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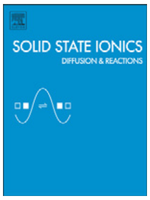

Donor-substituted $SrTi_{1+x}O_{3-\delta}$ anodes for SOFC

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ABSTRACT

Nonstoichiometric Nb-substituted $SrTiO_3$ compounds were investigated in order to discuss the influence of nonstoichiometry at the sample properties in the light of recent results reported in the literature. Structural and electrical properties of samples were characterized. Investigated compounds were also applied as anodes for Solid Oxide Fuel Cells and their reactivity with YSZ electrolyte was examined. The defect chemistry explaining observed phenomena was suggested and the probability of Sr-site vacancies formation compared to Ti-site vacancies was discussed.

1. Introduction

The traditionally used anode for Solid Oxide Fuel Cells (SOFCs) is Ni-YSZ cermet that suffers from many limitations. Hence, it is necessary to investigate some alternative materials, like perovskite-related structures. Among them $SrTiO_3$ is one the most promising compositions, but in a pure form it is a dielectric material. Its conductivity increases significantly at low oxygen partial pressure according to a change in the titanium valence from Ti^{4+} to Ti^{3+} [1]. Also substitution with donor dopants can affect the value of $SrTiO_3$ conductivity [2–11]. The most popular Sr-site donor dopants are La, Y and Al, whereas Ti-site is often substituted with Nb and Ta. Also the nonstoichiometry in the ABO_3 perovskite structure has a very big influence on the conductivity, grain size and phase purity of the perovskite material. In this paper the nonstoichiometric Nb-doped $SrTiO_3$-based samples reduced in hydrogen atmosphere will be discussed in detail.

1.1. Defect chemistry of $SrTiO_3$-based materials

Many scientific groups have performed investigations on nonstoichiometric strontium titanate [12–17]. In spite of comparable experimental results, there can be found significantly different explanations of defect chemistry and phenomena taking place in this kind of material.

Blennow et al. [12] discusses the defect chemistry of reduced $SrTiO_3$. Author shows that conductivity of strontium titanate is associated with Ti^{4+}/Ti^{3+} state. The equilibrium state is described with Eq. (1) that can be shifted to one of the sides depending on the oxygen partial pressure [12]:

$$2Ti_{Ti}^{x}+O_{o}^{x}\overset{SrTiO_3}{\longleftrightarrow}2Ti_{Ti}^{'}+V_{O}^{\bullet\bullet}+\frac{1}{2}O_2(g) \tag{1}$$

Mostly, Ti^{3+} ions are formed under reducing conditions. However, the concentration of Ti^{3+} ions can be additionally increased by A-site deficiency. In this compound both $V_{Sr}^{''}$ and $V_{O}^{\bullet\bullet}$ exist and Ti^{3+} ions are formed as a consequence of oxygen vacancies $V_{O}^{\bullet\bullet}$ presence. As a result, this Sr depleted sample will have higher concentration of Ti^{3+} and higher conductivity than stoichiometric composition according to the Eq. (2) [12]:

$$(1-x)SrTiO_3+xTiO_2\overset{H_2}{\rightarrow}Sr_{1-x}Ti_{1-2y}^{4+}Ti_{2y}^{3+}O_{3-y-x}+\frac{y}{2}O_2 \tag{2}$$

Horikiri et al. [13] bases his considerations about reduced $SrTiO_3$ on the site-mixing concept [14], in which it is assumed that Sr ions may enter the B-site, because the vacancy on the 6-oxygen coordinated B-site is less stable than on the 12-coordinated A-site. Thus, the equilibrium state of pure $SrTiO_3$ can be expressed by the Eq. (3) [13]:

$$Sr_{Sr}^{x}+V_{Ti}^{''''}\rightleftharpoons V_{Sr}^{''}+Sr_{Ti}^{''} \tag{3}$$

with the equilibrium shifted almost completely to the right-hand side.

In this case, when there is Sr-deficiency in the $Sr_{1-x}TiO_3$ structure, some amount of TiO_2 is formed as a second phase. Then strontium occupying the B-site $Sr_{Ti}^{''}$ may be driven out by titanium, because $Sr_{Ti}^{''}$ is

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less stable than Ti_{Ti}^{x}. In consequence, some additional electrons are released and the conductivity of the material increases. This situation may be written as [13]:

$$V_{Sr}^{''} + Sr_{Ti}^{''} + TiO_2 \rightarrow Sr_{Sr}^{x} + Ti_{Ti}^{x} + 2O_o^{x} + 4e^{'} \tag{4}$$

On the basis of this hypothesis, the A-site deficiency results in the reduction of acceptor electrical barrier existing at grain boundaries [5,13] and in the increase of total conductivity of the material.

Bäurer et al. [15] suggests that for A-site deficient $Sr_{1\text{-}x}TiO_3$ a TiO_2 excess is partly accommodated by the formation of $V_{Sr}^{''}$ and $V_O^{\bullet\bullet}$ vacancies according to the Eq. (5) [15]:

$$nSrTiO_3 + TiO_2 \leftrightarrow nSrTiO_3 + Ti_{Ti}^{x} + 2O_o^{x} + V_{Sr}^{''} + V_O^{\bullet\bullet} \tag{5}$$

whereas A-site excess is accommodated in SrO intergrowth layers called Ruddlesden–Popper (RP) phases, without forming vacancies [15]:

$$nSrTiO_3 + SrO \leftrightarrow nSrTiO_3 + SrO_{RP} \tag{6}$$

Zhao et al. [16] for Y-doped A-site deficient strontium reports that the increase of $V_{Sr}^{''}$ concentration leads to the decrease of the amount of yttrium occupying strontium position ($Y_{Sr}^{\bullet}$). The created charge imbalance will be compensated by the increase of $V_O^{\bullet\bullet}$ concentration and, in consequence, will result in the decrease of Ti^{3+} concentration. Thus, the A-site deficient sample should present lower electrical conductivity than the stoichiometric one, but could have higher ionic conductivity [16].

On the other hand, the same group in the paper of Gao et al. [17] analyses the defect chemistry of so-called B-site deficient Y-doped $SrTi_{1\text{-}x}O_3$. By analogy to the previous considerations the author suggests that Ti deficiency will generate oxygen vacancies $V_O^{\bullet\bullet}$ and, for charge compensation, the decrease of Ti^{3+} concentration. Experimentally, this theory suggests that B-site deficiency in $SrTi_{1-x}O_3$ will result in the increased ionic conductivity and unchanged electronic conductivity, what disagrees with the results obtained by Gao et al. [17]. It should be noted that the energy of titanium defect ($V_{Ti}^{''''}$) formation is significantly higher than the energy of strontium defect ($V_{Sr}^{''}$) formation [1,18–21]. Thus, it seems that Ti vacancies ($V_{Ti}^{''''}$), which presence is much less probable in the structure, should not be taken into account in defect chemistry of $SrTiO_3$.

The aim of this work is to discuss the influence of nonstoichiometry at the properties of donor-substituted $SrTiO_3$ and to confront with previously reported defect chemistry in the light of obtained experimental results. There are two possible types of stoichiometric notations. First notation with Sr-site normalized to unity can be denoted as 'nominal notation', whereas notation after Ti-site normalization, and thus suggesting the presence of Sr-site defects, is denoted as 'equivalent notation.' In the discussion part of this paper the latter notation will be applied.

2. Experimental

The Nb-substituted strontium titanate samples nominally noticed as $Sr(Ti,Nb)_{1+x}O_{3-\delta}$ ($x \in <-0.05;0.10>$) were prepared using a conventional solid-state reaction method [5]. The $SrCO_3$ (Sigma Aldrich, 99.9+%), TiO_2 (Sigma Aldrich, 99+%) and Nb_2O_5 (Fluka, 99.9+%) powders were mixed in the suitable stoichiometric ratios and ball milled with ethanol for 24 h. After drying the mixture was pressed into bars (~280 MPa) and calcined in air at 1200 °C for 12 h. Then, the pellets were reground to obtain better samples quality, uniaxially pressed at 560 MPa and sintered at 1400 °C for 12 h in air. It has been shown [5] that an optimal amount of Nb is 2 mol%, as it gives the highest conductivity in comparison with the other investigated compositions. In this paper only the most representative compounds will be presented. Nominal notations, equivalent notations and abbreviations of the samples are listed in Table 1.

The investigations were performed on both the bulk samples and on samples fabricated as 40 μm-thick porous layers on yttria-stabilized zirconia (YSZ) electrolyte (half cells). The latter were prepared by mixing powder with a 5 wt.% of carbon black and an organic binder ESL403 (ElectroScience). The resulting paste was deposited onto the surface of the YSZ electrolyte support (~0.8 mm thick). In order to burn out the organic binder, the prepared pellets were calcined at 700 °C for 3 h in air [22]. To improve the electrical properties several samples were reduced at 1400 °C for 10 h in dry hydrogen.

The phase composition of the bulk samples was analyzed by an X-ray diffraction method by the X'Pert Pro MPD Philips diffractometer using Cu K_α (1.542 Å) radiation at room temperature. The XRD patterns were also analysed by the Rietveld refinement method using a version of the LHPM1 program [23] with the pseudo-Voigt profile function applied. As a starting point of the analysis, crystal structure parameters of $SrTiO_3$ (Pm-3m space group) [24] and TiO_2 (P 42/mnm space group) were used [25]. The morphology of the samples was characterized by the Hitachi TM3000 scanning electron microscope (SEM), using secondary electron (SE) detector. To recognize the elements and their distribution in composite the Energy-Dispersive X-ray Spectroscopy (EDX) was performed by the BRUKER AXS Quantax 200 spectrometer operating with Zeiss EVO40 SEM at 20 kV, WD = 12–17 mm in particular areas of each sample. The electrical conductivity of polished bar samples (size $1 \times 2 \times 10\ mm^3$) was measured using the four terminal DC method over temperature range of 400–950 °C in humidified hydrogen (97% H_2/3% H_2O) under the pressure $p(O_2) = 4.183E\text{-}22$ atm (calculated in Factsage software). The measurements were performed at constant heating and cooling rates (3 °C/min). To ensure that the measurements were performed in equilibrium conditions, it was found that the results obtained in this way were identical with those taken after holding at each temperature for 30 min.

3. Results and discussion

3.1. Phase characterization and defect structure

Sample XRD results are shown in Fig. 1. Both S091TNO and S095TNO compositions gave comparable results, but only the latter is shown in Fig. 1. Also the stoichiometric STNO composition is not shown as it was reported recently [5] and contains no additional phases, regardless of the heat treatment. In both non-reduced and reduced S095TNO samples (Fig. 1a and b) a trace amount of TiO_2 and Sr_2NbO_4 phases was identified. In the interior of S105TNO pellet no additional phases can be found, as presented in Fig. 1c and d. However, it should be noticed that process of high temperature reduction of this sample results in the formation of a yellow-colour surface layer. The EXD spectrum of this layer compared to EDX spectrum of S105TNO interior is shown in Fig. 2. It shows that Sr/Ti ratio is four times higher in the layer than in the interior. Surprisingly, in both the layer and the interior almost no trace of niobium was detected. According to paper of Sudireddy et al. [26] this niobium could have migrated to the grain boundaries and have formed small particles

Table 1
Nominal notations, equivalent notations and abbreviations of Nb-doped $SrTi_{1+x}O_{3-\delta}$ ($x \in <-0.05;0.1>$) ceramics.

Nominal notation	Equivalent notation	Abbreviation
$SrTi_{1.08}Nb_{0.02}O_{3-\delta}$	$Sr_{0.909}Ti_{0.982}Nb_{0.018}O_{3-\delta}$	S091TNO
$SrTi_{1.032}Nb_{0.021}O_{3-\delta}$	$Sr_{0.95}Ti_{0.98}Nb_{0.02}O_{3-\delta}$	S095TNO
$SrTi_{0.98}Nb_{0.02}O_{3-\delta}$	$SrTi_{0.98}Nb_{0.02}O_{3-\delta}$	STNO
$SrTi_{0.933}Nb_{0.019}O_{3-\delta}$	$Sr_{1.05}Ti_{0.98}Nb_{0.02}O_{3-\delta}$	S105TNO