



Sung Hun Woo¹, Kyeong Eun Song¹, Seung-Wook Baek², Hyunil Kang³, Wonseok Choi³, Tae Ho Shin⁴, Jun-Young Park⁵ and Jung Hyun Kim^{1,*}

- ¹ Department of Advanced Materials Science and Engineering, Hanbat National University, 125, Dongseodae-ro, Yuseong-gu, Daejeon 34158, Korea; ws99345@gmail.com (S.H.W.); 30201188@edu.hanbat.ac.kr (K.E.S.)
- ² Interdisciplinary Materials Measurement Institute, Korea Research Institute of Standards and Science (KRISS), 267, Gajeong-ro, Yuseong-gu, Daejeon 34113, Korea; baeksw@kriss.re.kr
- ³ Department of Electrical Engineering, Hanbat National University, 125, Dongseo-Daero, Yuseong-gu, Daejeon 34158, Korea; hikang@hanbat.ac.kr (H.K.); wschoi@hanbat.ac.kr (W.C.)
- ⁴ Energy and Environmental Division, Korea Institute of Ceramic Engineering and Technology (KICET), 101, Soho-ro, Jinju-si 52851, Korea; ths@kicet.re.kr
- ⁵ HMC, Department of Nanotechnology and Advanced Materials Engineering, Sejong University, 209, Neungdong-ro, Gwangjin-gu, Seoul 143-747, Korea; jyoung@sejong.ac.kr
- * Correspondence: jhkim2011@hanbat.ac.kr; Tel.: +82-42-821-1239

Abstract: In this study, the phase synthesis and electrochemical properties of $A'A'/A''/B_2O_{5+d}$ (A': Lanthanide, A'': Ba, and A'': Sr) layered perovskites in which Pr and Sm were substituted at the A/-site were investigated for cathode materials of Intermediate Temperature-Operating Solid Oxide Fuel cells (IT-SOFC). In the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1-0.9) systems, tetragonal (x < 0.4) and orthorhombic ($x \ge 0.5$) crystalline structures were confirmed according to the substitution amount of Pr, which has a relatively large ionic radius, and Sm, which has a small ionic radius. All of the layered perovskite oxide systems utilized in this study presented typical metallic conductivity behavior, with decreasing electrical conductivity as temperature increased. In addition, $Pr_{0.5}Sm_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO55), showing a tetragonal crystalline structure, had the lowest conductivity values. However, the Area-Specific Resistance (ASR) of PSBSCO55 was found to be 0.10 Ω cm² at 700 °C, which is lower than those of the other compositions.

Keywords: intermediate; temperature-operating; solid; oxide; fuel; cell; electrical conductivity; electrochemical properties; X-ray photoelectron spectroscopy

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are energy converters that directly convert the chemical energy of oxygen and hydrogen into electrical energy at high temperatures. Because they are made of ceramic and run at high temperatures (600–1000 °C), SOFCs have the advantage of not requiring any additional precious metal catalyst. There is a problem, however, in their long-term performance, such as in the chemical reaction of the electrode and the poisoning of Cr when devices are operating at high temperatures [1–4].

To solve these problems, many domestic and overseas research institutes are focusing on research and development toward Intermediate Temperature-Operating Solid Oxide Fuel Cells (IT-SOFCs). In the case of these IT-SOFCs, however, problems such as relatively lower ion conductivity and Oxygen Reduction Reaction (ORR) of the cathode when operating at a relatively low temperature have been reported, making it essential to develop advanced cathode materials.

For example, the properties of $PrBaCo_2O_{5+d}$ (PBCO), in which the lanthanide site of $LnBaCo_2O_{5+d}$ was replaced by Pr, were reported; the compound was found to show excellent Area-Specific Resistance (ASR). The layered perovskite oxide system formed a



Citation: Woo, S.H.; Song, K.E.; Baek, S.-W.; Kang, H.; Choi, W.; Shin, T.H.; Park, J.-Y.; Kim, J.H. Pr- and Sm-Substituted Layered Perovskite Oxide Systems for IT-SOFC Cathodes. *Energies* 2021, *14*, 6739. https:// doi.org/10.3390/en14206739

Academic Editor: Bahman Amini Horri

Received: 24 August 2021 Accepted: 14 October 2021 Published: 16 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). crystalline structure for the layered order of $[CoO_2]$ -[BaO]- $[CoO_2]$ - $[LnO_6]$, in which it was shown that two types of cobalt coordination environments such as pyramidal CoO₅ and octahedral CoO₆ co-existed. Oxygen vacancy in the $[LnO_d]$ layer was acknowledged to prevent spin glass behavior, resulting in excellent oxygen mobility and surface properties [5,6].

Based on these studies, our group synthesized SmBa_{0.5}Sr_{0.5}Co₂O_{5+d} (SBSCO) using a cathode mixed with Ce_{0.9}Gd_{0.1}O₂ (CGO91) and SBSCO at a mass ratio of 1:1; a cathode material with an ASR of 0.019 Ω cm² at a temperature of 700 °C was developed [7–9]. In addition, from the composition of Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co₂O_{5+d} (x = 0.1–0.9) that our group recently reported, the crystalline structure was confirmed through the ionic radius substituted at the A[/]-site in the chemical composition of the layered perovskite oxide system A[/]A^{//}A^{///}B₂O_{5+d} (A[/]: Lanthanide, A^{//}: Ba and A^{///}: Sr). In particular, Sm_{0.2}Nd_{0.8}Ba_{0.5}Sr_{0.5}Co₂O_{5+d} (SNBSCO8), reported as having a tetragonal crystalline structure, was found to have an excellent ASR of 0.092 Ω cm² at 700 °C [10].

In this study, in order to develop a cathode that can be used in IT-SOFC, $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxide systems were synthesized by substituting Pr, with a larger ionic radius than that of Sm, in the A[/]-site based on SBSCO of the layered perovskite oxide system. Phase synthesis, electrical conductivity, electrochemical analysis, and X-ray Photoelectron Spectroscopy (XPS) analyses of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) were conducted for the cathode materials of IT-SOFC.

2. Materials and Methods

2.1. Solid State Reaction, X-ray Diffraction Measurement, and Microstructure Analysis

 $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–1) layered perovskite oxide systems were synthesized by means of a traditional solid-state reaction (SSR).

To ensure an accurate experiment, reagent-grade oxides and carbides such as Praseodymium Oxide (Pr_6O_{11} , High Purity Chemicals, Kojundo, Japan), Samarium Oxide (Sm_2O_3 , Alfa Aeser, Haverhill, MA, USA), Cobalt Oxide (Co_3O_4 , Alfa Aeser), Barium Carbonate (BaCO₃, Alfa Aeser), and Strontium Carbonate ($SrCO_3$, Alfa Aeser) were dried in an electric furnace for 1 h under 150 °C conditions and then accurate weights were obtained. Table 1 summarizes the chemical compositions and abbreviations used in this study.

Chemical Compositions	Abbreviations
SmBa _{0.5} Sr _{0.5} Co ₂ O _{5+d}	SBSCO
$Pr_{0.1}Sm_{0.9}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	PSBSCO19
Pr _{0.3} Sm _{0.7} Ba _{0.5} Sr _{0.5} Co ₂ O _{5+d}	PSBSCO37
$Pr_{0.5}Sm_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	PSBSCO55
Pr _{0.7} Sm _{0.3} Ba _{0.5} Sr _{0.5} Co ₂ O _{5+d}	PSBSCO73
Pr _{0.9} Sm _{0.1} Ba _{0.5} Sr _{0.5} Co ₂ O _{5+d}	PSBSCO91
PrBa _{0.5} Sr _{0.5} Co ₂ O _{5+d}	PBSCO

Table 1. Abbreviations of specimens.

A $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–1) layered perovskite composition was mixed through physical methods such as agate mortar and ball mill processes using an ethanol solvent, and then calcined at 1000 °C and 1100 °C for 6 h and 8 h, respectively, under air condition.

X-ray diffraction (XRD) patterns of the calcined samples were obtained by means of an X-ray diffraction analyzer (Model D/MAX 2500, Rigaku). An XRD measurement system was operated at 45 kW and 200 mA. The data were collected from $2\theta = 10$ to 90° and the obtained data were matched with reference data for the identification of crystal structures [7–10].

3 of 18

The microstructure of a symmetrical half-cell was investigated using field-emission scanning electron microscopy (FE-SEM, JSM-7600 F, JEOL) combined with energy-dispersive spectroscopy.

2.2. Electrical Conductivity Analysis

To measure the electrical conductivity of the layered perovskite oxide systems, $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide systems were put into a metal mold with a size of 6 mm × 25 mm and compressed to prepare rectangular-shaped bars. After sintering at 1100 °C for 3 h, bars showing sizes of 5 mm × 4 mm × 25 mm were prepared.

The bar-type samples were then connected using Pt-wire and Pt paste for a general 4-terminal DC method. These were measured at 50 $^{\circ}$ C intervals in a temperature range of 50–900 $^{\circ}$ C via a Keithley 2400 source meter.

2.3. Electrochemical Characterization

In order to fabricate a half cell, 2.5 g of $Ce_{0.9}Gd_{0.1}O_2$ (CGO91, Rhodia, Frankfurt, Germany) powder, an electrolyte material, was weighed and compression-molded at a pressure of 2×10^3 kg/m²; it was then sintered at 1450 °C for 6 h. $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–1) layered perovskite oxide systems, synthesized by SSR for electrochemical analysis, were fabricated as a cathode ink using Alpha-terpineol (KANTO CHEMICAL), Butvar (SIGMA Aldrich), and acetone. Afterwards, this ink was coated on the CGO91 electrolyte substrate by screen printing. After this material was sintered at 1000 °C for 1 h, a half-cell was finally prepared.

The electrochemical properties of the fabricated layered perovskite oxide half-cell were measured by means of an electrochemical analyzer (Model nStat, HS Technologies, Cavite, Philippine) under a frequency range of 0.05 Hz to 2.5 MHz and air conditions in a 500–900 °C temperature range with steps of 50 °C at a rate of 5 °C/min.

2.4. X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out on Pr_xSm_{1-x} Ba_{0.5}Sr_{0.5}Co₂O_{5+d} samples calcined at 1100 °C for 8 h.

For analysis of these samples, XPS was performed on a PHI VersaProbe XPS Microprobe with a monochromatized Al Ka source (hv = 1486.6 eV) under conditions of 25 W and 15 kV. The XPS data were analyzed using PeakFit version 4. Calibration of the binding energy (BE) was conducted with respect to the C 1s peak fixed at 284.4 eV.

3. Results and Discussion

3.1. XRD Analysis and Microstructure

Based on $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+d}$ (SBSCO), the XRD results of $\text{Pr}_x\text{Sm}_{1-x}\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+d}$ (x = 0–0.9), which stepwise-substituted Praseodymium (Pr) with a relatively large ionic radius in the place of Samarium (Sm), are summarized in Figure 1.

From Figure 1, when the specific peaks of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ oxide systems measured at about 23, 33, 41, 47, 59, 69, and 78° were compared with those of SBSCO, these XRD patterns corresponded to the same peaks of SBSCO, implying that these oxide systems were synthesized as a layered perovskite crystal structure [7,8].

In a similar research result, the composition of $Nd_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) that our group recently reported represented a change in the crystalline structure due to the splitting and merging of XRD peaks. In other words, in the chemical composition of $A/A^{//}A^{//}B_2O_{5+d}$ (A': Lanthanide, A'': Ba and A''': Sr), a layered perovskite oxide system, an orthorhombic crystalline structure was found when the A/-site was substituted by Sm, which had a relatively small ionic radius, while a tetragonal crystalline structure was formed when Nd, which had a relatively large ionic radius, was substituted.

Upon comparison of the previous results described above and the results summarized in Figure 1, it can be seen that all the XRD peaks were split in the case of $Pr_{0.3}Sm_{0.7}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO37) and $Pr_{0.1}Sm_{0.9}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO19). This showed the same phenomenon as the split XRD patterns of SBSCO, SmBaCo₂O_{5+d}

(SBCO), GdBaCo₂O_{5+d} (GBCO), and GdBa_{0.5}Sr_{0.5}Co₂O_{5+d} (GBSCO), which were reported as orthorhombic crystalline structures [7–9,11–14].



Figure 1. XRD patterns of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) oxide systems calcined at 1100 °C for 8 h.

In the cases of $Pr_{0.9}Sm_{0.1}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO91), $Pr_{0.7}Sm_{0.3}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO73), and $Pr_{0.5}Sm_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO55), it was confirmed that all the peaks of the XRD were merged. This was confirmed to be consistent with the merged XRD pattern of NdBaCo₂O_{5+d} (NBCO), NdBa_{0.5}Sr_{0.5}Co₂O_{5+d} (NBSCO), PrBaCo₂O_{5+d} (PBCO), and PrBa_{0.5}Sr_{0.5}Co₂O_{5+d} (PBSCO), which were reported to be tetragonal crystal structures [13,15–19].

Therefore, the crystal structures of PSBSCO37 and PSBSCO19, with a lower molar ratio of Pr than Sm, existed in the orthorhombic form in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–0.9) oxide systems. However, the structures of PSBSCO91, PSBSCO73, and PSBSCO55, with the same or higher Pr substitution compared to that of Sm, existed in a tetragonal from.

The field-emission scanning electron microscopy (FE-SEM) images in Figure 2 show the cross-section view of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide systems of a symmetrical half-cell. It was confirmed that all of the cathode materials sintered a good balance of the conflicting electrode requirement of maintaining a porous and cathode thickness.

3.2. Electrical Conductivity of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$

The electrical conductivity results of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) layered perovskite oxide systems are summarized in Figure 3.

As was confirmed in Figure 3a, all compositions of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) showed typical metallic conductivity behavior in which the conductivity decreased with an increasing temperature, similar to results reported for SBSCO and SNBSCO in the existing literature [7–10,20].

Perovskite or layered perovskite, which both have high electrical conductivity values in the relatively low-temperature region, were mainly associated with the change of the charge state of cobalt (Co) substituted at the B-site. For example, changes from a charge state of Co^{3+} to Co^{2+} and Co^{4+} were observed; from this, it could be interpreted that an increase in the concentration of Co^{4+} , which could be explained by small-polaron hopping, caused the higher electrical conductivity in the low-temperature region compared with the high-temperature region [10,11].



Figure 2. SEM images of cross-section view in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide systems of symmetrical half-cell. The oxide systems are sintered at 1000 °C for 1 h. (a) $Pr_{0.1}Sm_{0.9}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO19), (b) $Pr_{0.3}Sm_{0.7}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO37), (c) $Pr_{0.5}Sm_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO55), (d) $Pr_{0.7}Sm_{0.3}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO73), and (e) $Pr_{0.9}Sm_{0.1}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO91).



(a)

Figure 3. Cont.

2.8

2.7

2.6

2.5

2.4

Pr 0.1

Sm 0.9

0.2

0.8

0.3

0.7

(b)

0.4

0.6

0.5

0.5

Various amounts of Pr (from 0.0 to 1.0) or Sm (from 1.0 to 0.0)

log(electrical conductivity)(S/cm)



0.7

0.3

0.8

0.2

0.9

0.1

Figure 3. (a) Electrical conductivity results of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) cathode materials from 50 °C to 900 °C in air and (b) summarized electrical conductivity results with respect to various amounts of Pr or Sm substitutions.

0.6

0.4

On the other hand, electrical conductivity decreased in the high-temperature region. This could be interpreted as showing a decrease in the charge state from Co^{4+} to Co^{3+} and a sharp increase in the oxygen vacancy concentration, which increased as a function of the temperature inside the layered perovskite lattice, causing the decrease in electrical conductivity [10,11]. It can be seen that the electrical conductivity slope in the low-temperature region and the conductivity reduction tendency in the high-temperature region changed in the temperature range of 300–350 °C.

This temperature range was interpreted as the boundary between the low and hightemperature regions. This same phenomenon was found in the SBSCO composition in this study. Further, results of the Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) show that the temperature range of 300–350 °C was the same temperature range in which weight loss of the layered perovskite occurred. This phenomenon was related to the rapid occurrence of oxygen vacancies [11].

Therefore, the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) oxide system applied to this study could also be judged to have the same characteristics as the existing results. In other words, the decrease in electrical conductivity at 300–350 °C found in the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ composition was interpreted as being due to the rapid generation of oxygen vacancies in the crystal.

The electrical conductivity values of each composition at specific temperatures (500, 600, 700, and 900 °C) are summarized in Figure 3b. In the case of the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide system, differences in conductivity occurred depending on the composition. As the substitution amount of Pr existing in A⁷ of A⁷A⁷⁷B₂O_{5+d} in the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ increased (as the substitution amount of Sm decreased), the conductivity decreased and the lowest conductivity properties were found in PSBSCO55, which had substitution ratios of 1 for Pr and Sm. Hence, it can be inferred that as the substitution amount of Pr decreased (as the substitution amount of Sm increased), the value of electrical conductivity increased.

For example, the conductivity values of PSBSCO91 were 1346, 668, 419, 323, and 263 S/cm at 50, 500, 600, 700, and 900 °C. However, PSBSCO55 showed the lowest values of 1091, 580, 471, 374, and 236 S/cm, while PSBSCO19, compared to the PSBSCO55,

showed increased electrical conductivity values of 1360, 675, 545, 446, and 283 S/cm. In other words, the percolation phenomenon of electrical conductivity according to the compositions occurred in the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide system [21].

In summary, it was confirmed that the electrical conductivity was decreased when Pr was substituted in the layered perovskite SBSCO. Therefore, the lowest conductivity values of the PSBSCO55 composition of the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide system have been found. However, these values were meant to be higher than the minimum electrical conductivity (100 S/cm) required for the IT-SOFCs cathode material [22]. Furthermore, all compositions were confirmed to have lower electrical conductivity values than those of SBSCO and PBSCO, but higher conductivity values than that of NBSCO [7,8,17,19].

3.3. Electrochemical Characterization

Figure 4 summarizes the impedance plots of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9), measured at 700 °C. In cases of compositions of the layered perovskite oxide systems PSB-SCO19 and PSBSCO37 with orthorhombic crystalline structures, the ASR values at 700 °C are 0.21 and 0.12 Ω cm². For the compositions of PSBSCO55, PSBSCO73, and PSBSCO91 with tetragonal crystalline structures, the ASR values at 700 °C were measured and found to be 0.10, 0.15, and 0.29 Ω cm². These experimental results show that PSBSCO37, PSBSCO55, and PSBSCO73 have relatively lower ASR values than the SBSCO (0.204 Ω cm²) layered perovskite cathode material. Under the same temperature conditions (700 °C), it was confirmed that the ASR values were lower than those of PrBa_{0.5}Sr_{0.5}Co₂O_{5+d} (0.286 Ω cm²), NdBa_{0.5}Sr_{0.25}Ca_{0.25}Co₂O_{5+d} (0.13 Ω cm²), and the required ASR value (0.15 Ω cm²) for IT-SOFC cathode materials [7,8,10,23,24].



Figure 4. Impedance plots of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) oxide systems measured at 700 °C in air on dense CGO91 electrolyte. The number in these plots corresponds to the logarithm of frequency.

Figure 5 summarizes the ASRs according to the temperatures of all $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxides. In contrast to the low ASRs of cathodes with high electrical conductivity, the lowest ASR value can be found in PSBSCO55, which has relatively low conductivity in the composition of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$. These properties will be further explained using the results of X-ray photoelectron spectroscopy surface analysis XPS.



Figure 5. Area-specific resistances (ASRs) of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) oxide systems from 550 to 900 °C in air.

The activation energy values, calculated at 550–900 °C, of tetragonal crystalline structures PSBSCO55, PSBSCO73, and PSBSCO91 (1.23, 1.17, and 1.23 eV) were relatively lower than those of the orthorhombic crystalline structures SBSCO (1.21 eV), PSBSCO19 (Ea = 1.37 eV), and PSBSCO37 (Ea = 1.26 eV). From these experimental results, it can be confirmed that, among the oxides of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite, the activation energy of the oxide system with a tetragonal crystalline structure presented the same tendency as the existing results, showing a value relatively lower than the activation energy of the orthorhombic crystalline structure (PSBSCO19, PSB-SCO37) [7,8].

Figure 6 provides a summary of the relationships between the crystalline structure and electrical conductivity—ASR property of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$.



Figure 6. Relationships between ASRs–electrical conductivity values of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) oxide systems measured at 600, 700, and 800 °C and crystalline structures.

Based on the layered perovskite SBSCO, it was confirmed that the electrical conductivity decreased when Pr was substituted for the A-site. In $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9), the tetragonal crystalline structure was identified when there was a relatively large ionic radius (Pr > Sm); lower electrical conductivity values were also obtained by replacing Pr by 50 mol % or more in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ perovskite oxide systems. In addition, the PSBSCO55 composition showed the lowest electrical conductivity values at all temperature conditions measured. However, PSBSCO55 showed the lowest ASR values in these experiments.

3.4. XPS Spectra of Cobalt

Figure 7 and Table 2 summarize the results of XPS analysis performed in the Co 2p range of $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxide systems.



Figure 7. Cont.



790

Binding Energy(eV)

(**d**)

800

810

Figure 7. Cont.

0 -

770

780

Intensity (Arb. unit)

Intensity (Arb. unit)



Figure 7. Measured cobalt 2p peaks and deconvolution peaks of (**a**) PSBSCO19, (**b**) PSBSCO37, (**c**) PSBSCO55, (**d**) PSBSCO73, and (**e**) PSBSCO91.

Table 2. Binding energy (BE), full width at half maximum (FWHM), and % area of the cobalt peaks from the XPS analysis of various samples.

Composi-	Binding Energy (BE) Distribution										2. 4	
tions	Co 2p _{3/2} BE (eV) EWHM Area %			Co 2p _{1/2} BE (eV) EWHM Area %			$Co^{2+} + Co^{4+}$ BE (eV) EWHM Area %			$Co^{3+} + Co^{4+}$ BE (eV) EWHM Area %		
	DL (CV)	1 //11//1	Alca /0	DL (CV)	1 //11//1	Alca /0	DL (CV)	1 **111	Alca /0	DL (CV)	1 ******	Alca /0
PSBSCO19	779.4	2.93	56.01	794.6	3.08	30.93	789.3	1.08	0.81	804.8	5.65	5.49
PSBSCO37	779.7	3.22	54.50	794.9	3.08	31.48	786.1, 789.0	0.95/1.09	0.76, 0.65	804.0	4.09	5.23
PSBSCO55	779.7	2.63	53.35	794.9	2.69	32.95	788.2	2.13	1.73	804.3	3.28	4.38
PSBSCO73	779.6	3.07	55.88	794.9	2.90	27.35	786.9 <i>,</i> 789.5	1.45/1.20	0.90, 0.47	804.6	3.70	5.27
PSBSCO91	779.5	2.73	50.67	794.8	2.62	31.88	787.5	1.17	0.95	804.3	3.90	5.45

In general, it is accepted that a Co 2p spectrum can be separated into a Co $2p_{3/2}$ spectrum with low binding energy (BE) and a Co $2p_{1/2}$ with high BE. In this study, it was likewise verified that all measured Co $2p_{3/2}$ spectra of the layered perovskite oxide systems were in the lower BE range of about 779.0–780.0 eV. In addition, it can be seen that Co $2p_{1/2}$ spectra existed in the higher BE range of about 794.0–795.0 eV [21,25,26].

Further, the range of 777.1–777.9 eV found in the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxide systems shown in Figure 7 was similar to the BE range of the 2p3/2 found at 777.3 eV for Co metal [21]. Furthermore, the BE region of 792.0–792.5 eV was similar to the BE range of Co metal $2p_{1/2}$ found at 792.4 eV. Therefore, all the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxide systems measured in this experiment showed that Co metal was present on the surface [21,27].

According to the XPS results corresponding to SBSCO which were studied by our group, relatively high electrical conductivity properties were present because a high concentration of Co^{4+} was apparent at relatively low temperatures in the layered perovskite oxide system in which Co was substituted at the B-site [21]. In other words, it was clear that the presence of Co^{4+} and high conductivity were directly proportional. In the case of the spectra located at 786.0–790.0 eV of SBSCO, the crystalline structure was orthorhombic,

and this property was caused by Co^{2+} and Co^{4+} ; at 804.0–805.0 eV, the phenomenon was caused by the coexistence of Co^{3+} and Co^{4+} [21,27,28].

The BEs of the Co^{2+} and Co^{4+} spectra of the PSBSCO19 and PSBSCO91 compositions, showing relatively high electrical conductivity, were located at 789.3 and 787.5 eV, respectively; the area % of the spectra was confirmed to be about 0.81 and 0.95, respectively, as shown in Table 2. The BEs of the Co^{3+} and Co^{4+} spectra were located at 804.8 and 804.3 eV, respectively, and the area % of the spectra was confirmed to be approximately 5.49 and 5.45%, respectively. On the other hand, in the case of PSBSCO55, which showed the lowest electrical conductivity, the BEs of Co^{2+} and Co^{4+} were located at 788.2 eV and the area % occupied by Co^{2+} and Co^{4+} in PSBSCO55 was 1.73. It was confirmed that the Co^{3+} and Co^{4+} spectra were located at 804.3 eV,

The relationships between the crystalline structure and the area percentage of Co, when Co has charge states of +2, +3, and +4, as calculated through the results of this experiment, with electrical conductivity of 50 °C, are summarized in Figure 8. The reason that the electrical conductivity was high in PSBSCO19 and PSBSCO91 and the electrical conductivity was low in PSBSC055 was the correlation between $Co^{3+} + Co^{4+}$ area % and $Co^{2+} + Co^{4+}$ area %. In other words, the effects of the electrical conductivity and the $Co^{2+} + Co^{4+}$ area % were inversely proportional. On the other hand, the electrical conductivity behavior was proportional to $Co^{3+} + Co^{4+}$ area %. It is clear that the property of high electrical conductivity was caused by Co^{4+} , which has a relatively high concentration at a high area % of $Co^{3+} + Co^{4+}$.



Figure 8. Electrical conductivity area % of Co with 2+, 3+, and 4+—Substitution of Pr or Sm relationship in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.0–0.9) oxide systems.

3.5. XPS Spectra of Oxygen

The XPS spectra of O1s for $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) are shown in Figure 9. It can be seen that all layered perovskite oxide systems were split into three spectra according to the binding energy (BE) differences.

In the low BE (LBE) region, the oxygen was inside the lattice. Oxygen ions inside the lattice became oxygen vacancies at high temperatures, which affected the adsorption and activation energy of oxygen molecules. In the high (HBE) BE region, this phenomenon was associated with the adsorption of hydroxyl species (OH-) and surfaces. Finally, in the intermediate BE (IBE) region, this phenomenon was associated with CO_3^{2-} [21,29,30].

Table 3 summarizes the peak shifts and areas for the corresponding deconvolution results shown in Figure 8. In the $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) layered perovskite oxide system, the LBE was in the range of 527.6–527.9 eV. The area % of orthorhombic structures of PSBSCO19 and PSBSCO37 was analyzed and found to be 17.07 and 18.51, with tetragonal structures PSBSCO55, PSBSCO73, and PSBSCO91 occupying approximately 20.29, 17.36, and 16.65 of area %.

For HBEs found between 530.7 and 530.8 eV, PSBSCO55 occupied the largest area % of 74.18. On the other hand, PSBSCO37 and PSBSCO19, whose substitution amounts of Sm were higher than that of PSBSCO55, showed a lower HBE area % value than that of PSBSCO55. This tendency was also found in the oxide systems, such as those of SBSCO and NdBaCo₂O_{5+d} (NBCO), in which the A-site was partially removed [21,31].



Figure 9. Cont.



(**d**)

Figure 9. Cont.



Figure 9. Measured oxygen 1s peaks and deconvolution peaks of (**a**) PSBSCO19, (**b**) PSBSCO37, (**c**) PSBSCO55, (**d**) PSBSCO73, and (**e**) PSBSCO91.

Table 3. Binding energy (BE), full width at half maximum (FWHM), and % area of the cobalt peaks from the XPS analysis of various samples.

Compositions		LBE		Binding Er	nergy (BE) D IBE	istribution	НВЕ		
	BE (eV)	FWHM	Area %	BE (eV)	FWHM	Area %	BE (eV)	FWHM	Area %
PSBSCO19	527.7	1.10	17.07	528.7	1.49	16.03	530.7	2.23	66.90
PSBSCO37	527.9	1.13	18.51	528.7	1.12	10.19	530.8	2.95	71.30
PSBSCO55	527.9	1.35	20.29	528.9	1.03	5.53	530.7	2.44	74.18
PSBSCO73	527.8	1.12	17.36	528.7	1.29	18.24	530.8	2.54	64.40
PSBSCO91	527.6	1.14	16.65	528.4	1.21	13.59	530.7	2.55	69.76

The results of XPS analysis and ASR performed at 700 °C are shown in Figure 10. In Figure 10, it can be seen that PSBSCO91 with a tetragonal structure and PSBSCO19 with an orthorhombic crystalline structure showed the highest ASR values. It can also be seen that PSBSCO55 with a tetragonal structure shows the lowest ASR value. The properties were inversely proportionate, as follows: When the area % in LBE was large, ASR had its lowest value; on the contrary, ASR had its highest value when the area % was small. In addition, PSBSCO55, which had the largest area % (74.18%) in the range of HBE, had the lowest ASR of all samples. Comparing these results, LBE and HBE with a high area % had effectively lower ASR values.

However, ASR is a resistance that occurs when oxygen molecules are electrochemically reduced from the three-phase boundary (TPB) of an electrolyte/cathode/oxygen to oxygen ions. In order to achieve low ASR properties, therefore, the interface properties where the area of the three-phase interface was relatively extended were very important. In other words, since the value of HBE is directly related to this property, it can be asserted that PSBSCO55, with its outstanding surface oxygen activity, had the lowest ASR properties. Therefore, compared to the properties of oxygen ions in the lattice, low ASR was directly related to the surface or interface HBE properties [21,29–31].



Figure 10. Area-specific resistances (ASRs)—Area % of LBE and HBE in oxygen spectra—Substitution of Pr or Sm relationship in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ oxide system.

4. Conclusions

In this study, $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9) was synthesized by substituting Pr, possessing a large ionic radius, and Sm, possessing a small ionic radius, at the A[/]-site in the chemical composition of A[/]A^{//}B₂O_{5+d} (A[/]: Lanthanide, A^{//}: Ba and A^{///}: Sr).

When Pr (x = 0.1 to 0.3) was substituted with Sm, an orthorhombic crystalline structure was formed. However, when the replacement amount of Pr (x = 0.5–0.9) was the same or higher than that of Sm, a tetragonal crystal structure was formed.

From electrical conductivity values of all chemical compositions, electrochemical analyses, and XPS analysis results, tetragonal $Pr_{0.5}Sm_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (PSBSCO55), possessing a low Co⁴⁺ concentration in the Co 2p range, presented the lowest electrical conductivity values of 1091, 374, and 236 S/cm at 50, 600, and 700 °C. For PSBSCO55, which had the largest area % of LBE and HBE spectra in $Pr_xSm_{1-x}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0.1–0.9), the ASR value was 0.10 Ω cm² at 700 °C, the best ASR among all chemical compositions, confirming that PSBSCO55 is suitable as a cathode material for IT-SOFCs.

Author Contributions: Conceptualization, S.H.W. and J.H.K.; formal analysis, S.H.W.; funding acquisition, S.-W.B., H.K. and W.C.; investigation, S.H.W., K.E.S., S.-W.B., H.K., W.C., T.H.S., J.-Y.P. and J.H.K.; project administration, J.H.K.; supervision, J.H.K.; writing—original draft, S.H.W., K.E.S., S.-W.B., H.K., W.C., T.H.S. and J.-Y.P.; writing—review and editing, S.H.W. and K.E.S. All authors have read and agreed to the published version of the manuscript.

Funding: The Korean government (MSIT) (No. 2019R1A2C1087534) and the research fund of Hanbat National University in 2019.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2019R1A2C1087534) and the research fund of Hanbat National University in 2019.

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

References

- 1. O'Hayre, R.; Cha, S.W.; Collella, W.; Prinz, F.B. Fuel Cell Fundamentals, 3rd ed.; Wiley: Hoboken, NJ, USA, 2006.
- Andersson, M.; Yuan, J.; Sunden, B. SOFC modeling considering hydrogen and carbon monoxide as electrochemical reactants. J. Power Sources 2013, 232, 42–54. [CrossRef]
- 3. Koide, H.; Someya, Y.; Yoshida, T.; Maruyama, T. Properties of Ni/YSZ cermet as anode for SOFC. *Solid State Ion.* 2000, 132, 253–260. [CrossRef]
- Jin, S.B.; Kim, K.S.; Baek, S.W.; Kim, H.S.; Kang, H.I.; Choi, W.S.; Kim, J.H. Characterization of Layered Perovskite Nanofibers using Electrospinning for Cathode Materials of Low Temperature-operating Solid Oxide Fuel Cell. *New. Renew. Energy* 2017, 13, 50–58. [CrossRef]
- Frontera, C.; Garcia-Munoz, J.L.; Llobet, A.; Manosa, L.; Aranda, M.A.G. Selective spin-state and metal-insulator transitions in GdBaCo₂O_{5.5}. J. Solid State Chem. 2003, 171, 349–352. [CrossRef]
- 6. Kim, G.; Wang, S.; Jacobson, A.J.; Reimus, L.; Brodersen, P.; Mims, C.A. Rapid oxygen ion diffusion and surface exchange kinetics in PrBaCo₂O_{5+x} with a perovskite related structure and ordered A cations. *J. Mater. Chem.* **2007**, *17*, 2500–2505. [CrossRef]
- Kim, J.H.; Cassidy, M.; Irvine, J.T.S.; Bea, J.M. Advanced Electrochemical Properties of LnBa_{0.5}Sr_{0.5}Co₂O_{5+d} (Ln = Pr, Sm, and Gd) as Cathode Materials for IT-SOFC. *J. Electrochem. Soc.* 2009, 156, B682–B689. [CrossRef]
- 8. Kim, J.H.; Cassidy, M.; Irvine, J.T.S.; Bea, J.M. Electrochemical investigation of composite cathodes with SmBa_{0.5}Sr_{0.5}Co₂O_{5+d} cathodes for intermediate temperature-operating solid oxide fuel cell. *Chem. Mater.* **2010**, *22*, 883–892. [CrossRef]
- Irvine, J.T.S.; Bea, J.M.; Park, J.Y.; Choi, W.S.; Kim, J.H. Electrochemical properties and durability of in-situ composite cathodes with SmBa_{0.5}Sr_{0.5}Co₂O_{5+δ} for metal supported solid oxide fuel cells. *Int. J. Hydrogen Energy* 2017, 42, 1212–1220. [CrossRef]
- Song, S.W.; Choi, W.S.; Kang, H.; Baek, S.W.; Azad, A.K.; Park, J.Y.; Kim, J.H. Synthesis and electrochemical properties of layered perovskite substituted with heterogeneous lanthanides for intermediate temperature-operating solid oxide fuel cell. *Int. J. Hydrogen Energy* 2018, 43, 11378–11385. [CrossRef]
- Kim, J.H.; Kim, Y.M.; Connor, P.A.; Irvine, J.Y.S.; Bae, J.M. Structural, thermal and electrochemical properties of layered perovskite SmBaCo₂O_{5+d}, a potential cathode material for intermediate-temperature solid oxide fuel cells. *J. Power Sources* 2009, 194, 704–711. [CrossRef]
- Xia, L.N.; He, Z.P.; Huang, Z.W.; Yu, Y. Synthesis and properties of SmBaCo_{2-x}Ni_xO_{5+δ} perovskite oxide for IT-SOFC cathodes. *Ceram. Int.* 2016, 42, 1272–1280. [CrossRef]
- Aksenova, T.V.; Gavrilova, L.Y.; Yaremchenko, A.A.; Cherepanov, V.A.; Kharton, V.V. Oxygen nonstoichiometry, thermal expansion and high-temperature electrical properties of layered NdBaCo₂O_{5+d} and SmBaCo₂O_{5+d}. *Mater. Res. Bull.* 2010, 45, 1288–1292. [CrossRef]
- 14. Marrero-Jerez, J.; Pena-Martinez, J.; Nunez, P. Study of the oxygen desorption from $GdBa_{1-x}Sr_xCo_2O_{5+\delta}$ (x = 0, 0.25, 0.5 and 1): Effect of the Sr-content on the oxidation state of cobalt ions. *J. Alloys Compd.* **2014**, *606*, 269–272. [CrossRef]
- 15. Chavez, E.; Mueller, M.; Mogni, L.; Caneiro, A. Study of LnBaCo₂O_{6-δ} (Ln = Pr, Nd, Sm and Gd) double perovskites as new cathode material for IT-SOFC. *J. Phys. Conf. Ser.* **2009**, *167*, 012043. [CrossRef]
- Kim, J.Y.; Choi, S.H.; Park, S.H.; Kim, C.M.; Shin, J.Y.; Kim, G.T. Effect of Mn on the electrochemical properties of a layered perovskite NdBa_{0.5}Sr_{0.5}Co_{2-x}Mn_xO_{5+δ} (x = 0, 0.25, and 0.5) for intermediate-temperature solid oxide fuel cells. *Electrochim. Acta* **2013**, *112*, 712–718. [CrossRef]
- 17. Subardi, A.; Liao, K.Y.; Fua, Y.P. Oxygen transport, thermal and electrochemical properties of NdBa_{0.5}Sr_{0.5}Co₂O_{5+δ} cathode for SOFCs. *J. Eur. Ceram. Soc.* **2019**, *39*, 30–40. [CrossRef]
- 18. Ding, H.; Xue, X. PrBa_{0.5}Sr_{0.5}Co₂O_{5+d} layered peroyskite cathode for intermediate temperature solid oxide fuel cells. *Electrochim. Acta* **2010**, *55*, 3812–3816. [CrossRef]
- 19. Lu, S.; Long, G.; Meng, X.; Ji, Y.; Lu, B.; Zhao, H. PrBa_{0.5}Sr_{0.5}Co₂O_{5+x} as cathode material based on LSGM and GDC electrolyte for intermediate-temperature solid oxide fuel cells. *Int. J. Hydrogen Energy* **2012**, *37*, 5914–5919. [CrossRef]
- 20. Kim, Y.M.; Schlegl, H.; Kim, K.S.; Irvine, J.T.S.; Kim, J.H. X-ray photoelectron spectroscopy of Sm-doped layered perovskite for intermediate temperature-operating solid oxide fuel cell. *Appl. Surf. Sci.* **2018**, *288*, 695–701. [CrossRef]
- 21. Huang, K.; Lee, H.Y.; Goodenough, J.B. Sr- and Ni- Doped LaCoO₃ and LaFeO₃ Perovskites: New Cathode Materials for Solid-Oxide Fuel Cells. *J. Electrochem. Soc.* **1998**, 145, 3220–3227. [CrossRef]
- Joung, Y.H.; Kang, H.I.; Choi, W.S.; Kim, J.H. Investigation of X-ray photoelectron spectroscopy and electrical conductivity properties of the layered perovskite LnBaCo₂O_{5+d} (Ln = Pr, Nd, Sm, and Gd) for IT-SOFC. *Electron. Mater. Lett.* 2013, *9*, 463–465. [CrossRef]
- 23. Azad, A.K.; Kim, J.H.; Irvine, J.T.S. Structural, electrochemical and magnetic characterization of the layered-type PrBa_{0.5}Sr_{0.5}Co₂O_{5+δ} perovskite. *J. Solid State Chem.* **2014**, 213, 268–274. [CrossRef]
- Yao, C.; Zhang, H.; Liu, X.; Meng, J.; Zhang, X.; Meng, F.; Meng, J. Investigation of layered perovskite NdBa_{0.5}Sr_{0.25}Ca_{0.25}Ca_{0.25}Co₂O_{5+δ} as cathode for solid oxide fuel cells. *Ceram. Int.* 2018, 44, 12048–12054. [CrossRef]
- Galenda, A.; Natile, M.M.; Krishnan, V.; Bertagnolli, H.; Glisenti, A. LaSrCoFeO and Fe₂O₃/LaSrCoFeO Powders: Synthesis and Characterization. *Chem. Mater.* 2007, 19, 2796–2808. [CrossRef]
- 26. Ivanovskaya, M.I.; Kotikov, D.A.; Pan'kov, V.V.; Zyryanov, V.V. Structure of SrCo_{0.5}Fe_{0.5}O_{3 δ}-based composites prepared by sol-gel and mechanochemical processes. *Inorg. Mater.* **2009**, *45*, 910–915. [CrossRef]

- 27. Tan, B.J.; Klabunde, K.J.; Sherwood, P.M. XPS studies of solvated metal atom dispersed (SMAD) catalysts. Evidence for layered cobalt-manganese particles on alumina and silica. *J. Am. Chem. Soc.* **1991**, *113*, 855–861. [CrossRef]
- 28. Nitadori, T.; Muramatsu, M.; Misono, M. Valence control, reactivity of oxygen, and catalytic activity of lanthanum strontium cobalt oxide (La_{2-x}Sr_xCoO₄). *Chem. Mater.* **1989**, *1*, 215–220. [CrossRef]
- Merino, N.A.; Barbero, B.P.; Eloy, P.; Cadus, L.E. La_{1-x}Ca_xCoO₃ perovskite-type oxides: Identification of the surface oxygen species by XPS. *Appl. Surf. Sci.* 2006, 253, 1489–1493. [CrossRef]
- 30. Noboru, Y.; Yasutake, T.; Tetsuro, S. TPD and XPS study on thermal behavior of absorbed oxygen in La_{1-x}Sr_xCoO₃. *Chem. Lett.* **1981**, *10*, 1767–1770.
- Yi, K.; Sun, L.; Li, Q.; Xia, T.; Huo, L.; Zha, H.; Li, J.; Lü, Z.; Bassat, J.M.; Rougier, A.; et al. Effect of Nd-deficiency on electrochemical properties of NdBaCo₂O_{6-δ} cathode for intermediate-temperature solid oxide fuel cells. *Int. J. Hydrogen Energy* **2016**, *41*, 10228–10238. [CrossRef]