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Overcoming phase instability of $RBaCo_2O_{5+\delta}$ (R = Y and Ho) by Sr substitution for application as cathodes in solid oxide fuel cells

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ABSTRACT

Phase instabilities of the $RBaCo_2O_{5+\delta}$ (R = Y and Ho) layered-perovskites and their decompositions into $RCoO_3$ and $BaCoO_{3-z}$ at 800 °C in air were investigated. The phase instability will restrict their high temperature applications such as cathodes in solid oxide fuel cells (SOFC). However, appropriate amount of Sr substitution (≥60% for R = Y and ≥70% for R = Ho) for Ba successfully stabilized the $R(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ phase at elevated temperatures. This can be explained to be due to the decrease in oxygen vacancies in the R–O layer, decrease in R–O bond length, and consequent improvement in structural integrity. In addition, the Sr substitution (x = 0.6–1.0) for Ba provided added benefit with respect to the chemical stability against $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) electrolyte, which is a critical requirement for the cathodes in SOFC. Among the various compositions investigated, the $Y(Ba_{0.3}Sr_{0.7})Co_2O_{5+\delta}$ + GDC composite cathode delivered the optimum electrochemical performances with a stable phase, demonstrating the potential as a cathode in SOFC.

1. Introduction

Recently, the $RBaCo_2O_{5+\delta}$ (R = lanthanide and Y) layered-perovskite oxides have drawn much attention due to the wide variations in oxygen content (5 + δ), where 0 ≤ δ ≤ 1, and promising mixed ionic–electronic conducting (MIEC) properties [1–6]. The $RBaCo_2O_{5+\delta}$ oxides have the R–O and Ba–O layers alternating along the *c*-axis, and the difference in the ionic radii between the R^{3+} and Ba^{2+} ions plays a dominant role in determining the oxygen content values and the crystal structure [1–3,7]. For example, the amount of oxygen vacancy localized in the R–O layer increases with decreasing size of the R^{3+} ions in the air-synthesized $RBaCo_2O_{5+\delta}$ samples. At a given R^{3+} ions, however, the amount of oxygen vacancies also varies depending on temperature and atmosphere (oxygen partial pressure). The size of the R^{3+} ions, oxygen contents, and corresponding crystal structures influences the thermal and electrochemical properties of $RBaCo_2O_{5+\delta}$. [1,8,9] As a result, there has been growing interest to explore various $R(Ba_{1-x}A_x)Co_{2-y}M_yO_{5+\delta}$ (A = Ca, Sr, and M = Fe, Ni, Cu) compounds with improved cathode performance and lower thermal expansion coefficient for SOFC application [7,10–15].

Among the various $RBaCo_2O_{5+\delta}$ samples investigated, R = Y has drawn attention because it forms various superstructures due to an ordering of oxygen vacancies [16,17]. It was proposed that the formation of superstructure in the $YBaCo_2O_{5+\delta}$ is determined by its oxygen content value (δ); $2a_p \times 1a_p \times 1a_p$ (*p* refers to perovskite) superstructure for δ ≥ 0.5, $3a_p \times 3a_p \times 1a_p$ superstructure for 0.25 ≤ δ ≤ 0.44, and no superstructure for 0 ≤ δ ≤ 0.19 [16]. This large amount of oxygen vacancies in $YBaCo_2O_{5+\delta}$ may be beneficial to the oxygen transport in the lattice, which is one of the important requirements for cathodes in SOFC [3,18]. However, $YBaCo_2O_{5+\delta}$ had a side-reaction problem in contact with $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ electrolyte at 1000 °C [1]. Alternatively, Xue et al. [19] reported that $YBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ composition showed no such side reaction with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{2.85}$ electrolyte at 950 °C.

To date, however, the phase stabilities of $YBaCo_2O_{5+\delta}$ and $HoBaCo_2O_{5+\delta}$ at the operation temperature of SOFC (600 °C ≤ *T* ≤ 800 °C) have not been adequately investigated. This is the first report which describes the phase instability of the $YBaCo_2O_{5+\delta}$ and $HoBaCo_2O_{5+\delta}$ at 800 °C, to the best of our knowledge. In addition, it is necessary to examine the chemical stability of $YBaCo_2O_{5+\delta}$ against other standard electrolytes such as GDC. With an aim to overcome the phase instability problem and apply them as cathodes in SOFC, we present here an investigation of $R(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ (R = Y and Ho) system. The effects of Sr substitution for Ba in $R(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ on the high temperature phase stability, chemical stability with GDC electrolytes, thermal and electrochemical properties are characterized and discussed.

2. Experimental

The $R(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ powders (R = Y and Ho, x = 0–1.0) were synthesized by a conventional solid-state reaction method. Required

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amounts of Y_2O_3, Ho_2O_3, $BaCO_3$, $SrCO_3$, and Co_3O_4 were thoroughly mixed in a mortar and pestle and calcined at 1000 °C for 12 h in air. The calcined powders were then ground, pressed into pellets, and sintered at 1075–1125 °C for 12–24 h in air. The synthesized materials were characterized by X-ray diffraction (XRD, Scintag and PANalytical) using a Cu Kα radiation. The room-temperature oxygen content values were determined by iodometric titration [20]. Thermogravimetric analysis (TGA, Netzsch STA) of the $Y(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ samples was carried out in air.

The polarization resistances (R_p) of the $Y(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ + $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC, Nextech, Micro-grade) composite (1:1 wt. ratio) cathodes in contact with GDC electrolytes were measured using symmetrical cells by ac-impedance spectroscopy (Solartron 1260 FRA). All the cathode materials were mixed with an organic binder (Heraeus V006) to form a slurry (1:1 wt. ratio), screen-printed on each side of the GDC electrolytes, and then heated at 1000 °C for 3 h. The composite cathodes ($Y(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ + $Gd_{0.2}Ce_{0.8}O_{1.9}$) showed similar particle sizes of around 1 μm in diameter. For the SOFC performance test, anode-supported single cells consisting of composite cathode/GDC/Ni + GDC anode were prepared. Here, the composite cathode was again attached at 1000 °C for 3 h. The experimental details are available elsewhere [21]. Pt meshes and wires were attached to each electrode using Pt paste as a current collector. During the single cell fuel cell operation, humidified H_2 (~3% H_2O at 25 °C) and air were supplied, respectively, as fuel and oxidant. After the fuel cell performance tests, the microstructures of the cathodes were observed with a scanning electron microscope (SEM, JEOL JSM-5610).

3. Results and discussion

3.1. Phase instability of $RBaCo_2O_{5+\delta}$ (R = Y and Ho) at high temperatures in air

Fig. 1 compares the room-temperature XRD patterns of the $YBaCo_2O_{5+\delta}$ and $HoBaCo_2O_{5+\delta}$ powders. Iodometric titration indicates the room temperature oxygen content to be 5.31(1) for R = Y and 5.14(1) for R = Ho. Most of the XRD reflections of the $YBaCo_2O_{5+\delta}$ could be indexed based on a tetragonal unit cell with a = 3.878(1) Å and c = 7.498(1) Å. Extra reflections marked with "s" belong to the 3 × 3 × 1 superstructure caused by the ordering of oxygen vacancies in Y–O layer [16,17,22]. The $HoBaCo_2O_{5+\delta}$ sample exhibited XRD pattern very similar to that of $YBaCo_2O_{5+\delta}$ and also could be indexed based on the tetragonal unit cell with a = 3.882(1) Å and c = 7.488(1) Å. In particular, the inset in Fig. 1 illustrates that $HoBaCo_2O_{5+\delta}$ also has superstructure reflections similar to that of $YBaCo_2O_{5+\delta}$. This can be explained by a similar ionic radii between Y (r = 1.019 Å (8-fold coordination), 1.08 Å (11-fold coordination)) and Ho (r = 1.015 Å (10-fold coordination), 1.12 Å (12-fold coordination)) [23]. However, further electron diffraction analysis will be necessary to understand the superstructures of the $HoBaCo_2O_{5+\delta}$ sample. Neutron diffraction studies are also underway to better understand the various super-structures formed due to the ordering of oxygen vacancies.

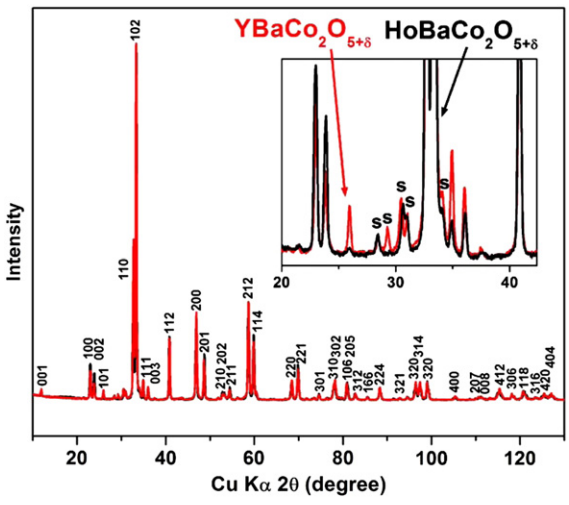

Fig. 1. Comparison of the XRD patterns of $YBaCo_2O_{5+\delta}$ and $HoBaCo_2O_{5+\delta}$.

Fig. 2 illustrates the in situ XRD patterns of the $YBaCo_2O_{5+\delta}$ sample recorded during heating from 25 to 800 °C in air. Although the pristine $YBaCo_2O_{5+\delta}$ phase was stable up to 700 °C, it showed several reflections (marked as *) from secondary phases at 800 °C, which developed with dwelling time. To analyze the secondary phase more clearly, fresh $YBaCo_2O_{5+\delta}$ powders were placed on top of a Pt crucible and heated at 800 °C in air for extended times. After heating at 800 °C for 12 h, a significant amount of the secondary phases was developed, which could be indexed as $BaCoO_3$ (JCPDS 52-1612) [24], $YCoO_3$ (JCPDS 52-0137) [25], along with a small amount of unknown impurities in Fig. 3(a). Furthermore, the pristine $YBaCo_2O_{5+\delta}$ layered-perovskite phase was fully decomposed after dwelling at 800 °C for 3 days. Similarly, $HoBaCo_2O_{5+\delta}$ showed phase decompositions into $BaCoO_3$ (JCPDS 52-1612), $HoCoO_3$ [26], and a small amount of unknown impurities in Fig. 3(b). From these results, it can be concluded that the following major decomposition reactions occur at 800 °C in air:

$$YBaCo_2O_{5+\delta} \rightarrow YCoO_3 + BaCoO_{3-z} \quad (1)$$

$$HoBaCo_2O_{5+\delta} \rightarrow HoCoO_3 + BaCoO_{3-z} \quad (2)$$

The decomposition of the $RBaCo_2O_{5+\delta}$ (R = Y and Ho) at 800 °C in air is reported here for the first time to the best of our knowledge. However, both $YBaCo_2O_{5+\delta}$ and $HoBaCo_2O_{5+\delta}$ samples were stable as indicated by their XRD patterns after heating up to 800 °C in nitrogen

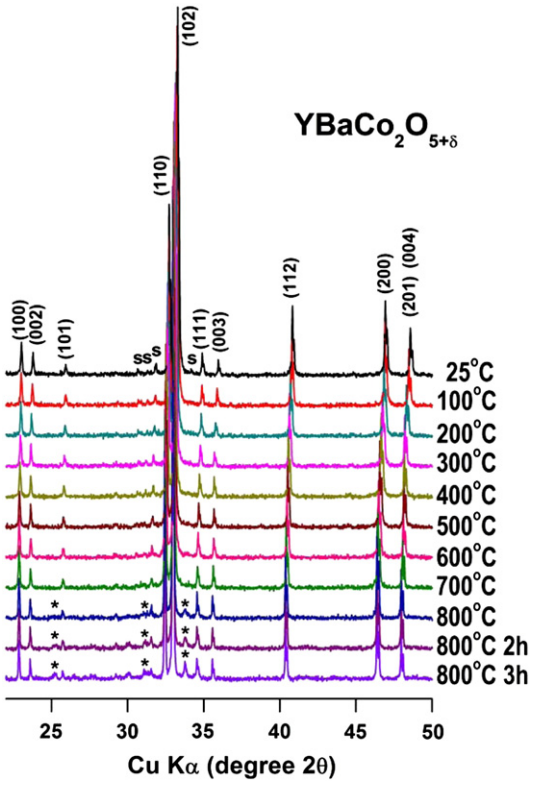

Fig. 2. In situ XRD patterns of $YBaCo_2O_{5+\delta}$ recorded on heating in air. Reflections belonging to superstructure and secondary phases are marked with "s" and *, respectively.