Effect of Nb doping on chemical stability of BSCF-based solid solutions

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Abstract

Effects of Nb doping on the chemical stability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ based solid solutions under high oxygen partial pressure ($p(\text{O}_2)$) and CO_2 -containing atmospheres were studied. BSCF and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCN) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCFN) were prepared and investigated by using TG-DTA analysis under $p(\text{O}_2) = 1$ and 10^{-3} bar with or without of CO_2 . The results showed the Nb substitution effectively improved the chemical stability under high oxidation condition and also improves the CO_2 -tolerance of BSCF-based materials.

Keywords: BSCF, chemical stability, Nb-doping, CO₂ tolerance

1. Introduction

Cubic perovskite Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) is expected as one of the most high-performance cathode materials for IT-SOFCs or oxygen permeable membranes [1]. The high oxygen vacancy concentration and the relatively low activation barrier for the vacancy diffusion bring high ionic conductivity and, consequently, excellent oxygen reduction properties [2-3]. However recent studies suggested the chemical instability of BSCF below the critical temperature of 1123K in air [4-9]. Another material instability problem with BSCF is its high reactivity with CO₂ resulting in the formation of (Ba,Sr)CO₃ [10–11]. These instability issues lead to the severe performance degradation as an SOFC cathode or an oxygen permeable membrane [4, 12-13]. Therefore, it is necessary to make a clear assessment on BSCF regarding the chemical stability under high $p(\text{O}_2)$ and CO₂-containing atmosphere at operating temperature of IT-SOFCs or oxygen permeable membranes. However, there are only a few estimations on the stability of BSCF in the limited temperature range in air. The chemical stability of BSCF in a wide ranges of $p(\text{O}_2)$ and temperature has not been understood so far.

In our previous work [14], the chemical stability of BSCF was investigated as a function of $p(\text{O}_2)$ (1 to 10⁻²² bar) and temperature (300 to 1373K) by HT-XRD,

HT-gravimetry and coulometric titration. The decomposition of the cubic perovskite phase of BSCF was confirmed in connection with the oxidation/reduction of Co ions due to the oxygen nonstoichiometry (δ) change. We found the cubic perovskite phase of BSCF decomposed when cobalt ions were oxidized to higher oxidation state than trivalence in high $p(\text{O}_2)$ or were reduced to lower oxidation state than divalence in low $p(\text{O}_2)$ condition. These results suggested the cubic perovskite phase of BSCF can be stabilized by controlling the oxidation state of Co. Nagai *et al.* demonstrated that Nb was the most effective dopant for stabilization of the cubic structure in $\text{SrCo}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ (M= Ni, Cu, Zn, Cr, Fe, Al, Ga, In, Ce, Ti, Zr, Sn, V and Nb) [15-16]. They suggested that the sequence of the stabilization effect in high $p(\text{O}_2)$ was $\text{Cu}^{2+} < \text{Cr}^{3+}, \text{Al}^{3+}, \text{Ga}^{3+} < \text{La}^{3+}$ (substituting A site) $< \text{Fe}^{3.108+} < \text{Ti}^{4+} < \text{Nb}^{5+}$. S.M. Fang *et al.* [17] found the phase instability of BSCF in air condition is suppressed at the substitution of 5 mol% of Nb for the (Co, Fe)-site. These results give us a hypothesis that the stability of the perovskite structure is enhanced by substituting the B-site cations by higher valence cations. These works indirectly support our speculation [14] that lowering the Co mean valence improves the stability of Co-containing perovskite oxides in high $p(\text{O}_2)$ condition. However, the information about the doping effect of higher valence cation Nb on the chemical stability of BSCF-based materials under high $p(\text{O}_2)$ and

CO₂-containing atmospheres is insufficient.

Therefore, in this work, we substituted higher valence cation, Nb⁵⁺, for B-site of BSCF-based solid solutions to improve the chemical stability. The effect of the Nb substitution on the chemical stability under high $p(\text{O}_2)$ and CO₂-containing atmospheres was investigated through thermal analysis by using TG-DTA measurements under $p(\text{O}_2)$ = 1 and 10⁻³ bar with or without 5 vol% CO₂.

2. Experimental

2.1 Synthesis materials

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) was synthesized by Pechini method. Nitrate solutions of Ba²⁺, Sr²⁺, Co²⁺ and Fe³⁺ were prepared by dissolving BaCO₃, Co₃O₄, SrCO₃ and Fe(NO₃)₃·9H₂O (all reagents with A.R. purity) in nitric acid or deionized water. The concentrations of the Ba, Co and Sr ions were determined by the chelate titration using EDTA. The concentration of the Fe ions was measured by the inductively coupled plasma atomic emission spectroscopy (Optima 3300, Perkin Elmer, Yokohama, Japan). After mixing the solutions in the appropriate stoichiometric ratios, excess amounts of ethylene glycol and citric acid were added to the mixed solution. The solution was heated to 523 K and dried, followed by calcining at 1273 K for 10 h and

sintering at 1373 K for 10h. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCN) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCFN) were synthesized by solid state reactions. BaCO_3 , Co_3O_4 , Fe_2O_3 , Nb_2O_5 (all reagents with A.R. purity) were weighted according to their stoichiometry and mixed. The mixtures were calcined at 1273K for 10 h. The primary powders were crashed finely in an agate mortar, and sintered at 1373 K for 10 h. Obtained powder of BSCN and BSCFN 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 Thermoanalysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with BSCF, BSCN and BSCFN samples by the Bruker2000s thermal analyzer 300-1273 K at a heating/cooling rate of $5\text{ K}\cdot\text{min}^{-1}$ with a gas rate of $100\text{ ml}\cdot\text{min}^{-1}$. Oxygen partial pressure $p(\text{O}_2)$ controlled by flowing pure O_2 , N_2 , CO_2 and a mixture gas of 1000 ppm $\text{O}_2\text{-N}_2$. The $p(\text{O}_2)$ was monitored at the outlet of the TG-DTA chamber by a zirconia sensor. All the samples were preheated at 1273 K for 1 hour in 1000 ppm $\text{O}_2\text{-N}_2$. The usual sample for TG-DTA measurement was 98-100 mg.

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

X-ray diffractometer (D8 Advance with LYNXEYETM Super Speed Detector, Bruker AXS, and CuK α radiation) was used for *in situ* high-temperature powder X-ray diffraction (HT-XRD) measurements. The BSCF powder was set on a platinum heater inside the XRD chamber. In order to investigate the chemical stability in pure O₂, the XRD patterns were measured in the $p(\text{O}_2)$ range of $p(\text{O}_2) = 1 \times 10^{-4}$ to 1 bar using O₂-N₂ mixture gases. The XRD patterns were obtained at every 100 K with 20 min dwell time.

3. Results and Discussion

3.1 Phase stability under high $p(\text{O}_2)$

Fig. 1 shows the TG and DTA curves of BSCF, BSCN and BSCFN during two heating and cooling thermal cycles in 1000 ppm O₂. As seen in Fig.1, the weights of all samples decreased with increasing temperature from RT to 1273K and then increased monotonously with cooling temperature back to RT. About 1% weight changes were observed for all three samples in the thermal cycles. Such a weight change is considered due to the oxygen vacancy formation and oxygen cooperation. These results indicated that all samples were stable in 1000ppm O₂-N₂ atmosphere.

Fig. 2 shows the TG and DTA curves of BSCF, BSCN and BSCFN in pure O₂ gas.

When the temperature was increased up to around 500 K, a slight weight gain was observed for all three samples due to oxygen absorption of the relaxation process from the metastable quenched state to equilibrium state of sample. This was probably because of the oxygen nonstoichiometry compensation owing to the different $p(\text{O}_2)$ employed in calcination, $p(\text{O}_2)=10^{-3}$ bar , and TG-DTA measurements, $p(\text{O}_2)=1$ bar. Around 500 K, an obvious exothermic peak was observed in DTA curves of the BSCF. Simultaneously, an apparent weight increase was observed in the TG curve of BSCF from 500 to 680 K. The exothermic peak and the weight change indicated decomposition of BSCF in high $p(\text{O}_2)$. This agreed with HT-XRD results shown in Fig. 3, BSCF decomposed to mixture phases when temperature heating up to higher than 673 K. This decomposition is probably driven by oxidizing of Co ionic in high $p(\text{O}_2)$. Therefore, this decomposition absorbs more oxygen to cooperate with high oxidation state Co ionic. In Fig. 2 no obvious exothermic peaks were observed in the DTA curves of BSCN and BSCFN. These indicate the substitution of Nb into the B-site improved the stability of cubic perovskite phase of BSCF under high $p(\text{O}_2)$. In our previous work [14], we found the oxidation of Co ions caused the decomposition of the cubic BSCF under high $p(\text{O}_2)$. It is considered that the doping of high valence Nb into the B-site lowered the Co mean valence and consequently improved the chemical stability of BSCF under high $p(\text{O}_2)$.

3.2 Chemical stability against CO₂ poisoning

Fig. 4 shows the TG-DTA results of BSCF, BSCN and BSCFN samples during two heating and cooling cycles between 300 and 1273 K in 1000ppm O₂-N₂ containing 5 vol% CO₂. A significant weight gain, approximately 4%, was observed with BSCF at 750 K to 1125 K. This weight gain was caused by formations of Ba and Sr carbonate. When temperature heated up to above 1123K, a significant weight loss and simultaneously exothermic peaks of BSCF were observed owing to the carbonate decomposition and formation of oxygen vacancies Vo^{••}. The TG curves of BSCN and BSCFN in Fig. 4 showed obviously different weight change behaviors from that of BSCF. This indicated the Nb substitution in the B-site effectively suppressed the formation of carbonates in 5vol% CO₂ containing atmosphere. However, although the chemical stability of BSCF against CO₂ had greatly improved by Nb doping, a small amount of carbonate might be formed in BSCN and BSCFN in CO₂-containing atmosphere, because the weight losses of BSCN and BSCFN were slightly smaller compared with those under the same $p(\text{O}_2)$ condition without CO₂, Fig.1.

Fig. 5 shows the TG-DTA results of BSCF, BSCN and BSCFN in O₂ with 5 vol% CO₂. Small weight gains were observed with all three samples during heating up to 500 K. During further heating BSCF showed a large weight increase from 750 to 1120 K.

On the other hand BSCN and BSCFN showed a gradual weight decrease with increasing temperature up to 1273K and then increased monotonously with cooling temperature back to RT. The TG-DTA results in Fig.5 demonstrated once again that the Nb substitution in the B-site effectively improved the chemical stability of BSCF-based materials against CO₂. The weight change of BSCF due to the carbonate formation was relatively smaller in pure O₂ than 1000ppm O₂. In other words, BSCF in pure O₂ gas containing 5 vol% CO₂ atmospheres showed better stability than in 1000ppm O₂ gas containing 5 vol% CO₂ atmospheres. This suggested $p(O_2)$ also affect carbonate formation. The primary cause is the relative high valence state of Co ions in high $p(O_2)$ increased the acidity of BSCF and reduced carbonate formation.

Let us first discuss the $p(O_2)$ effect on carbonate formation of pure BSCF. For decomposition of oxides containing trivalent Co ions in CO₂, we should consider reduction of Co ions. For instance, the decomposition of alkaline earth cobaltite can be expresses by the following reaction:

where M is alkaline earth metal. Then the equilibrium constant of this reaction, K_c , can be written as:

$$K_c a_{MCoO_{3-\delta}} p(CO_2) = a_{MCO_3} a_{CoO} [p(O_2)]^{(1-\delta)/2} \quad (2)$$

where $a_{MCoO_{3-\delta}}$, a_{MCO_3} and a_{CoO} are the activities of $MCoO_{3-\delta}$, MCO_3 and CoO , $p(CO_2)$ and $p(O_2)$ are the partial pressures of CO_2 and O_2 , respectively. Eq. (2) tells us the stability of the alkaline earth carbonate is related to $p(CO_2)$ and $p(O_2)$. At a constant $p(CO_2)$, more carbonate are formed in lower $p(O_2)$ condition. This corresponds well with TG-DTA results in Figs. 4 and 5. The maximum weight gain due to the carbonate formation was from 4% in pure O_2 , while it was 1.8% in 1000ppm O_2 - N_2 .

As already mentioned, BSCF becomes more stable by doping Nb into B-site. The reactivity of a material with an acidic gas, such as CO_2 can be related to its acidity, and higher acidity of the material leads to better resistance against CO_2 [18]. The following order of the acidity of metal oxides has been reported: $Nb^{5+} > Co^{4+} > Co^{3+} > Fe^{3+} > Co^{2+} > Fe^{2+}$ [19]. In our previous work, we found Co ion in BSCF show nearly trivalent in high $p(O_2)$ conditions [14]. The high valence state of Co ions increased the acidity of BSCF and reduced carbonate formation. Therefore BSCF shown better CO_2 -resistans in high $p(O_2)$. When the Nb ions substituted for the B-site, the valence sate of Co ions is considered to decrease. However, as suggested by N.C. Jeong *et al.* [19], Nb^{5+} shows very high acidity and thus it was considered Nb doping could improve the chemical stability of BSCF against CO_2 .

4. Conclusions

In this study, the influence of the Nb-doping on the chemical stability of BSCF, BSCN and BSCFN under high $p(\text{O}_2)$ and CO_2 -containing atmospheres were examined. An obvious exothermic peak on DTA and an apparent weight increase in TG from 500 to 680 K during heating in pure O_2 proved the instability of BSCF in high $p(\text{O}_2)$ condition. On the other hand, neither DTA peaks nor weight gains were observed in the TG-DTA of BSCN and BSCFN. These results indicated the doping of Nb for the B-site improved the chemical stability of BSCF under high $p(\text{O}_2)$ condition. TG-DTA results in CO_2 -containing atmosphere demonstrated the Nb-doping improved the CO_2 -tolerance of BSCF-based solid solution. In conclusion, the Nb-doped BSCF exhibited relatively high chemical stability under high $p(\text{O}_2)$ as well as CO_2 containing atmospheres.

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Figure Captions

Fig. 1: TG and DTA curves of BSCF (solid line), BSCN (dash line) and BSCFN (dot line) of two heating-cooling thermal cycles in 1000ppmO₂-N₂.

Fig. 2: TG and DTA curves of BSCF (solid line), BSCN (dash line) and BSCFN (dot line) of two heating-cooling thermal cycles in 100% O₂.

Fig. 3 Powder XRD patterns of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} during heating in $p(\text{O}_2) = 1$ bar. Closed Inverted triangle indicates the impurity phase.

Fig. 4: TG and DTA curves of BSCF (solid line), BSCN (dash line) and BSCFN (dot line) of two heating-cooling thermal cycles in 1000ppm O₂-N₂ containing 5 vol% CO₂.

Fig. 5: TG and DTA curves of BSCF (solid line), BSCN (dash line) and BSCFN (dot line) of two heating-cooling thermal cycles in 5vol%CO₂-95vol% O₂.

Fig. 1

Gas: 1000ppmO₂-N₂

(Heating/cooling rate is 5K/min)

Fig. 2

Gas: 100% O₂

(Heating/cooling rate is 5K/min)

Fig. 3

Fig. 4

Fig. 5

Gas: 5% CO₂-95% O₂

(Heating/cooling rate is 5K/min)