expected to increase, results in higher resistance to re-oxidation since the oxidation kinetics should be proportional to the oxygen diffusion rate.

According to the defect chemistry, donor substitution generally inhibits the creation of oxygen vacancies, and hence causes slow oxygen diffusion and slow redox kinetics. Since the electrical conductivity of Ti-based materials is a function of oxygen partial pressure (P$_{O_2}$), the slow redox kinetics may cause erroneous measurement if the material is not allowed to reach equilibrium with the ambient atmosphere. For example, attempts to study the P$_{O_2}$-dependence of the electrical conductivity of relatively dense Nb-substituted SrTiO$_3$ samples yielded somewhat odd results (8). In this case, the microstructure played an important role. Fine-grained, porous samples exhibited faster redox kinetics than the coarse-grained, dense samples. With this in mind, the reported unusual re-oxidation kinetics for Y- and Co-substituted SrTiO$_3$ may be related to its unique microstructure, which usually varies with the material preparation and processing procedures. Furthermore, for these SrTiO$_3$-based materials, the charge compensation mechanism, which determines the electrical property, depends remarkably on the composition and the P$_{O_2}$ during the sintering or annealing process (4,11). Therefore, further work is required to evaluate the feasibility of yttrium-substituted SrTiO$_3$ as a possible redox-stable anode material, especially with respect to the redox behaviour.

In this paper, the 10 mol% yttrium-substituted SrTiO$_3$ (with and without 5 mol% Co co-substitution) were studied in more detail, emphasizing the complex dependence of electrical conductivity and redox behaviour on the preparation and processing procedures.

**EXPERIMENTAL**

The target compositions were Sr$_{0.85}$Y$_{0.10}$TiO$_3$ (SYT) and Sr$_{0.85}$Y$_{0.10}$Ti$_{0.95}$Co$_{0.05}$O$_3$ (SYTC). These two compositions were chosen simply for a better comparison with the previous work by Hui and Petric (6), although the solubility limit of Y in SrTiO$_3$ was reported to be around 8 mol% (5). In fact, Hui and Petric (6) found that the electrical conductivity of Sr$_{0.85}$Y$_{0.10}$Ti$_{0.95}$Co$_{0.05}$O$_3$ is much higher than that of Sr$_{0.88}$Y$_{0.08}$Ti$_{0.95}$Co$_{0.05}$O$_3$.

Both the conventional solid-state reaction (SSR) and the Pechini method (12) were used to synthesize the powder. Compared with SSR, the Pechini method is able to yield more homogeneous and ultra-fine powders at much lower calcination temperatures. For SSR, the mixtures of the starting chemicals (SrCO$_3$, Y$_2$O$_3$, TiO$_2$ and Co$_3$O$_4$) were first ball-milled in ethanol for 48 h. After drying, the powder was pressed uni-axially into pellets and calcined at 1400°C for 10 h in air. The pellets were then crushed and pressed into bars with dimensions of about 2.5×5×40 mm$^3$, and finally sintered at 1500°C for 8 h in air.
or forming gas (Ar-4%H₂). For the Pechini method, nitrates of Sr, Y and Co, titanium isopropoxide were used as the starting chemicals. The as-prepared powders were then pressed into bars and sintered at different temperatures to obtain samples with different densities. Some air-sintered samples were subsequently reduced at different temperatures in forming gas before the electrical conductivity measurement.

The crystalline phase composition was determined by powder X-ray diffraction (XRD, Siemens D5000) with Cu Kα radiation. A laser diffraction grain size analyser (Fritsch Analysette 22) was used to measure the particle size distribution, and the stoichiometric composition was determined by inductively coupled plasma with optical emission spectroscopy (ICP-OES, TJA-IRIS-INTREPID spectrometer). The density or porosity was measured by the Archimedes's method. The microstructure was observed with scanning electron microscopy (SEM, Joel T300). The standard d.c. four-probe method was used to measure the electrical conductivity in air or reducing atmospheres (Ar-4%H₂) between 25°C and 910°C.

RESULTS AND DISCUSSION

Particle Size and Stoichiometric Composition

The average particle sizes of the SSR-prepared powders are about 30 μm, which are over one order of magnitude larger than that prepared by the Pechini process (about 1 μm). As for the stoichiometric composition, the SSR-prepared SYTC powder has much lower Co content (3.4 mol%) than the target value (5 mol%), which is attributed to the volatile loss of Co during the high-temperature calcination process since the SSR precursor contains the expected Co content. Other elements (Sr, Y, Ti) do not show any noticeable volatile loss. Within the error of ICP-OES, the Pechini-prepared powders show the expected stoichiometric compositions.

Phase Assemblage

The powder preparation methods (SSR and Pechini) have no effect on the final phase assemblage for the same composition and with the same processing procedures. Fig. 1 shows the XRD patterns for Pechini-prepared samples subjected to different processing procedures. Due to the solubility limit of Y in SrTiO₃, all patterns contain the impurity pyrochlore phase Y₂Ti₂O₇. It is very interesting to compare the phase assemblage for samples sintered in different atmospheres. For SYT, sintering in air at 1400°C results in an additional small amount of TiO₂ (Fig. 1a). The appearance of TiO₂ will be further explained in the following sections. After sintering in forming gas (Ar-4%H₂), however, the diffraction intensity of Y₂Ti₂O₇ is decreased and no TiO₂ is observed (Fig. 1d). The reduction of air-sintered sample at different reduction temperatures also clearly shows this tendency (Fig. 1: b-c), i.e., as the reduction temperature increases, the diffraction intensity of Y₂Ti₂O₇ decreases. This behaviour indicates that the solubility of Y in SrTiO₃ increases at lower P₀₂ and higher reduction temperature.
Figure 1. XRD patterns for Pechini-prepared samples subjected to various processing procedures. 

- **a**: SYT, sintered in air at 1400°C for 5 h; 
- **b**: a reduced in Ar-4%H₂ at 1220°C for 20 h; 
- **c**: a reduced in Ar-4%H₂ at 1320°C for 20 h; 
- **d**: SYT, sintered in Ar-4%H₂ at 1350°C for 5 h; 
- **e**: SYTC, sintered in air at 1400°C for 5 h; 
- **f**: reduced in Ar-4%H₂ at 950°C for 20 h; 
- **g**: SYTC, sintered in Ar-4%H₂ at 1350°C for 5 h. 

For SYTC, air-sintered samples show not only Y₂Ti₂O₇ impurity, but also another minor impurity, which is assigned to Co₂TiO₄ (Fig. 1 e). The comparison between Fig. 1 a and e indicates that the addition of Co also increases the Y solubility. The solubility enhancement of Y with reduction, and with the addition of the Co, can be understood as follows. The donor substitute (Y₂O₃) tends to bring excess oxygen into the lattice, and anything that will reduce that, loss of oxygen due to reduction, or the presence of acceptor substitutes, will enhance the solubility of the donor. Here the presence of the Y₂Ti₂O₇ impurity serves as an "indicator" for the solubility change under different conditions. In the previous work (6), 5 mol % Co at Ti site was assumed to be stable in the reducing atmosphere based on the concept that a small amount of unstable transition metal ions would be stabilized by inserting them into a stable perovskite host lattice. However, in this work, the appearance of metallic Co upon reduction (Fig. 1 f and g) indicates that the Co-containing composition seems unstable in the reducing atmosphere. The comparison of Fig. 1 f and g also indicates that more Co is extracted out of the host lattice as the reduction temperature increases.
**Reduction Kinetics of Air-sintered Samples**

Fig. 2 shows the electrical conductivity of SYTC samples with different densities / microstructures as a function of reduction time in Ar-4%H₂ at 910°C (P₀₂ «1 O'2 0 bar). Very slow reduction kinetics is observed for relatively dense samples. For instance, the conductivity of sample a (89% relative density) still has not reached equilibrium even after 240 h of reduction. In contrast, for samples c and d (82% and 62% relative density), it takes a very short time to reach 0.2-0.3 S/cm, showing much faster reduction kinetics.

During the reduction process of air-sintered SrTiO₃-based materials, the removal of oxygen from the lattice as well as the valence change of Ti ions can be represented by

\[
O_2^+ \leftrightarrow V_{\text{O}}^\ast + 2e^- + 1/2O_2(g) \tag{1a}
\]

\[
\text{Ti}^{4+} + e^- \leftrightarrow \text{Ti}^{3+} \tag{1b}
\]

The reduction kinetics is thus determined by the bulk diffusion of oxygen, i.e., the diffusion from the grain interior to the grain boundary and/or to the gas/solid interface. For diffusion-controlled process, the kinetics can be expressed as a function of a single dimensionless parameter \( t D/L^2 \), where \( t \) is the time, \( D \) is the diffusion coefficient, and \( L \) is the size scale. This means the time \( t \) required to reach equilibrium is proportional to the square of diffusion length \( L \). Therefore, porous samples with fine grains (short diffusion length) require much shorter time to reach equilibrium than dense samples with coarse grains (long diffusion length). Fig. 3 shows the SEM micrographs for the four samples corresponding to Fig. 2. Sample a has more pores than sample b, but not all the pores are well connected and the average pore-to-pore distance is rather long (> 50 μm). In contrast, samples c and d have very fine microstructures, e.g., the pores are well connected and the average pore-to-pore distances are in the order of 1 μm. If samples b and d were compared, with a diffusion length of about 1 mm (the sample thickness) and 1 μm respectively, the required diffusion time for sample b would have to be six orders of magnitude longer than for sample d.

It should be noticed that, even for samples c or d, the conductivity seems to rise endlessly with reduction time. In comparison to the fast increase at the initial stage, the process that takes place subsequently should be an extremely slow one. According to the discussion below, this process should involve cation diffusion, which has been shown by Moos et al. (3) to occur with a considerable rate only at temperatures above 1150°C. Therefore, to obtain the equilibrium conductivity values in the reducing atmosphere, high-temperature heat treatment in this atmosphere is necessary, which can be realized either by post-reduction after sintering in air or by direct sintering in the reducing atmosphere.

**Electrical Conductivity of High-temperature Reduced Samples**

Samples that experienced a high-temperature reduction process show significantly improved electrical conductivity in Ar-4%H₂. In this work a typical temperature program for the conductivity measurement included a heating up process at 10 K/min to 910°C, holding at 910°C until the conductivity became stable, and then cooling down at 5 K/min to room temperature step by step (with temperature intervals of 100 K and holding time...
Figure 2. Reduction kinetics (at 910°C in Ar-4%H₂) of air-sintered SYTC samples sintered at different temperatures to obtain different relative densities (d_{rel}).

Figure 3. SEM micrographs (fracture) for SYTC samples corresponding to Figure 2.
of 1 h at each step). By this way the apparent equilibrium conductivities (not necessarily the true equilibrium values as discussed below) at least at one temperature (910°C) were obtained. At other temperatures, sometimes only non-equilibrium values could be obtained (in this case values toward the end of each temperature step were chosen for plotting). Fig. 4 show three example runs for SYT samples with different processing procedures. The temperature dependence of the conductivity obtained in this way is
shown in Fig. 5 for various samples. The processing procedures as well as the resulted densities and open porosities of samples shown in Fig. 4 and 5 are listed in Table 1.

Table 1. Relative densities and open porosities of Pechini-prepared samples (corresponding to Fig. 4 and 5) subjected to various firing conditions.

| Sample Code | Composition | Firing conditions | Relative density | Open porosity |
|-------------|-------------|-------------------|------------------|---------------|
| SYTC-1230S  | SYTC        | Sintered at 1230°C/5 h/Ar-H2 | 65%              | 35%           |
| SYTC-1300S  | SYTC        | Sintered at 1300°C/5 h/Ar-H2 | 82%              | 18%           |
| SYTC-1350S  | SYTC        | Sintered at 1350°C/5 h/Ar-H2 | 84%              | 0.5%          |
| SYT-1230S   | SYT         | Sintered at 1230°C/5 h/Ar-H2 | 61%              | 39%           |
| SYT-1300S   | SYT         | Sintered at 1300°C/5 h/Ar-H2 | 72%              | 28%           |
| SYT-1350S   | SYT         | Sintered at 1350°C/5 h/Ar-H2 | 95%              | 0.1%          |
| SYT-1220R   | SYT         | Sintered at 1400°C/5 h/air, then reduced at 1220°C/20 h/Ar-H2 | 99%              | 0.1%          |
| SYT-1320R   | SYT         | Sintered at 1400°C/5 h/air, then reduced at 1320°C/20 h/Ar-H2 | 99%              | 0.1%          |

Appendantly samples sintered (in Ar-4% H2) or reduced at higher temperatures show higher electrical conductivity. This cannot be explained simply in terms of relative densities. For example, air-sintered SYT reduced at 1320°C and 1220°C shows conductivity of 113 and 53 S/cm at 810°C, respectively, but their relative densities are the same (99%). Also for SYTC, as the sintering temperature is increased from 1300°C to 1350°C, the relative density only increases by 2% (from 82% to 84%), but the conductivity increases by almost 100% (from 39 to 76 S/cm at 810°C). To understand this, the defect chemistry of this material will be discussed below.

A Kroger-Vink diagram (13) is a useful representation when discussing the electrical conductivity in oxides with added dopants. Being similar to other donor-substituted SrTiO3 (e.g., Sr1-xLa2TiO3 (2)), the equilibrium defect concentrations as a function of P02 for Y-substituted SrTiO3 can be schematically shown in Fig. 6. It should be noticed that, in this paper, we merely assume the occupation of Y at the Sr site, acting as a donor. There may be some arguments that Y can also occupy the Ti site, acting as an acceptor. In fact, this really takes place in the case of BaTiO3 due to the intermediate ionic radius of Y3+. For instance, Lee et al. (14) and Xue et al. (15) found that Y and Er can occupy both Sr and Ti sites in ratios that depend on the Ba/Ti ratio. They act as acceptors in the presence of excess BaO, but as donors in the presence of excess TiO2. In this work, the compositions are Sr site deficient, which will favour the occupation of Y at Sr site. The high electrical conductivity also suggests the donor-like behaviour.

Y3+ substitution of Sr2+ in SrTiO3 results in an excess of positive charge, which has to be compensated to ensure the electroneutrality in the material. In oxidizing atmosphere (corresponding to region III in Fig. 6), it is compensated by negatively charged strontium vacancies. With high-resolution transmission electron microscopy, Battle et al. (16) have observed the strontium vacancy ordering in Sr1.3x/2La4TiO3.

The ionic compensation mechanism results in very low electronic conductivity in air. In the present work, at 810°C and in air, the electrical conductivity of air-sintered SYT and
SYTC is only in the order of $10^{-2}$ and $10^{-4}$ S/cm, respectively. With this compensation mechanism, the appearance of TiO$_2$ impurity in the air-sintered SYT can also be explained. Since not all of the Y used in the starting materials can be dissolved into the SrTiO$_3$ lattice, the un-dissolved Y prefers to form the pyrochlore Y$_2$Ti$_2$O$_7$. Due to the limitation of the compensation mechanism, $Y_{sr}^* = 2[V_{sr}^+]$, a small amount of TiO$_2$ is expected as a separate phase according to

$$\text{Sr}_{0.85} Y_{0.10} \text{TiO}_3 \xrightarrow{\text{air-sinter}} y\text{(Sr}_{0.85}/yY_{(0.1-\alpha)}/y\text{Ti}^{IV}\text{O}_3}) + \alpha/2\text{Y}_2\text{Ti}_2\text{O}_7 + \alpha/2\text{TiO}_2$$

where $y=1-1.5\alpha$ and $\alpha$ indicates the amount of Y that cannot be dissolved into the SrTiO$_3$ perovskite lattice in oxidizing atmosphere. The left side only indicates the starting nominal composition and should not be considered as any single-phase material. It is noticeable that no TiO$_2$ impurity is observed for air-sintered SYTC. This may be explained by the appearance of another impurity phase (Co$_2$TiO$_4$) as described above.

In modest reducing atmosphere, electrons are generated as Ti$^{4+}$ is reduced to Ti$^{3+}$ according to reaction [1a] and [1b], thus the compensation mechanism moves from ionic compensation to electronic compensation (corresponding to region II in Fig. 6). The electronic conductivity is then improved by several orders of magnitude. In this region, the electron concentration is determined by the donor doping level, i.e., $n = [Y_{sr}^+]$, and the concentration of strontium vacancy is very low.

One should keep in mind that the defect concentrations shown in Fig. 6 are in thermodynamic equilibrium with the P$_{O2}$, i.e., the transition from one region to another region due to the P$_{O2}$ variance will take place without any kinetic limitations. At lower temperatures, however, such kind of transition will be practically limited by kinetic factors. For instance, the transition for SYT from ionic compensation to electronic
compensation involves the cation diffusion to reduce the concentration of strontium vacancy. This transition can be represented by:

$$\text{Sr}_{1-3x/2} \left( V_0^+ \right)_{x/2} Y'_x \text{TiO}_3 \rightleftharpoons \left( 1-x/2 \right) \text{Sr}_{1-x/2} \left( V_0^+ \right)_{x/2} \text{TiO}_3 + x/2 \text{TiO}_2 + x/4 \text{O}_2(g) \quad [3]$$

where $x$ is the yttrium content in the SYT perovskite lattice ($x<0.1$) and $z=x/(1-x/2)$. It should be noticed that an electronically compensated perovskite (ABO$_3$) tends to have a composition with a unit A/B ratio, as indicated by Smyth (17). This rule is supported by the work of Makovec et al. (18), where a Ba-rich phase Ba$_2$TiO$_4$ has been observed when the air-sintered donor-substituted BaTiO$_3$, Ba$_{1-x}$La$_x$ Ti$_{1-\delta}$($V_0^+$)$_{\delta}$O$_3$ (with titanium vacancies as compensation defects) is reduced at 1350°C for 50 h in N$_2$-10% H$_2$.

At high reduction temperatures, the transition can be finished within reasonable time (20 h), resulting in quite high electrical conductivity. At lower reduction temperatures, e.g., the conductivity measurement temperatures in this work, ≤ 910°C, the transition cannot be finished within reasonable time due to the extremely slow cation diffusion, resulting in low electrical conductivity, as shown above.

In highly reducing atmospheres, oxygen vacancies will become the predominant ionic defects, and more electrons than the donor can supply are produced to counterbalance the oxygen vacancies, i.e., $n = 2[V^n_0]$ (corresponding to region I in Fig. 6). The composition of SYT in this region can be expressed as $\text{Sr}_{1-z} Y'_x \text{Ti}_{1-2z} \text{O}_3$, where $\delta$ indicates the oxygen vacancy concentration. The fact that the conductivity of SYT reduced at 1320°C is much higher than that reduced at 1220°C indicates that the material is possibly in region I under this reducing condition. The mass-action law of reaction [1a] can be formulated as:

$$[V^n_0]^n \text{O}_2^{1/2} = K_{\text{Red}} \exp(-\Delta H_{\text{Red}}/kT) \quad [4]$$

where $\Delta H_{\text{Red}}$ is the reduction enthalpy. According to the work by Moos et al. (3), $\Delta H_{\text{Red}}$ has a positive value ($6.1 \pm 0.2$ eV determined from undoped SrTiO$_3$). Thus reaction [1a] will turn right-hand as the reduction or sintering temperature increases, producing more electrons. The reduction at high temperatures cannot be fully reversed during the subsequent cooling process due to the short time and slow oxygen diffusion at lower temperatures. Therefore it is assumed that most of the “extra” electrons produced by the high-temperature reduction process remain in the conduction band down to lower temperatures. In our measurement procedure, the temperature is decreased step by step. When the temperature is decreased, reaction [1a] tends to turn left-hand, absorbing oxygen and decreasing the electron concentration. While this process may not be observed with dense samples due to slow oxygen diffusion rate, it is indeed observed with porous samples, as shown in Fig. 4. The dense samples (SYT-1220R and SYT-1320R) show conductivity platforms but the porous sample (SYT-1230S) shows degradation, at each temperature step, indicating the occurrence of oxygen uptake. Thus the observed conductivity platforms at each temperature should not be simply regarded as signs of true equilibrium and may be only a result of very slow kinetics.

The above discussion also indicates that some TiO$_2$ impurity should be present as a result of high-temperature reduction according to reaction [3]. However, in this study, no TiO$_2$
impurity phase is observed by XRD for high-temperature reduced samples. Nevertheless, the significant conductivity improvement after reduction indeed indicates the transition from ionic compensation to electronic compensation. This discrepancy is possibly due to that the amount of TiO$_2$ is too small to be detected by XRD.

![Graph showing redox behaviour of electrical conductivity](image)

Figure 7. The redox behaviour of electrical conductivity (at 910°C between Ar-4%H$_2$ and air) for two SYT samples sintered in Ar-4%H$_2$ at 1350°C and 1300°C, with relative density (open porosity) of 95% (0.1%) and 72% (28%), respectively. The oxidation segments are indicated on the graph.

Redox Reversibility

Fig. 7 shows the redox behaviour of two SYT samples sintered in Ar-4%H$_2$ at 1350°C and 1300°C, and with relative densities (open porosities) of 95% (0.1%) and 72% (28%), respectively. Again the effect of microstructure on the redox kinetics was observed. For the dense sample, after oxidation in air at 910°C for 9 h, the conductivity decreased from 86.4 to 77 S/cm. In contrast, for the porous sample, the conductivity decreased abruptly by more than 3 orders of magnitude when the atmosphere was switched from Ar-4%H$_2$ to air, indicating a much faster kinetics than the dense sample.

The conductivity started to increase upon the subsequent reduction process. However, it seemed that the conductivity could not be recovered completely at least within reasonable time. Although the possibility of complete recovery after sufficient long time cannot be excluded, a more possible explanation would be based on the thermodynamic consideration. It is assumed that samples reduced at high temperatures are actually not in thermodynamic equilibrium with the P$_{O_2}$ at lower temperatures (e.g., at the measurement temperature, 910°C). The equilibrium conductivity should be lower than the non-equilibrium one. While the re-equilibration may be extremely slow in reducing atmosphere, the oxidation in air might be able to accelerate it. Nevertheless, other
possibilities such as the deterioration of the microstructure upon redox cycling could also contribute to the observed conductivity degradation. Further study is required to clarify the mechanism of redox irreversibility.

CONCLUSIONS

The present investigation indicates that the electrical properties of yttrium-substituted SrTiO$_3$ depend to a very large extent on the preparation and processing procedures, i.e., the particular histories they experienced. This is mainly attributed to the limitation of the re-equilibration kinetics after the environment (e.g., temperature and oxygen partial pressure) of these materials is changed, e.g., the application environment is different from that under which the material is fabricated. Therefore one should take caution when characterizing such kind of materials.

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