X-ray photoelectron spectroscopy of Sm-doped layered perovskite for intermediate temperature-operating solid oxide fuel cell

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ABSTRACT

Chemical states of Sm doped layered perovksite, $SmBa_{1-x}Sr_xCo_2O_{5+d}$ ($x = 0$ and 0.5), have been investigated by X-ray Photoelectron Spectroscopy (XPS). Substitution of Sr in $SmBa_{1-x}Sr_xCo_2O_{5+d}$ oxide system shifts the binding energy of Sm $3d_{5/2}$ to the more positive side and the charge state of Sm remained Sm^{3+}. Therefore, the substitution of Sr into the $SmBa_{1-x}Sr_xCo_2O_{5+d}$ oxide system does not change the charge state of Sm. Three types of oxygen species were observed in $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) and SBCO from the O 1s spectra comprised of lattice oxygen, carbonated species and adsorbed oxygen species with respect to the measured binding energy ranges. The more Sr was substituted into the Sm doped layered perovskite, the larger the binding energy values became. In case of the Co spectra of SBSCO, two satellite peaks were observed at the range of 786.0–789.0 eV and at 804.93 eV. The evidence of Co^{3+} and Co^{4+} indicated that Co is existing in the chemical form of mixed valence state including Co^{3+} and Co^{4+} in SBCO and SBSCO oxide systems.

1. Introduction

Mixed ionic and electronic conductors (MIEC) have presented very useful properties for cathode materials for solid oxide fuel cell (SOFC) because the ability to transport both types of species, electrons and oxygen ions, allows the oxygen reduction reaction to be extended beyond the triple phase boundary (TPB) and can result in an overall reduction in the cathode polarisation resistance [1–5]. Of these types of material, perovskite type materials based on the general formula $LnBaCo_2O_{5+d}$ and $LnBa_{1-x}Sr_xCo_2O_{5+d}$ (Ln: lanthanides) have lately been receiving growing interest as cathode materials for Intermediate Temperature-operating solid oxide fuel cell (IT-SOFC) due to their excellent electrochemical properties [6–8]. This structure often leads to these materials being termed as layered perovskites and it is the presence of these layers which facilitates the rapid transport properties often observed in these materials [9]. Recently, we reported that kind of behavior for $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (PBSCO) and $NdBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (NBSCO) [10]. From these literatures, PBSCO and NBSCO contain oxygen vacancies in the $[PrO_\delta]$ and $[NdO_\delta]$ layers and form $2a_p \times 2a_p \times 2a_p$ superstructure based on the ordering of these oxygen anions along with the cation

layers at room temperature [10]. We have also investigated the structural, thermal and electrochemical properties of $SmBaCo_2O_{5+\delta}$ (SBCO) and of the composite cathode with SBCO and $Ce_{0.9}Gd_{0.1}O_{2-d}$ (CGO91) [11] and the electrochemical properties of members of the series $LnBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (Ln = Pr, Sm, and Gd) as cathode materials for IT-SOFC [12]. Significantly, a 1:1 mix of $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) and CGO91 (50 wt% SBSCO and 50 wt% CGO91, SBSCO:50) results in the lowest area specific resistance (ASR) of $0.10\,\Omega\,cm^2$ at $600\,°C$ and $0.013\,\Omega\,cm^2$ at $700\,°C$ [13]. The ASR of another composite cathode (50 wt% of SBCO and 50 wt% of CGO91, SBCO:50) on a $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte was observed to be $0.05\,\Omega\,cm^2$ at $700\,°C$ [14,15].

The chemical states in surface layer properties of cathode materials are generally different from the properties of the cathode bulk. Therefore, it is important to determine the nature of the cathode surface, because the TPB, where the electrochemical reaction occurs, is the layer part of the cathode surface which is connected with the electrolyte. Significantly, the occurrence of different oxygen species and the charge states of cobalt based perovskite are of great influence to the rate limiting steps of the oxygen reduction process at the cathode. Therefore, it is very important to investigate the Co charge state and the oxygen species of the cathode oxide materials. However, most of the researches in cathode materials of SOFC are focused on impedance tests, electrical conductivity measurements and power density comparisons. In this study, we have

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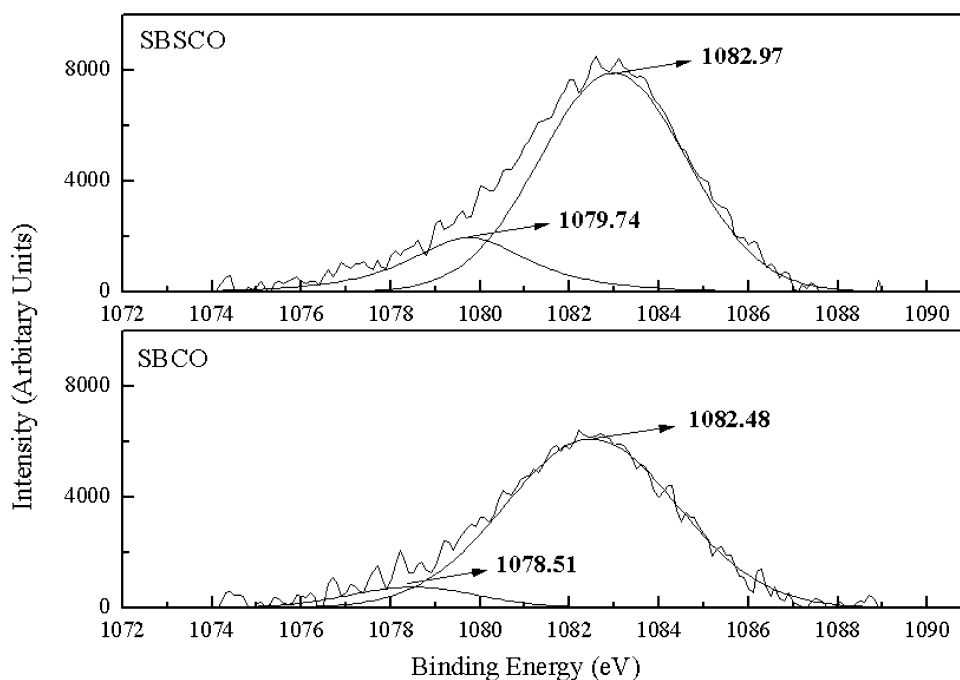E-mail address: jhkim2011@hanbat.ac.kr (J.H. Kim).

Fig. 1. Measured Sm 3d$_{5/2}$ peaks and deconvolution peaks of SBSCO and SBCO.

performed a more detailed investigation of the chemical state of the layered perovskite oxides (SmBa$_{1-x}$Sr$_x$Co$_2$O$_{5+d}$ ($x = 0$ and 0.5)) by using X-ray Photoelectron Spectroscopy (XPS) analysis in order to show the relationship between charge state or chemical species and electrochemical properties.

2. Experimental

Samarium oxide (Sm$_2$O$_3$), strontium carbonate (SrCO$_3$), cobalt oxide (Co$_3$O$_4$), and barium carbonate (BaCO$_3$) were used for the synthesis of the Sm doped layered perovskite oxides expressed as SmBa$_{1-x}$Sr$_x$Co$_2$O$_{5+d}$ ($x = 0$ and 0.5). Single phases were prepared by means of conventional solid state reaction as follows: the weighed powders were placed inside a muffle furnace and heated from room temperature to 1000 °C using various ramp rates, then held at this temperature for 8 h as a first calcination step to decompose the carbonates after mixing and grinding in a mortar with a pestle. The heat treatment for the single phases was repeated at 1100 °C for 36 h after ball milling (bar type) for 24 h with acetone, and then the samples were cooled to room temperature. The bar type rectangular-shaped (5 mm × 5 mm × 18 mm) samples for the XPS measurement of the layered perovskite oxides were pressed and sintered at 1100 °C for 12 h in air. A PHI VersaProbe XPS Microprobe spectrometer was used in the XPS experiments and Mg $K\alpha$ radiation (1253.6 eV) was used as the excitation source for the narrow scan and the wide scan. The binding energy (BE) of the elements was calibrated with respect to the C $_{1s}$ component of the C 1s peak fixed at 284.4 eV. The data treatment was performed with PeakFit version 4.

3. Results and discussion

Fig. 1 shows the Sm 3d$_{5/2}$ core level spectra and the peak deconvolution results of SmBa$_{1-x}$Sr$_x$Co$_2$O$_{5+d}$ ($x = 0$ and 0.5). The Sm 3d$_{5/2}$ peak has a shoulder at the side of the lower binding energies in the vicinity of 1078–1079 eV and these peaks may be caused by the shake off satellite effect [15]. The binding energies of Sm 3d$_{5/2}$ in SmBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_{5+d}$ (SBSCO) and SmBaCo$_2$O$_{5+d}$ (SBCO) are

observed at 1082.97 eV and 1082.48 eV, consistent with the normal oxidation state of Sm^{3+} because the binding energy of core level for Sm$_2$O$_3$ is generally observed at 1083.2 eV which indicates that the substitution of Sr into the SmBa$_{1-x}$Sr$_x$Co$_2$O$_{5+d}$ oxide system cannot change the charge state of Sm. In addition, comparing the binding energy shift of SBSCO to the one of SBCO, the substitution of Sr in the SmBa$_{1-x}$Sr$_x$Co$_2$O$_{5+d}$ oxide system shifts the binding energy ranges of Sm 3d$_{5/2}$ to the more positive side as shown in Fig. 1.

Fig. 2(a) shows the measured XPS spectra and the deconvolution results of Sr 3d$_{5/2-3/2}$ in SBSCO. Generally, the Sr 3d peaks were shown as mainly two distinctive peaks of 3d$_{5/2}$ at lower binding energy ranges and 3d$_{3/2}$ at relatively higher binding energy ranges [16]. However, the measured result shows only one merged peak shown as Fig. 2. (a). Considering the one broad peak to be deconvoluted, deconvolution analysis can be carried out and the results of the deconvoluted Sr 3d spectra was comprised of 4 peaks at 130.18, 131.50, 133.21 and 135.35 eV, respectively. According to the XPS results of Sr in various materials containing the element Sr, two pairs of spin-orbit doubles were observed at 132.8 eV, 134.6 eV and 133.8 eV, 135.8 eV [17–19]. The Sr spectra peaks at 132.8 eV and 134.6 eV are ascribed to the presence of SrO [18] and the peaks at 133.8 eV 135.8 eV to the existence of SrCO$_3$ [19]. The position of the lower binding energy in the Sr 3d$_{5/2}$ which is located at around 131.6 eV is originated from the formation of the peovskite phase showing a charge state of Sr^{2+} [17]. For example, in case of the SrCo$_{0.5}$Fe$_{0.5}$O$_{3-d}$, the binding energy of Sr at 133.5 eV corresponds to the perovskite structure and at 136.0 eV to the carbonate species [20]. Therefore, the main peaks in SBSCO measured at about 131.50 eV and 133.21 eV were originated from Sr 3d$_{5/2}$ and 3d$_{3/2}$, which correspond to the perovskite structure. The Sr spectra peak at 135.35 eV shown in Fig. 2(a) corresponds to the carbonate species because the SBSCO oxide is susceptible to surface carbonate-hydration and therefore metal carbonate species are exposed to the surface of SBSCO. In this sense, SrCO$_3$ and SrO were formed on the surface of SBSCO. In order to classify the carbonate species (SrCO$_3$ and SrO) of the surface layer in SBSCO, spectra of Sr 3d were carried out with six peaks in Fig. 2(b). Comparing the main separated peaks of Sr 3d$_{5/2}$ and 3d$_{3/2}$ in Fig. 2(b) to the