Tailoring the Chemical Stability of Cobalt-rich Perovskite Mixed Conductor

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Abstract

In this paper we try to tailor the chemical stability of cobalt-rich perovskite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) by B-site doping Sb. The chemical stability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (BSCFS) were investigated by studying the oxygen nonstoichiometry, crystal structure and oxidation state by means of coulometric titration, high-temperature X-ray diffraction (HT-XRD) and soft-X-ray absorption spectroscopy (s-XAS) in various oxygen pressure ($p(\text{O}_2)$) and temperatures. The results prove chemical stability of BSCFS is successfully improved in intermediate temperature solid oxide fuel cell working condition owing to Co valence change which is controlled by high valence cation doping.

Keywords: BSCF, chemical stability, oxygen nonstoichiometry, soft XAS

1. Introduction

To lower the working temperature of SOFC, the performance of the cathode is a large limiting factor for SOFC.[1-4] Therefore, the development of novel cathode materials attracts much interests from a vast number of researchers for intermediate temperature

SOFC. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (denoted as BSCF) is a widely known cobalt-rich perovskite oxide that is a very promising cathode material for IT-SOFC because of high electrochemical performance. [5-6] Although BSCF is promising for low-temperature SOFCs, its use is limited because of its poor long-term stability. The unstable structure of BSCF leads to a phase transition from a cubic to a less conductive hexagonal structure at around 800 °C. [7] This issue of the material instability led to the severe performance degradation when working as SOFC cathode. For the practical application of BSCF cathode material for IT-SOFC, it is necessary to make clear the assessment of the chemical stability under SOFC operation conditions. Many works investigated the long-term stability of BSCF, but many of them were performed only in air condition or in limited temperature range. In our previous work, the chemical stability of BSCF was studied in a wide range of $p(\text{O}_2)$ (1 to 10^{-22} bar) and temperature (300 to 1373 K). [8-9]. The crystal structure and oxygen nonstoichiometry were studied by high temperature XRD, thermogravimetry and coulometric titration. It was found the decomposition of the cubic perovskite phase of BSCF was related to the oxidation/reduction of Co ions originating from the oxygen nonstoichiometry (δ) change. The cubic phase of BSCF decomposed when trivalent cobalt ions were oxidized to higher oxidation state in high $p(\text{O}_2)$ or when divalent cobalt ions were reduced to lower oxidation state in low $p(\text{O}_2)$. The oxidation state of Co governed the stability of BSCF. [9] The decomposition of BSCF in high $p(\text{O}_2)$ was found more fatal than in low $p(\text{O}_2)$ when one consider the use of BSCF as an SOFC cathode. One approach to improve the chemical stability of cobalt-rich perovskite is the B-site doping in ABO_3 . Nagai *et al.* studied B-site doping in one cobalt-rich system $\text{SrCo}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ (M=Ni, Cu, Zn, Cr, Fe, Al, Ga, In, Ce, Ti, Zr, Sn, V and Nb) [10-11]. Their results suggested that the cubic phase become more stable

in pure O₂ in the order of B-site doping of Cu²⁺ < Cr³⁺, Al³⁺, Ga³⁺ < Fe^{3.108+} < Ti⁴⁺ < Nb⁵⁺. Wang *et al.* studied structure, conductivity, thermal expansion and electrochemical performance of Nb doped SrCoO_{3-δ} cathode found the SrCo_{1-y}Nb_yO_{3-δ} has improved cubic phase stability and performance. [12] The results indicated the high valence cations doping can improve the stability of high performance cubic of cobalt-rich perovskite SrCoO_{3-δ} materials. B-site doping with Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, B, Al, Sr, Y, Zr, Nb, Ba, La, Ho and Y of cobalt-rich perovskite BSCF system were also be studied. [13-21] Lu *et al.* measured crystal structure, oxygen permeability and stability of BSCF and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}M_{0.1}O_{3-δ} (M=Fe, Cr, Mn, Zr) and found Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Cr_{0.1}O_{3-δ} shows best oxygen permeation stability and improved structure stability in He, 1%O₂/He, air and O₂ at 1073 K. [13] Yakovlev *et al.* studied phase transformation and oxygen equilibration kinetics of BSCF and Zr-doped BSCF and found 3 mol% Zr doping is sufficient to prevent the cubic-to-hexagonal phase transition and preserve high oxygen exchange and transport properties at 1073 K by electrical conductivity relaxation method. [14] Fang *et al.* investigated the phase stability, thermal expansion, electrical conductivity and oxygen permeation of Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Nb_xO_{3-δ} (x = 0- 0.2) and found 5mol% substitution of Nb for (Co,Fe) can suppressed the phase instability in air and N₂ at 1023 K, however the oxygen permeation is reduced by 10% comparing with pure BSCF. [15] Babakhani *et al.* researched structure stability and oxygen permeability of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}M_{0.1}O_{3-δ} (M = Al, Mn, Fe, Ce, Cr, Ni, Co) and found Al, Ni and Ce cation increase the oxygen permeability and the phase transition was not observed only for Ni doping sample. [16] Porras-Vazquez *et al.* studied the stability and conductivity of oxyanion-doped BSCF

with B and P. The XRD results show 0.5 mol % B doping sample is stable after annealing at 1023 K for 144 h in air. [17] Kwak *et al.* investigated a series of B-site doping BSCF cathode materials for SOFC. They indicated Zn addition stabilizes the structure of BSCF, reduced the thermal expansion coefficient and provided stable long-term performance. [18] Above works investigated the stability, electrochemical and oxygen transport properties of various B-site doped BSCF-based materials and found B-site doping can change the stability of BSCF-based materials. However, most of these stability studies were performed only in limited $p(\text{O}_2)$ condition or in limited temperature range. The effect of B-site doping on the chemical stability of BSCF-based materials in a wide range of $p(\text{O}_2)$ and temperature has not been systematically investigated so far and the explanation of stability change mechanism is still not clear. Based on our previous results, the cobalt valence is the key factor of materials stability of cobalt-rich perovskite. Thus, to fully study the chemical stability of cobalt-rich perovskite materials, the oxidation state variation of cobalt by cation doping and in different $p(\text{O}_2)$ and temperatures must be clarified. Therefore, in this work, we use high valence Sb doped BSCF for the systematic study on the effect of B-site cation doping on chemical stability of BSCF-based materials in a wide range of $p(\text{O}_2)$ and temperature. To explore the methodology for chemical stability and decomposition mechanism of cobalt-rich perovskite functional materials we also investigate the oxidation state of cobalt under various $p(\text{O}_2)$ and temperatures. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (BSCFS) were prepared and the chemical stability in a wide range of $p(\text{O}_2)$ and temperature was investigated by using HT-XRD, coulometric titration and soft-X-ray absorption spectroscopy(s-XAS). By using the oxygen nonstoichiometry and crystal structure results we established chemical stability map of BSCFS with oxidative and reductive

stable boundaries. The Co valence change by B-site doping and the effect on chemical stability of doped BSCF were also discussed by using s-XAS results.

2. Experimental

2.1 Synthesis and materials preparation

BSCF and BSCFS were synthesized by solid state reactions. SrCO_3 , BaCO_3 , Co_3O_4 , Fe_2O_3 and Sb_2O_3 (all reagents with A.R. purity) were weighted according to their stoichiometry and mixed in an agate mortar for 1.5 h. The mixtures were calcined at 1273K for 10 h with a heating/cooling rate of $3 \text{ K} \cdot \text{min}^{-1}$. Then, the primary powders were **crushed** finely in an agate mortar, and sintered at 1373 K for 10 h. Obtained powder of BSCF and BSCFS were confirmed to be single phase perovskites by X-ray powder diffraction (XRD) (D2 Phase: Cu $K\alpha$ radiation, Bruker AXS, Germany) at room temperature in air.

2.2 High-temperature X-ray diffraction (HT-XRD)

X-ray diffractometer (D8 Advance with LYNXEYETM Super Speed Detector, Bruker AXS, and Cu $K\alpha$ radiation) was used for *in situ* high-temperature powder X-ray diffraction (HT-XRD) measurements as a function of $p(\text{O}_2)$, temperature and annealing time. The BSCFS powders were set on a platinum heater inside the XRD chamber. In order to investigate the chemical stability depending on $p(\text{O}_2)$, the XRD patterns were measured in the $\log(p(\text{O}_2)/\text{bar}) = 0$ and -4 using $\text{O}_2\text{-N}_2$ mixture gases. The $p(\text{O}_2)$ was monitored at the inlet and the outlet of the XRD chamber by two zirconia sensors. The XRD patterns were obtained at every 100 K with a temperature range of RT to 1373 K. At each temperature, XRD measurements were repeated until XRD pattern did not show

any apparent changes and the equilibrium was ensured. The holding times were 20, 20, 15, 10, 5, 5, 5, and 5 hours at every 100 K between 673 and 1373 K, respectively.

2.3 Coulometric titration

The oxygen nonstoichiometry of in the lower $p(\text{O}_2)$ range ($< 1 \times 10^{-4}$ bar) at 873-1173 K was measured by coulometric titration. The change in the oxygen content $\Delta\delta$ was controlled by passing an electric charge, C , through the sample using a coulometer (Model 3320, Toho Technical Research, Japan):

$$\Delta\delta = \frac{C}{2Fn} \quad (1)$$

where F is the Faraday constant ($96485.3 \text{ C mol}^{-1}$) and n is the number of moles of the BSCF sample. The $p(\text{O}_2)$ at the sample, $p(\text{O}_2)_{\text{II}}$, could then be calculated from the equilibrium electromotive force, E , of the galvanic cell under open circuit condition according to the Nernst equation:

$$E = \frac{RT}{4F} \ln \left(\frac{p(\text{O}_2)_{\text{II}}}{p(\text{O}_2)_{\text{I}}} \right) \quad (2)$$

where R is the ideal gas constant ($8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$), and $p(\text{O}_2)_{\text{I}}$ is the reference $p(\text{O}_2)$ in air.

2.4 Soft X-ray absorption spectroscopic (s-XAS) measurements

For comparison the Co valence in BSCF and BSCFS, we applied s-XAS measurements at beam line BL27SU at SPring-8, JASRI, Japan. The s-XAS measurements at Co L -edge (770-805 eV) and O K -edge (524-555 eV) were performed for BSCF and BSCFS with the fluorescence yield mode at R.T. The BSCF and BSCFS samples were pre-annealed in $\log(p(\text{O}_2)) = -3$ at 1073 K for 8 hours and quenched to R.T,

respectively.

3. Results and Discussion

Fig.1. (A) and (B) show the *in situ* HT-XRD patterns of BSCFS. Fig.1. (A) shows the XRD results of BSCFS during cooling from 1373 to 773 K in pure O₂. The holding times were 20, 15, 10, 5, 5, 5, and 5 hours at every 100 K between 773 and 1373 K, respectively. All the peaks in Fig.1.(A) matched with cubic structure during cooling from 1373 to 773 K in pure O₂. This indicated that the cubic perovskite phase of BSCFS was thermodynamically stable under high $p(\text{O}_2)$ condition. Fig.1.(B) shows the HT-XRD results of the cubic phase BSCFS during heating in $\log(p(\text{O}_2)) = 10^{-4}$ bar. As shown in Fig.1 (B), a small amount of the impurity phase of Ba₂CoO₄ (ICSD-#92321, marked with closed inverted triangles) was observed at 1373 K. While in other temperature no impurity appeared when heating up to 1273 K. This indicated that the cubic perovskite phase of BSCFS is unstable when temperature is higher than 1273 K in $\log(p(\text{O}_2)) = 10^{-4}$ bar.

Oxygen nonstoichiometry ($3-\delta$) of BSCF and BSCFS were shown in Fig.2. (A) and (B) as a function of $p(\text{O}_2)$ at 1173, 1073 K, 973 K and 873 K. **Oxygen content decreased monotonically** at the beginning in both BSCF and BSCFS, corresponding to the gradual reduction from relatively high to intermediate $p(\text{O}_2)$ for each measured temperatures. From intermediate to low $p(\text{O}_2)$, the oxygen content showed a small twist followed by a large inflection for further reducing. Since the decomposition of an oxide occurs at a constant potential during the coulometric titration and thus $p(\text{O}_2)$ did not change until the decomposition is completed. Therefore, the inflections in Fig.2. (A) and (B) are considered to demonstrate the material decompositions as indicated by the vertical lines. The two step decompositions are due to the two step reduction of the transition metal

ions in intermediate/low $p(\text{O}_2)$ conditions. [9] Based on the oxygen nonstoichiometry results, the instable conditions of cubic BSCFS can be estimated as $p(\text{O}_2) = 5.77 \times 10^{-13}$, 1.45×10^{-10} , 8.51×10^{-9} and 2.47×10^{-7} bar at 873, 973, 1073 and 1173 K, respectively.

As shown in Fig. 3. the chemical stability diagram of BSCFS was established by summarizing the results of HT-XRD in $\log(p(\text{O}_2)) = 0$ and -4, oxygen nonstoichiometry measurements in relatively low $p(\text{O}_2)$. For clearly showing the improvement of chemical stability of BSCFS we also include the stable boundaries of BSCF (two solid black lines) in Fig.3. The cross symbols in Fig.3 show the conditions where the decomposition of cubic BSCF was observed by HT-XRD and CT. [9] The open circles show the stable conditions of cubic BSCF were observed by HT-XRD analysis. [9] Based on these instable conditions, we can draw the stable boundaries for the oxidation and the reduction environment as the two solid black line in Fig.3. The high stability of cubic BSCFS in O_2 at the temperature range of 300 to 1173 K was proved by HT-XRD marked as open triangle in Fig.3. The open inverted triangle show the stable conditions of cubic BSCFS were observed by HT-XRD in $\log(p(\text{O}_2)) = -4$. The instable conditions of cubic BSCFS was marked as a closed inverted triangle which was observed by HT-XRD in $\log(p(\text{O}_2)) = -4$ at 1373 K. The reductive decomposition conditions of cubic BSCFS were marked as open stars on approximately 5.77×10^{-13} , 1.45×10^{-10} , 8.51×10^{-9} and 2.47×10^{-7} bar at 873, 973, 1073 and 1173 K, respectively. By using these stable and decomposition conditions we can summarize the two stable boundaries of cubic BSCFS as shown of two dash line in Fig.3. The stability boundaries of BSCFS are similar to pure BSCF, but both showed shift to relative higher oxidizing range. The stability diagram of BSCFS is divided into three regions by these two boundaries: (1) the oxidation decomposition region, (2) the chemical stable region, and (3) the reduction

decomposition region. According to the chemical stability diagram obtained in this work, the stability improvement of BSCF under IT-SOFC operating conditions are achieved by Sb doping.

To investigate the decomposition mechanism and confirm valence change of B-site transition metal in BSCF-based materials, we measure the oxidation state of BSCF and BSCFS dense pellets by s-XAS at the Co L_{III} -edge in high vacuum at R.T. Fig. 4 show the s-XAS results. The spectra were normalized to equalize the intensity at 779 eV. It is known that around 778 eV, the peak is corresponding to Co^{2+} , and around 783 eV, the peak is related to Co^{3+} . The intensity of Co^{3+} peak of BSCFS is less than the intensity of Co^{3+} peak of BSCF when $\log(p(O_2)) = -3$. It demonstrates that by high valence Sb doping, Co valence can be controlled to keep lower oxidation state in relative higher $p(O_2)$ condition which means the higher stability in IT-SOFC cathode working conditions.

4. Conclusions

The chemical stability of BSCFS have been investigated in a wide range of $p(O_2)$ and temperature by crystal structure, oxygen nonstoichiometry and oxidation state analysis by HT-XRD, coulometric titration and s-XAS. The chemical stability map of BSCFS is first time established and confirms the significant improvement of chemical stability in IT-SOFC working conditions. The s-XAS results clearly reveal the decomposition driving force of cubic BSCF-based materials are mainly depending on the oxidation state of Co ion. We proved that through controlling the Co valence by high valence cation doping the chemical stability of cobalt-rich perovskite BSCF-based materials can be tailored for stable long-term functional applications.

Acknowledgements

This work was supported by the CREST from the Japan Science and Technology Agency (JST) and Grant-in-Aid for Scientific Research of MEXT, Japan and was partly supported by A-STEP, JST, Japan.

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Figure Captions

Fig.1. HT-XRD patterns of BSCFS powder in (A) $\log(p(\text{O}_2)) = 0$ during cooling from 1373 K to 773 K and (B) in $\log(p(\text{O}_2)) = -4$ during heating from R.T. to 1373 K.

Fig.2. Comparison of oxygen nonstoichiometry ($3-\delta$) of (A) $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and (B) $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Sb}_{0.1}\text{O}_{3-\delta}$.

Fig.3. Chemical stable map of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Sb}_{0.1}\text{O}_{3-\delta}$ in a wide range of $p(\text{O}_2)$ and temperature (chemical stability map of BSCF [9] also shown in this figure as a reference).

Fig.4. s-XAS spectra of Co L_{III} -edge of BSCF and BSCFS samples which were pre-annealed in $\log(p(\text{O}_2)) = -3$ at 1073 K.

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Fig.4. s-XAS spectra of Co L_{III} -edge of CoO, BSCF and BSCFS samples which were pre-annealed in $\log(p(\text{O}_2)) = -3$ at 1073 K.