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Insulative Phase Formation and Polarization Resistance of $\text{PrBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ under Thermal Stress

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Abstract: The degradation behavior of $\text{PrBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ ($x = 0, 0.2, 0.5$) under thermal stress was investigated in terms of phase formation and polarization resistance. The tetragonal phase was indexed in all compositions of PBCCu_x , and the secondary phase, BaO , was identified after thermal degradation in the crystal structure analysis. BaO formation is induced by the nature of perovskite to terminate the surface with AO layer. For pristine specimens, the oxygen vacancy peak ratio was increased from 57% to 60% according to the decrease in the average oxidation number of the B-site ion with Cu doping. After thermal deterioration, the oxidation number of B-site ions was increased, and the $\text{M}=\text{O}$ bonding peak increased due to the decrease in oxygen vacancies and BaO formation according to the thermal stress. In all compositions, the electrical conductivity decreased from 1000 S/cm to 17 S/cm, and the polarization resistance increased approximately 200 times. These results are considered to be related to the increase in the oxidation number of B-site ions along with the formation of secondary phases.

Keywords: layered perovskite; thermal stress; B-site oxidation state; oxygen species; conductivities

Citation: Jo, K.; Ha, J.; Lim, T.; Lee, H. Insulative Phase Formation and Polarization Resistance of $\text{PrBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ under Thermal Stress. *Appl. Sci.* **2022**, *12*, 151. <https://doi.org/10.3390/app12010151>

Received: 19 October 2021

Accepted: 23 December 2021

Published: 24 December 2021

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion systems that directly convert chemical energy into electrical energy because of their high energy conversion efficiency, environmental friendliness and fuel flexibility. Despite these advantages, high operating temperatures (800~1000 °C) cause several drawbacks, such as interfacial reactions among the fuel cell components, structural deformation, chemical/thermal degradation and high material costs [1,2].

Despite the high efficiency at high temperature, significant efforts have been made to develop intermediate temperature-SOFCs (IT-SOFCs) that can be operated at 500~800 °C [3–5]. To decrease the operating temperature will reduce the degradation of other components and extend the selection range of economical material, and also enhance SOFC durability. However, decreasing the operating temperature makes the electrode kinetics sluggish and increases interfacial polarization resistances. It is most prominent for the oxygen reduction reaction (ORR) that occurs in the cathode side. To satisfy the acceptable conductivities of the cathode, a sufficient electronic and oxygen ion conductivity must be maintained, as well as a high electrochemical reaction such as ORR [6–10].

Mixed ionic-electronic conductors (MIECs) have received considerable attention as promising cathode materials capable of achieving high performance for intermediate temperature-SOFCs (IT-SOFCs, below 800 °C). Among the MIECs studied so far, $\text{AA}'\text{B}_2\text{O}_{5+\delta}$ -type layered perovskite oxides have received increasing consideration, where continuous layers of $|\text{BO}_2|$ - $|\text{AO}_\delta|$ - $|\text{BO}_2|$ - $|\text{A}'\text{O}|$ are stacked along the c-axis of the lattice. This layered structure improves the oxygen ion diffusivity by reducing the oxygen bonding strength of the $[\text{AO}_\delta]$ layer and generating an oxygen ion pathway [11,12].

$\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln = Pr, Nd, Sm, etc.) has high electrical conductivity, fast oxygen surface exchange and ion diffusion properties in the intermediate temperature range [13].

Several researchers have investigated the effect of ion substitution on the properties of the $\text{LnBaCo}_2\text{O}_{5+\delta}$. McKinlay et al. reported that the conductivity of $\text{YBaCo}_2\text{O}_{5+\delta}$ increased significantly when Ba was substituted with Sr [14]. The substitution of Co with Fe enhances the structural stability due to increase in electrical conductivity and decrease in polarization resistance. Wei et al. reported that $\text{PrBaCo}_2\text{O}_{5+\delta}$ is considered one of most promising potential cathode materials for IT-SOFCs because of its low cathode polarization by rapid oxygen reduction reaction at 500–700 °C [15,16].

For improving cathode performance $\text{LnBaCo}_2\text{O}_{5+\delta}$ material, A/B-site modification is a useful method. Ba cation-deficient layered-perovskite oxide $\text{PrBa}_{0.92}\text{Co}_2\text{O}_{5+\delta}$ (PB0.92CO) was evaluated as a new cathode material for IT-SOFCs. PB0.92CO has high conductivities of 580–195 $\text{S}\cdot\text{cm}^{-1}$ at temperatures of 200–800 °C in air. ASR values of PB0.92CO cathodes on GDC electrolytes range from 0.093 $\Omega\cdot\text{cm}^2$ at 600 °C to 0.0068 $\Omega\cdot\text{cm}^2$ at 800 °C with an activation energy of 1.05 eV [17]. For B-site modification, Xue et al. [18] have reported that increased Fe doping ($0 < x < 0.6$) deteriorates the cathode performance of $\text{YBaCo}_2\text{O}_{5+\delta}$. Ryu et al. have shown that Cu doping to $\text{PrBaCo}_2\text{O}_{5+\delta}$ induces reduction of Co^{3+} ion into Co^{2+} ion and enhances electrochemical properties [19].

In our previous study, we investigated whether the polarization resistance of $\text{PrBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ (PBCCu $_x$, $x = 0, 0.2, 0.5$) decreases with Cu doping [20]. In this study, thermal stress was applied to PBCCu $_x$, and the changes in electrochemical properties were investigated in terms of crystal structure and electronic structure changes. The crystal and electronic structures of the deteriorated powder were analyzed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and the electrochemical property changes were confirmed by measuring the conductivity and polarization resistance.

2. Materials and Methods

PBCCu $_x$ ($\text{PrBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$, $x = 0, 0.2, 0.5$) powders were synthesized through an EDTA-citrate complexing process. $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, St. Louis, MO, USA), $\text{Co}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ (98%, Sigma-Aldrich, St. Louis, MO, USA) and $\text{Ba}(\text{NO}_3)_2$ (99%+, Alfa Aesar, Haverhill, FL, USA) metal precursors were dissolved in deionized water. EDTA (99.5%, Alfa Aesar, Haverhill, FL, USA) was added to a 1 N NH_4OH (Junsei Chemical Co., Tokyo, Japan) solution to obtain an NH_3 -EDTA buffer solution. The NH_3 -EDTA solution and crystallized citric acid (99.5%, Samchun Chemical, Pyeongtaek, Korea) powders were applied to the metal precursor solution to make a sol for a total metal ion:EDTA: citric acid molar ratio of 1:1:2. The solution was heated to 75 °C while adjusting the pH to 9 with NH_4OH , and the solvent was evaporated to obtain clear gels. These gels were precalcined at 450 °C and calcined in air at 850 °C. Thermal stress was applied to PBCCu powder at 1050 °C for 100 h in electronic furnace in air atmosphere.

Symmetric cells (PBCCu | SDC (Sm doped Ceria, $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_2$) | PBCCu) were prepared to investigate the electrochemical properties of the PBCCu $_x$. The SDC pellets were sintered at 1400 °C for 4 h using SDC powder (SDC20-HP, Fuelcellmaterials, Lewis Center, OH, USA). The PBCCu powders were mixed with a binder prepared from α -terpineol and ethyl-cellulose to form PBCCu pastes, which were screen-printed onto both sides of the SDC pellets. After drying, the symmetric cells were calcined at 950 °C for 2 h in air.

To examine the crystal structures of the calcined powders and sintered powders, powder X-ray diffraction (XRD, PANalytical X'pert-Pro MPD PW3040/60) was performed at room temperature using a step scan procedure (0.02°/2 θ step, time per step 0.5 s, Cu K α radiation, $\lambda = 1.54\text{\AA}$) in the 2 θ range of 10–90°. The PBCCu surface was characterized by XPS using Al K α radiation ($h\nu = 1486.6\text{ eV}$) under ultrahigh vacuum conditions.

The electrical conductivity was measured using a DC 4-terminal technique between 300 and 950 °C in air. Four terminals were formed to wind the Pt electrode wires, and Pt paste was applied to the wires and terminals to ensure a tight connection between the specimen and electrode. The samples were calcined at 1000 °C for 1 h. Direct current was supplied

to them by a current source (Keithley 2400, Cleveland, OH, USA), and the corresponding voltage drops were collected using a multimeter (Agilent, 34401A, Santa Clara, CA, USA). Impedance measurements were conducted using an IviumStat (Ivium, Noord-Brabant, Eindhoven, The Netherlands) instrument over the frequency range from 106 to 0.01 Hz with 10 mV excitation voltage at operating temperatures of 600 °C under open circuit conditions in air.

3. Results and Discussions

Figure 1 shows the XRD patterns of PBCCu_x powders before and after the application of thermal stress. All the peaks were indexed as a single phase of the tetragonal lattice structure with a space group of P4/mmm for the pristine specimen [21,22]. In the XRD pattern after thermal stress application, as shown in Figure 1b, additional peaks corresponding to the secondary phase, BaO, were observed. Thermal degradation formed the BaO secondary phase, which is an insulating phase that could lead to a reduction in the conductivity of PBCCu_x [13,14]. This result corresponds to study of Li et al., which is that A– metal ions are easily precipitated on the surface in an oxidizing atmosphere, air atmosphere, and this is due to the nature of the perovskite oxide to terminate the surface with the AO layer [23].

Figure 1. XRD patterns of PBCCu_x: (a) Pristine and (b) After applying thermal stress for 100 h on 1050 °C.

Figures 2 and 3 exhibit XPS core level spectra for pristine PBCCu_x and PBCCu_x after applying thermal stress for 100 h on 1050 °C. The core level spectra of the Co 2p_{3/2} and Ba 3d_{5/2} states were observed at 775 eV to 785 eV and a weak satellite shake-up peak induced by Co²⁺ and Co³⁺ appeared at 785 eV to 790 eV in Figure 2 [24–27]. Cu 2p_{3/2} and Pr 3d_{5/2} core-level spectra were detected in the range of 922 eV to 938 eV in Figure 2 [28,29]. Table 1 shows the oxidation values of the B-site metal ions in the specimen before and after the application of thermal stress which is calculated by area ratio shown in Figures 2 and 3. For both specimens, the average oxidation value exhibited a decreasing trend as the Cu content increased, and it was calculated that the average oxidation value increased in all specimens after thermal stress was applied. As BaO forms on the surface, the A-site metals have fixed oxidation states, whereas the B-site transition metals Co and Cu can change their

oxidation states more easily [30,31]. The charge imbalance induced by BaO formation can be compensated by increasing the oxidation value of the B-site metal ion in Equation (1):

Pristine

Figure 2. Core-level spectra (black solid line) together with the fit results (colored area) for pristine PBCCu_x, Ba 3d_{5/2} and Co 2p_{3/2}: (a) PBCO; (b) PBCCu0.2; (c) PBCCu0.5, Pr 3d_{5/2} and Cu 2p_{3/2}: (d) PBCO; (e) PBCCu0.2; (f) PBCCu0.5.

Thermal stress application

Figure 3. Core-level spectra (black solid line) together with the fit results (colored area) for PBCCu_x after applying thermal stress for 100 h on 1050 °C, Ba 3d_{5/2} and Co 2p_{3/2}: (a) PBCO; (b) PBCCu0.2; (c) PBCCu0.5, Pr 3d_{5/2} and Cu 2p_{3/2}: (d) PBCO; (e) PBCCu0.2; (f) PBCCu0.5.

Table 1. Ionic ratio of B-site metal ions and average oxidation state for pristine and thermally degraded specimens.

		Pristine			After Applying Thermal Stress for 100 h on 1050 °C		
		PBCCu0	PBCCu0.2	PBCCu0.5	PBCCu0	PBCCu0.2	PBCCu0.5
Co	Co ²⁺ (%)	5.39	4.18	3.69	5.97	4.66	4.05
	Co ³⁺ (%)	63.13	62.05	70.81	35.96	46.95	50.27
	Co ⁴⁺ (%)	31.48	33.77	25.5	58.07	48.39	45.68
Cu	Cu ¹⁺ (%)	—	12.41	6.59	—	28.42	25.31
	Cu ²⁺ (%)	—	87.59	93.41	—	71.58	74.69
Average oxidation number		3.26	3.15	2.89	3.52	3.26	2.99

Figure 4 shows the O 1 s core-level spectra before and after the application of thermal stress. Peaks due to lattice oxygen at 528.28 eV, oxygen vacancies at 530.8 eV, M = O at 529.4 eV, and OH adsorbed on the surface at 533.1 eV were observed [25,26,28]. The ratio of oxygen vacancy in O 1 s spectra was calculated by Equation (2):

$$(\text{Oxygen vacancy})(\%) = \frac{\text{Area}_{\text{Oxygen vacancy}}}{\text{Area}_{\text{Lattice oxygen}} + \text{Area}_{\text{Oxygen vacancy}} + \text{Area}_{\text{M=O bond}} + \text{Area}_{\text{OH}}} \quad (2)$$

Figure 4. O 1 s core level spectra (black solid line) together with the fit results (colored area) for PBCCu: (a) Pristine and (b) After applying thermal stress for 100 h on 1050 °C.

Comparing the pristine and thermal stress–applied specimens, the oxygen vacancies in PBCCu0 decreased from 57% to 43%, and PBCCu0.2 and PBCCu0.5 also decreased by approximately 1% and 3%, respectively; therefore, the electrochemical catalytic capacity is expected to decrease accordingly. In the case of the M = O peak, the ratio of the M = O peak doubled in all compositions after thermal stress application. This result is attributed to the formation of the BaO secondary phase, which is confirmed by the crystal structure analysis in Figure 1b.

As shown in Figure 5a, PBCCux showed a conductivity of up to 1200 S/cm. However, after applying thermal stress, as shown in Figure 5b, the electrical conductivity was 11~17 S/cm, and the conductivity gradually increased as the temperature increased.

Figure 5c shows the electrochemical impedance spectra of PBCCu x measured using a symmetric cell. The polarization resistance value was calculated through the distance between the intersection point and Z' when Z'' was 0. The polarization resistance of PBCCu x was $0.91 \Omega \text{ cm}^2$ (PBCCu0), $0.53 \Omega \text{ cm}^2$ (PBCCu0.2) and $0.26 \Omega \text{ cm}^2$ (PBCCu0.5). As the amount of Cu is increased, the polarization resistance gradually decreases, and PBCCu0.5 is approximately 71.43% smaller than PBCCu0. This result indicates that Cu doping contributed to the reduction of polarization resistance by inducing an increase in oxygen vacancies and an improvement in the interaction with adsorbed oxygen [32]. Figure 5d shows the polarization resistance after applying thermal stress. Before and after thermal stress application, the polarization resistance gradually decreased as the content of Cu increased, and the polarization resistance increased up to $244.5 \Omega \text{ cm}^2$. The degradation of PBCCu x by thermal stress is induced by the formation of BaO.

Figure 5. Electrochemical performance of PBCCu x : Electrical conductivity of specimens: (a) Pristine and (b) After applying thermal stress for 100 h on 1050°C at $300\sim 900^\circ\text{C}$. Polarization resistance of specimens: (c) Pristine and (d) After applying thermal stress for 100 h on 1050°C at 600°C .

4. Conclusions

We investigated the crystal structure and electronic structure change of PBCCu x ($x = 0, 0.2, 0.5$) under thermal stress. The tetragonal phase was confirmed in all PBCCu x samples, and an insulating phase, BaO, was formed after thermal stress application. As the Cu content in PBCCu x increased, the average oxidation value of B-site ions decreased from 3.26 to 2.89, and the formation of additional oxygen vacancies was confirmed by increasing the oxygen vacancy ratio of the O 1s spectra. After thermal stress, the average oxidation value of B-site ions increased by approximately 0.1 for all compositions, the ratio of the oxygen vacancy peak decreased by approximately 5%, and the M = O peak ratio increased twice. Accordingly, the electrical conductivity decreased from 1200 S/cm to approximately 17 S/cm , the behavior also changed from metallic to insulative, and the polarization resistance increased approximately 200 times. BaO formation induced a decrease in the

electrochemical properties of PBCCu_x by interfering with the electron conduction and hindering the reaction point on the surface.

Author Contributions: Conceptualization, H.L.; Funding acquisition, H.L.; Investigation, K.J.; Methodology, J.H. and T.L.; Visualization, J.H. and T.L.; Writing—original draft, K.J. and J.H.; Writing—review & editing, H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by a Korea Institute for Advancement of Technology grant funded by the Korean Government (MOTIE) (P0008335, The Competency Development Program for Industry specialist).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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