

Evaluation of A-site doped $\text{Sr}_{1-x}\text{RE}_x\text{TiO}_{3+\delta}$ perovskites (RE = rare earth metals) as anodes in sulfur-based hybrid cycle for hydrogen production

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A sulfur-based hybrid cycle for electrolysis and thermal decomposition (SHC) in high temperature gas-cooled reactor is considered to be a highly efficient hydrogen producing process. Because in this cycle, hydrogen produces in the electrolysis ($\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{SO}_4$), electrodes must satisfy the following requirements; (i) high corrosion resistance in H_2SO_4 solution, (ii) high electrical conductivity, and (iii) low anodic overpotentials for the electrochemical reaction.

Since $\text{SrTiO}_{3+\delta}$ perovskite shows high corrosion resistance in 50 weight% H_2SO_4 solution [1], we expect this material to be an anode material of electrochemical cell in the SHC. However, $\text{SrTiO}_{3+\delta}$ shows no electrical conductivity at an operating temperature of approximately 80°C . This is due to Ti^{4+} ions with d_0 system in the perovskite. Therefore, the existence of Ti^{3+} ions in the perovskite leads to an appearance of electronic conduction.

It can be substituted with rare earth (RE) ions of higher ionic valence state at the A-site in the $\text{SrTiO}_{3+\delta}$ structure. RE-doping results in a charge-compensating by oxygen excesses in the perovskite. It is reported that the RE-doped $\text{SrTiO}_{3+\delta}$ releases oxygen under reducing atmospheres, this release results in a change from Ti^{4+} into Ti^{3+} ions. Thus, it can be expected that the electrical conductivity appears in these materials. The aim of this study is to clarify the solubility limit in the $\text{Sr}_{1-x}\text{RE}_x\text{TiO}_{3+\delta}$ systems (RE = rare earth metals) and to evaluate these materials as anodes in the SHC from the viewpoint of electrical conductivity and corrosion resistance.

Figure 1 shows the X-ray diffraction patterns of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta}$ after heating at 1500°C for 20 h in air. It is seen that no second phases were observed.

Figure 2 shows the cell volumes of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta}$ perovskite as a function of dopant content. The triangles represent the volumes after reducing at 1000°C for 1 h. The cell volume of the perovskite decreased with increasing the content of Pr in $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta}$ up to around 20 mol% in Pr. This suggests that the solubility limit of Pr in the perovskite is around 20 mol%.

It is expected that the electrical conductivity of the perovskites increases with increasing dopant content of higher valence ions. Figure 3 shows the relationship between dopant ionic radius and dopant content in the perovskite. Although the elements in the A-site of the perovskite structure have the dodecahedral coordination of oxygen, in this case the radii of the cations at the octahedral site are used. The dopant content in the perovskite structure trends to increase with increasing ionic radius of the dopant.

A further investigation on the electrical conductivity and corrosion resistance in H_2SO_4 solution is in progress.

References

[1] M. Mori, H. Kawamura, and M. Uotani, in *Proceedings of the 2003 Fall Meeting of the*

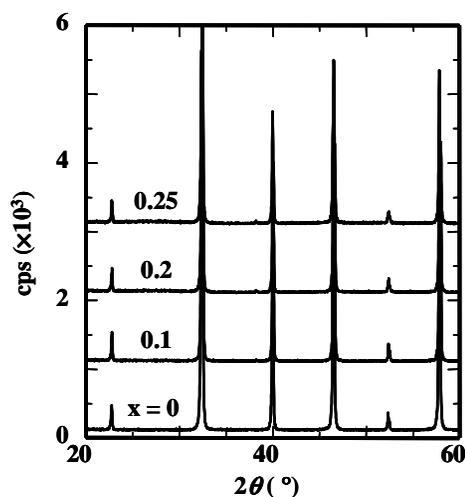


Fig. 1 XRD patterns of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta}$ as a function of dopant content after heating at 1500°C for 20 h in air.

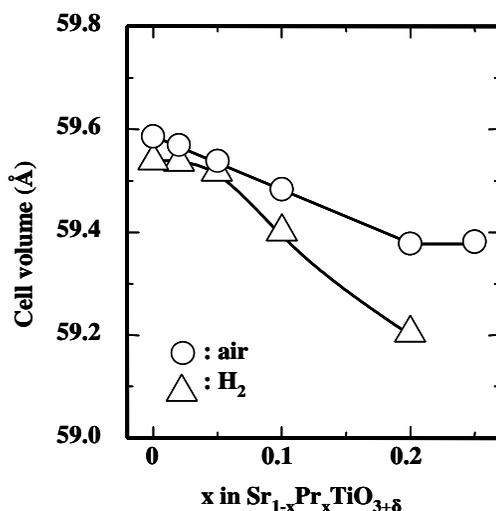


Fig. 2 Cell volumes of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta}$ as a function of dopant content. The triangles represent the cell volumes of the perovskites, after reducing at 1000°C for 1 h.

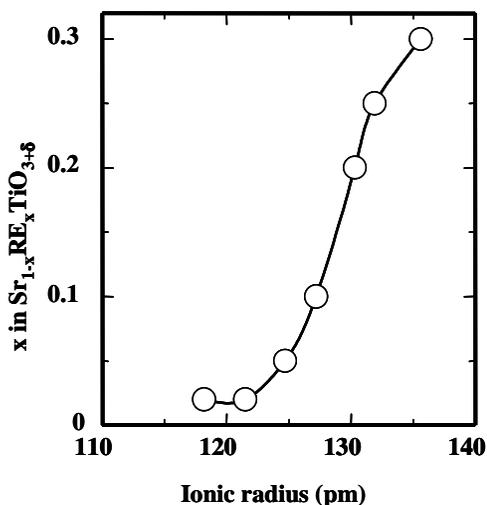


Fig. 3 Relationship between dopant ionic radius and dopant content in the $\text{Sr}_{1-x}\text{RE}_x\text{TiO}_{3+\delta}$ perovskite.