Stability and electrical conductivity of Nb- or Ta-doped SrTiO₃ perovskites for interconnectors in solid oxide fuel cells

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1. Introduction

Strontium titanate (SrTiO₃) perovskites are promising materials for interconnectors in segmented-in-series tubular solid oxide fuel cells because of their chemical and physical stability under both reducing and oxidizing atmospheres. The formula of these perovskites can be generally expressed as ABO₃, where SrTiO₃ by itself does not conduct electricity, but conductivity can be increased by doping a rare earth element into the A site of ABO₃ or a transition metal of higher valency than Ti⁴⁺ into the B site. The deficiency at the A site in La-doped or dopant-free SrTiO₃ has also been studied. We report that substitution of Sr on by La in SrTiO₃ effectively increases the electron conductivity while deficiency at the A site was also effective in enhancing the sintering density of the compacted powder. At the B site, when the Ti⁴⁺ in SrTiO₃ is substituted by Nb⁵⁺ or Ta⁵⁺, the dopant effectively increases electron density in the system, resulting in improved electrical conductivity. Karczewski et al. reported that maximum electrical conductivity was observed in a SrTi₉.98Nb₀.02O₃ sample at 650°C. However, there have been few systematic investigations into the stability of perovskite-type SrTiO₃ that have an incorporated A site deficiency and an aliovalent dopant at the B site. Identifying the stable regions in these materials is important, especially in commercial applications, because the appearance of a second impurity phase often results in a lowering of electrical conductivity. In addition, deterioration in mechanical strength of the sintered compact is also often observed, even though the deficiency and dopant have been introduced to improve sintering and electrical properties. In the case of La-doped SrTiO₃, our group has demonstrated that small grains of Sr-doped La₂O₃ were deposited on the surface of the La-doped SrTiO₃ matrix after firing the oxide precursor at 1400–1500°C for 5 h, even when the precursor was prepared using the citric gel method. This deposited second phase was confirmed to be the same impurity that appeared in La₀.₃Sr₀.₇TiO₃ during operation as an solid oxide fuel cell device at 900°C. This impurity was reported to cause degradation in electrical conductivity.

In this study, we investigated the phase stability of Nb- and Ta-substituted perovskite-type SrTiO₃ structures containing Sr deficiencies by means of X-ray diffractometry as well as scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) spectroscopy. The electrical conductivity of selected samples was also measured to clarify the effect of the dopant on electrical properties.

2. Experimental

The preparation of samples of Sr₁₋ₓTi₁₋ₓMₓO₃ (M = Nb and Ta) was carried out using a conventional solid-state reaction. SrCO₃, rutile TiO₂, and Nb₂O₅ (or Ta₂O₅) were mixed in an aluminum crucible with an aluminum pestle for 30 min and then calcined in air at 1200°C for 10 h. The sample was placed in a pot together with several alumina balls and then ball milled for 24 h with an appropriate amount of ethanol. After drying, the powder was fired in air at 1400°C for 5 h. The fired powder was ball milled again for 72 h with ethanol. After drying, the powder was...
formed into a pellet and the pellet was sintered in air at 1500°C for 10 h.

X-Ray diffraction measurements were performed using a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation at 40 kV and 150 mA. The X-ray intensity was monitored using a 1D D/teX Ultra 250 detector. Phases were identified with reference to the JCPDS database. Lattice parameters were calculated using the CellCalc Ver. 2.20 software.

The microstructure and cationic composition of the samples were analyzed by field emission SEM (FE-SEM, Hitachi S-4700) fitted with an EDX analyzer. These measurements were carried out with an applied accelerator voltage of 10 kV without carbon coating.

Electrical conductivity measurements were carried out with a DC four-probe system. The dimensions of rectangular samples were 10 mm long, 3 mm wide and 2 mm thick. Pt paste and wires were used for the electrodes. The measurements were conducted using the CellCalc Ver. 2.20 software.

When Ti was substituted by Nb or Ta, the lattice constant increased with increasing amount of the dopant. This trend is consistent with that reported by Ohta et al. and is possibly due to the ionic radius of Nb" and Ta" (both 64.0 pm) being larger than that of Ti" (60.5 pm). When x = 0.20, we can verify the observation that increasing Sr deficiency (y) leads to a reduction in lattice constant. This trend is consistent with previous reports for (La,Sr)TiO₃. With regard to the Ta-system, a similar relationship between the dopant concentration (x), Sr deficiency (y) and lattice constant is observed. Interestingly, as the amount of dopant (x) was increased, maximum values of lattice constant for perovskite-type Sr₁₋ₓTiₓ₋₉M₂O₃ structures were found to be 3.927 Å for M = Nb and 3.930 Å for M = Ta, regardless of Sr deficiency (y). Furthermore, the gradient of the linear relationship for a given value of y in Figs. 2(a) and 2(b) proved to be independent of dopant. This, in turn, means that the dopant (Nb or Ta) phase(s), the lattice constant did not change with increasing x.

3. Results and discussion

Stable regions of the perovskite-type structures in niobium-substituted or tantalum-substituted strontium titanates were initially studied. Figures 1(a) and 1(b) show X-ray diffraction patterns for SrTi₁₋ₓM₂O₃ [(a) M = Nb, (b) M = Ta] sintered at 1500°C for 10 h. Both doped titanate samples were monophasic for x = 0.1 and 0.2. However, SrTi₀.₇₅Nb₀.₂₅O₃ (x = 0.25) contained Sr₅TiNb₀.₇NbO₁₇ as an impurity phase, while the corresponding SrTi₀.₇₅Ta₀.₂₅O₃ was contaminated with Sr₂Ta₂O₇. Since SrTiO₃ (x = 0) was obtained as a pure single-phase material, we can conclude that stable monophasic perovskite-type SrTi₁₋ₓM₂O₃ (M = Nb, Ta) structures are obtained when 0 ≤ x ≤ 0.20. When the Sr deficiency (y) was increased in the absence of Nb or Ta as an additive (x = 0), rutile-type TiO₂ appeared as an impurity, even at y = 0.02.

Figures 2(a) and 2(b) show the dependence of lattice parameter a on the dopant concentration (x) in Sr₁₋ₓTiₓO₃ [(a) M = Nb, (b) M = Ta] sintered at 1500°C for 10 h. The Sr deficiency, y, was kept constant in each case. The lattice parameter for SrTiO₃ was determined to be 3.904 Å, which is in good agreement with the reported value. Within samples that demonstrated a single perovskite phase, the lattice parameters increased linearly with increasing x. In samples that developed an impurity

Fig. 2. Dopant concentration (x) dependence of lattice parameter a of Sr₁₋ₓTiₓO₃ (y = 0, 0.05 and 0.1, and M = Nb for (a) and M = Ta for (b), respectively) sintered at 1500°C for 10 h. Open and solid symbols mean lattice constants for impurity-free perovskite and those for perovskite with an impurity phase, respectively.
occupancy of the A site by Sr2+y increased. Sr deisond, Sr5TiNb4O17 was detected as an impurity for the analogous concentration of the dopant shifted toward higher tantalum were enriched while titanium was diluted in some substituting Ti by at least 20% in positive charge. It seems that Nb and Ta are capable of sub-

ing images of Sr L-, Ti K- and Ta M-lines (respectively) for the sintered SrTi0.9Ta0.1O3. Even within the single-phase region of the perovskite in SrTi0.9M0.1O3, electrical conductivity was improved by introducing the Sr deficiency. This is likely due to increased sintered density resulting from the Sr deficiency, which increases from 92 to 95% for M = Nb, and from 91 to 94% for M = Ta, and is probably due to an increase in effective carrier, a result of the introduction of Nb5+ or Ta5+.

Figures 3(a) and 3(b) summarize our X-ray results. These figures can be used to determine the stable, single-phase regions in these Sr1-xTi1-yMxO3 perovskite-type structures [(a) M = Nb; (b) M = Ta]. We also observed that the solubility limiting concentration of the dopant shifted toward higher Sr as Sr deficiency y increased. Sr deficiency decreases the positive charge due to occupancy of the A site by Sr2+. The inclusion of highly charged Nb5+ or Ta5+ may be preferable to compensate for this decrease in positive charge. It seems that Nb and Ta are capable of substituting Ti by at least 20% in SrTiO3. Strontium titanate doped with tantalum was observed to possess a wider stable region (against strontium deficiency) for achieving perovskite-type structures, compared to that doped with niobium. That is, at x = 0.25 and 0.30 in Sr1-xTi1-yTaO3, single phases were observed for perovskite-type structures even at y = 0.05 and 0.10. In comparison, SrTiNbO3 was detected as an impurity for the analogous Sr1-xTi1-yNbO3.

Figure 4(a) shows SEM images while Figs. 4(b)–4(d) show the EDX mapping images of Sr L-, Ti K- and Nb K-lines (respectively) associated with the sintered SrTi0.9Nb0.1O3. Figure 5(a) shows SEM images while Figs. 5(b)–5(d) show the EDX mapping images of Sr L-, Ti K- and Ta M-lines (respectively) for the sintered SrTi0.9Ta0.1O3. Even within the single-phase region of the perovskite in SrTi1-xMxO3 (M = Nb and Ta), the SEM images confirm that after firing at 1500°C for 10 h, strontium and tantalum were enriched while titanium was diluted in some SrTi0.9Ta0.1O3 grains, whereas no inhomogeneity was found in the case of SrTi0.9Nb0.1O3. The SrTi0.9Ta0.1O3 was found to be a single-phase system but a multi-phase system, with phase-separation. Since all the phases in the Ta-doped SrTiO3 could be assigned to the perovskite-type, no extra diffraction peaks were observed in the XRD pattern, and we could not identify the segregated phases. Even though the phases were segregated into two with a difference in the lattice constants by 0.1 Å, for example 3.91 and 3.92 Å, the difference in 2θ at the peak around 57.7° would be calculated to be only 0.1° [The average lattice constant of SrTi0.9Ta0.1O3 was 3.916 Å, as shown in Fig. 2(b).] In fact, the detection of such segregated phases was much harder since the lattice constant of the segregated phases may vary continuously according to the composition. The distribution of grain sizes was also different between the two systems. When the dopant was Nb, all grains appeared well grown with better size homogeneity when compared with grains doped with Ta.

Figures 6(a) and 6(b) depict the temperature dependence of electrical conductivity for selected samples of SrTi0.9M0.1O3 and Sr0.95Ti0.9M0.05O3 [(a) M = Nb; (b) M = Ta] fired at 1500°C for 10 h. The relative density of each sample was above 95%. For each dopant, higher conductivity was obtained in the Sr-depen
dent Sr0.95Ti0.9M0.05O3 (M = Nb and Ta). Comparing SrTi0.9M0.1O3 with Sr0.95Ti0.9M0.05O3, electrical conductivity was improved by introducing the Sr deficiency. This is likely due to increased sintered density resulting from the Sr deficiency, which increases from 92 to 95% for M = Nb, and from 91 to 94% for M = Ta, and is probably due to an increase in effective carrier, a result of the introduction of Nb5+ or Ta5+. The highly charged Nb5+ or
$\text{Ta}^{5+}$ may be preferred to compensate for the decrease in positive charge in the Sr-deficient perovskites.

In the case of this experiment, however, electron doping with the highly charged $\text{Nb}^{5+}$ or $\text{Ta}^{5+}$ would lead to overdoping of carriers because the measurements were done in a reducing condition so that electron conductivity was thought to deteriorate in SrTi$_{0.8}$Nb$_{0.2}$O$_3$. The introduction of one Sr vacancy results in the removal of two electrons,$^{13,20}$ to maintain charge neutrality, when we do not consider the change of oxygen amount. This means that electrons created by 10 mol% $\text{Nb}^{5+}$ or $\text{Ta}^{5+}$ doping will be absorbed by 5 mol% of Sr vacancy. This assumption leads to the fact that Sr$_{0.9}$Ti$_{0.9}$M$_{0.1}$O$_3$ possesses much smaller amount of carrier concentration than Sr$_{0.9}$M$_{0.1}$O$_3$. However, this absorption will give an appropriate carrier concentration to show the high conductivity under the reducing atmosphere. The electrical conductivity of SrTi$_{0.9}$Ta$_{0.1}$O$_3$, especially at low temperatures, will give an appropriate carrier concentration to show the high conductivity for both the cations.

4. Conclusion

Ta-substituted Sr$_{1-x}$Ti$_{1-x}$Ta$_x$O$_3$ perovskites are more stable over a wider compositional ($x$, $y$) region than the corresponding Nb-substituted Sr$_{1-x}$Ti$_{1-x}$Nb$_x$O$_3$, which were confirmed by XRD. However, compositional fluctuations caused by Ta substitution in the single-phase region of the perovskite are significant and can result in different contributions to electrical conductivity. In terms of the structural and electroconducting features, Nb is shown to be a better substitute for Ti in SrTiO$_3$.

References


