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고체 산화물 연료전지 공기극 물질인 $(Pr_{1-x}Sr_x)CoO_3$ (x=0.5 및 0.7)의 표면분석

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Surface analysis of $(Pr_{1-x}Sr_x)CoO_3$ (x=0.5 and 0.7) as a cathode material for Solid Oxide Fuel Cell

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Key words : Intermediate Temperature operating Solid Oxide Fuel Cell (IT-SOFC, 중저온형 고체산화물 연료전지), X-ray Photoelectron Spectroscopy (XPS, X-선 광전자분광기), Higher binding energy (HBE), Lower binding energy (LBE), Oxygen vacancy (산소 공공), cathode (공기극)

Abstract : The chemical states of oxygen on the surfaces of $Pr_{1-x}Sr_xCoO_3$ (x=0.5 and 0.7) oxide systems were investigated by X-ray photoelectron spectroscopy. Merged oxygen peaks of $Pr_{1-x}Sr_xCoO_3$ (x=0.5 and 0.7) oxides could be divided as five sub-peaks. These five sub-peaks could be defined as lattice oxygen (O_L), chemisorbed oxygen peaks (O_C) and hydroxyl condition oxygen peak (O_H). In case of the $Pr_{0.5}Sr_{0.5}CoO_3$ and $Pr_{0.3}Sr_{0.7}CoO_3$, the binding energy (BE) of oxygen lattice were located at same BE. However, the BE of chemisorbed oxygen peaks including oxygen vacancy shows different BE. Especially, it was found that BE of chemisorbed oxygen peaks was increased when more Sr were substituted. Comparing atomic percentages of oxygens of $Pr_{0.5}Sr_{0.5}CoO_3$ and $Pr_{0.3}Sr_{0.7}CoO_3$, the ratio of $Pr_{0.3}Sr_{0.7}CoO_3$ was higher than that of $Pr_{0.5}Sr_{0.5}CoO_3$. It showed more chemically adsorbed site including oxygen vacancies were existed in $Pr_{0.3}Sr_{0.7}CoO_3$.

1. Introduction

The Solid Oxide Fuel Cell (SOFC) is the most efficient energy device for conversion of chemical energy of hydrogen into electrical energy and shows high electric conversion efficiency, better environment performance than internal engine system, good quality exhausted heat usage, and fuel flexibility [1].

The conventional SOFC comprised of symmetrically deposited cathode and electrolyte based on yttria stabilized zirconia (YSZ) electrolyte operate at about 1000°C [2]. High temperature operation can cause thermal degradation, such as electrode densification, polarization and crack problems. High cost interconnect material for SOFC stack can confine mass production and limit commercialism. One possible way to solve this problem is to reduce the SOFC operating temperature to an intermediate temperature range of 800°C or lower [3].

An issue of significant importance for development of intermediate temperature range is the proper selection of cathode materials. Cathode material is the principal contributor to voltage loss from internal resistance in Intermediate Temperature operating Solid Oxide Fuel Cell (IT-SOFC) [4].

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The ABO_3 crystal structure type as a cathode material is named after perovskite and can be described as follows: The A-cations as rare-earth, alkaline-earth, alkali or other large ions are located at the corners of cube. O^{2-} ions occupy the face-cantered positions and one of the smaller B-cations usually filled with transition elements such as Co and Fe is located in the centre of cube. Hence, B-site cations are surrounded octahedrally by oxide ions. For an application as SOFC cathode, a material has to exhibit several general properties.

The basic requirement for any electrode material is high electronic conductivity. Further, the cathode material must be chemically stable under fuel cell operating conditions, particularly against the electrolyte. Compatibility with respect to the electrolyte refers not only to chemical inertness both during operation and preparation but also to the thermo-mechanical properties in the two contains materials. The key feature for a cathode material, however, is high catalytic activity with respect to the oxygen reduction reaction in order to decrease electrochemical polarization resistance.

$LaMnO_3$ doped with 10-25 mole % Sr ($La_{1-x}Sr_xMnO_{3-\delta}$, LSM), typical cathode material for SOFC, may be used as a cathode material for IT-SOFC due to high thermal property and stability [5]. However, it will not provide a required performance for IT-SOFC because a lower catalytic activity and electrical conductivity at an operating temperature range from 800 to 1000℃in LSM increases cathode polarization [6]. In contrast to LSM, $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) are another cathode material where La and Sr ions occupy the A-sites, Co ion the B-sites in the perovskite structure. LSC has been shown to increase the catalytic activity of the cathode for reduction of oxygen, larger ionic conductivity and producing mixed-conducting oxides at intermediate temperature ranges (600-800℃) [7].

The advanced Area-Specific Resistance (ASR) of $Pr_{0.5}Sr_{0.5}CoO_{3-\delta}$ as a new cathode material was recently studied for IT-SOFC[8]. This paper investigates the chemical state of perovskite oxides $Pr_{1-x}Sr_xCoO_3$ (x=0.5 and 0.7) using X-ray Photoelectron Spectroscopy (XPS). In this study, the relation between chemical states on the cathode surface and defect phenomena were analyzed for oxygen spectrum. Surface states on the cathode were also observed as a function of Sr substitution.

2 Experiment

2.1 Sample preparation

Praseodymium nitrate ($Pr(NO_3)_3$-xH_2O(x≈6, Alfa #12909), strontium nitrate ($Sr(NO_3)_2$-$6H_2O$, Sigma #24342-1), cobalt (II) nitrate($Co(NO_3)_2$-$6H_2O$, Sigma #36418), and glycine ($C_2H_5NO_2$, Sigma #G7126) have been used for cathode synthesis. These raw materials were dissolved and synthesized in deionized water by using the Glycine Nitrate Process (GNP) method[9]. The synthesized cathode powders are described in Table.1.

The X-ray diffraction patterns of the prepared samples after calcination at 1250°C for 1 hour were obtained in a RIGAKU D/MAX-IIIC (3kW) using Co $K\alpha_1$ radiation (λ=0.15418 nm) operated at 40kV and 45mA. The data were collected at 0.06° with a counting time of 1s per step, in the 2Θ range from 10° to 90°.

2.2 Surface characterization

The powders were uniaxially pressed into a disk (7.85mm in diameter and 0.52mm in thickness) and sintered at 1200°C. An ESCA 2000 spectrometer was used in X-ray Photoelectron Spectroscopy (XPS) experiments and Mg Kα radiation (1253.6eV) was used as excitation source for high resolution and wide scan. The data treatment was performed with PeakFit program version4. Binding Energy (BE) of elements was calibrated with respect to the C component of the C1s peak fixed at 248.8eV.

Composition	Abbreviated Composition
$(Pr_{0.3}Sr_{0.7})CoO_{3-\delta}$	PSC37
$(Pr_{0.5}Sr_{0.5})CoO_{3-\delta}$	PSC55

Table.1 The abbreviated specimens of experiments

3. Result and discussion

The XPS spectra of $Pr_{1-x}Sr_xCoO_3$ (x=0.5 and 0.7) for wide scan were shown in Fig.1. There were five relatively strong peaks, assigned to Sr3d, C1s, O1s, Co2p and Pr3d photoelectrons, respectively. The results of XPS spectra were in agreement with elementary composition of the specimens because C1s peak was located about 284.5eV.

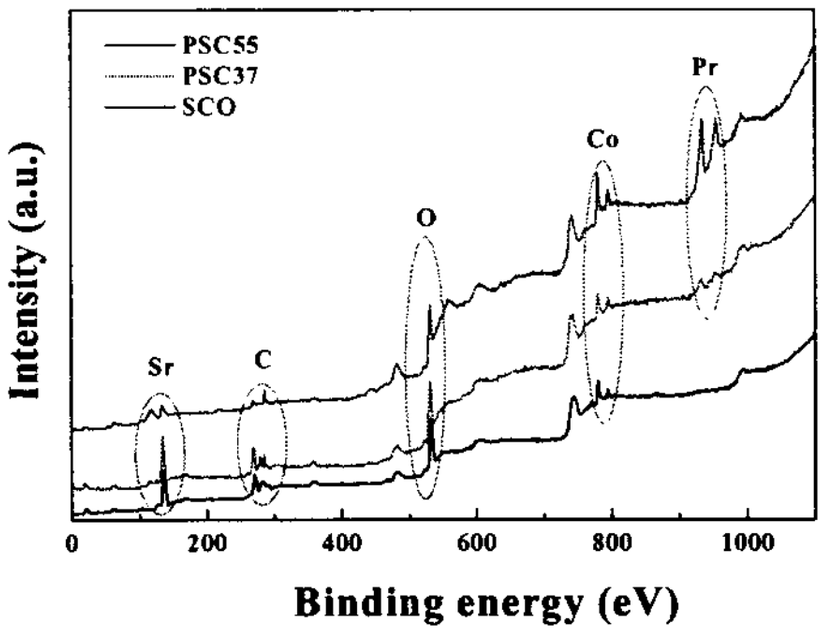

Fig. 1. XPS spectra of $Pr_{1-x}Sr_xCoO_3$ (x=0.5,0.7 and 1)

Quantitative analysis of cathode materials was investigated to survey chemical state on the surface. Back ground of raw data was removed in order to prevent measurement distortion. Linear background was applied by using linear background method connecting with first and final value[10]. In these experiments, linear two point background was used and fitting data were obtained by carrying out curve fitting based on Gaussian function from removed background process and used as quantitative data.

Oxygen peak of PSC55 showed two emerged asymmetry peaks with higher binding energy (HBE) and lower binding energy (LBE) in Fig.2. Emerged oxygen peak as O1s of PSC55 could be divided with 5 sub-peaks and they are summarized in Table.2.

The O1s peak at 527.9eV was attributed to the lattice oxygen (O_L) at the normal site of the perovskite structure [11]. The other peaks at 529.2, 531.1 and 531.7 in Fig.2 were assigned to the chemisorbed oxygen(O_C)[12] in the forms of O^{2-}, O^- and O_2^-, respectively [13]. One of the O1s peaks was assigned as O_H due to in hydroxyl condition.

The binding energy (BE) and full width at half maximum (FWHM) were summarized in Table.3.

Considering results in Table.3, the peaks of O_L were located with same BE in PSC37 and PSC55. However, the oxygen vacancies on the surface showed different oxygen state. The BE of peak 3 showed different BE. Comparing peak 3 of PSC55 with PSC37, BEs of O_L in PSC55 and PSC37 were existed at same BE. However, BEs of oxygen vacancies on the surface of cathode materials were located with different BE. When compared oxygen vacancies of PSC55 and PSC37, BE of oxygen vacancies of PSC55 and PSC37 were found at 530.8eV and 531.1eV. It showed that more substitution of Sr(x) in $PrCoO_3$ oxide system generated oxygen vacancy on the surface of cathode.

In order to investigate surface state difference between PSC55 and PSC37, atomic percentages of oxygen from PSC55 and PSC37 were surveyed. The atomic percentage of oxygen in different states on the oxide can be expressed as follows;

$$\sum O_i = Area\ of\ O_L + O_c + O_H$$

BE	Oxygen peaks of O_{1s}		Identification
Lower BE	OL		Lattice oxygen
↓	O^{2-}	O_c	Chemisorbed-oxygen
	O^-		
	O_2^-		
Higher BE	O_H		Oxygen in Hydroxyl enviroment

Table.2 Various oxygen peaks comprised of 5 peaks by using fitting data (hereafter, BE means Binding Energy)

where

$$O_c = O^{2-} + O^- + O_2^-$$

The atomic percentages of oxygen in different chemical states could be expressed as $(O_C)/\sum O_i(\%)$ and $(O_C + O_H)/\sum O_i(\%)$ can be used to adopt the environment effect as hydroxyl condition. The results of atomic percentages of oxygen from PSC55 and PSC37 were summarized in Table.4. Generally, oxygen vacancies were generated by substitution of Sr in $PrCoO_3$. Comparing the value of $(O_C)/\sum O_i(\%)$ and $(O_C + O_H)/\sum O_i(\%)$ of PSC 55 and PSC37, PSC37 had higher ratio in Table.4. It showed that more adsorbed site including oxygen vacancies were existed in PSC37.

4. Conclusion

The oxygen peaks of PSC37 and PSC55 using XPS were comprised as 5 sub-peaks. O_L peaks of PSC37 and PSC55 as lattice oxygen at the normal site of the perovskite had almost same BE. However, the BE of chemisorbed-oxygen peaks as Oc were increased when more Sr were substituted. According to atomic percentages of oxygen, the ratio of PSC37 was higher than that of PSC55. It showed PSC37 provided more

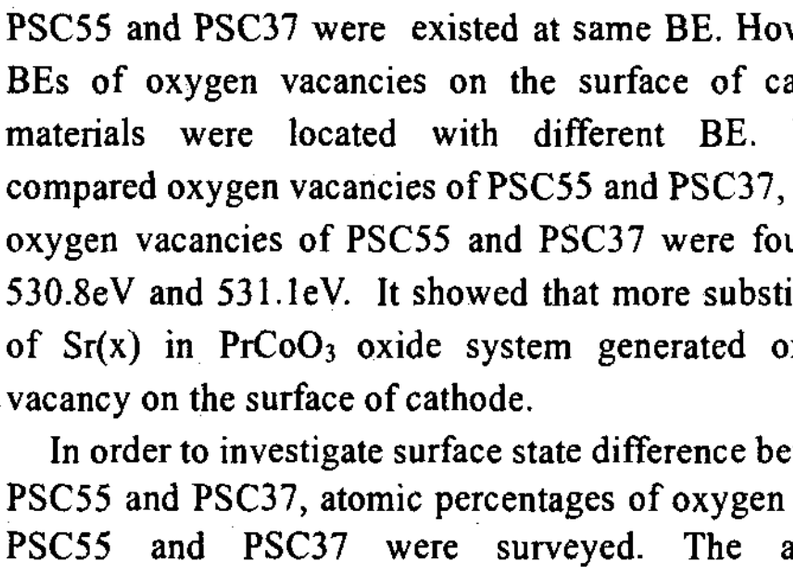

Fig.2. Oxygen peaks of PSC55 from XPS

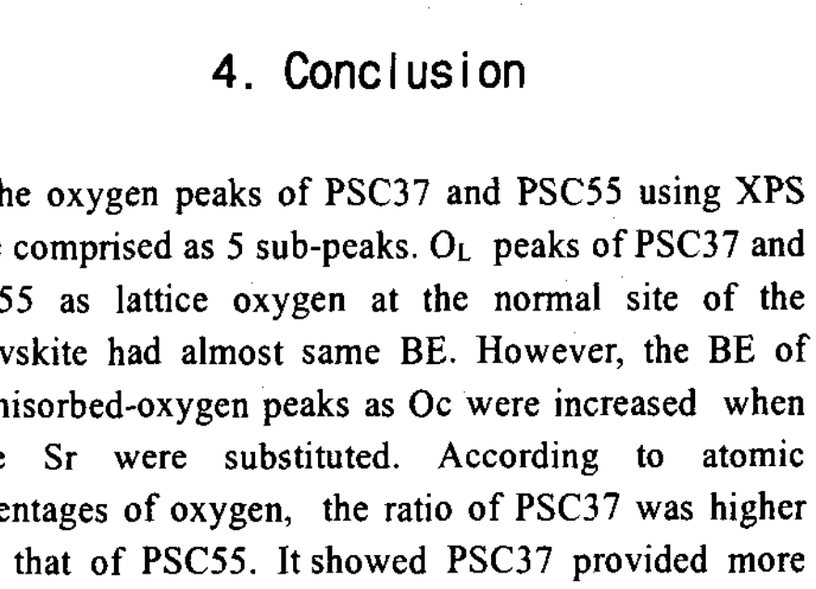

Fig. 3. Oxygen peaks of PSC37 from XPS

Composition		PSC37		PSC55	
		BE	FWHM	BE	FWHM
Peak	1	527.99	1.50	527.94	1.28
	2	529.48	2.19	529.23	1.94
	3	531.28	2.01	530.83	1.97
	4	532.63	1.62	531.99	1.98
	5	533.73	2.04	533.26	3.66

Table.3 Binding Energy (BE) and FWHM (Full width at half maximum) of PSC55 and PSC37 in O1s XPS peak

chemically adsorbed site including oxygen vacancies.

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Composition	Atomic percentage (%)					$(O_C)/\sum O_i(\%)$	$(O_C+O_H)/\sum O_i(\%)$
	O_L	O_c			O_H		
		O^{2-}	O^-	O_2^-			
PSC55	13.29	26.80	44.28	8.76	6.88	79.83	86.71
PSC37	6.86	24.24	42.56	12.29	14.05	79.09	93.14

Table.4 Atomic percentages of oxygen in different chemical states on PSC55 and PSC37 oxide