Structural and Oxygen-Transport Studies of Double Perovskites $PrBa_{1-x}Co_2O_{5+\delta}$ (x = 0, 0.05, 0.1) Toward Their Application as Superior Oxygen Reduction Electrodes

Feifei Dong[1,2], Meng Ni[2], Moses O Tade[3], Zongping Shao*[,1,3]

[1]*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu 210009, P. R. China*

[2]*Department of Building and Real Estate, The Hong Kong Polytechnic University, Hong Kong, P. R. China*

[3]*Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia*

Abstract

Here we present a comprehensive study of oxygen-deficient double perovskites $PrBa_{1-x}Co_2O_{5+\delta}$ (x = 0.00, 0.05, 0.10) to exploit their potential use as cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Special attention is paid to the structure, oxygen concentration and oxygen-ion transport properties, which are key factors related to the electrochemical performance. Based on results obtained from a series of high-resolution structural analysis techniques, such as XRD, SAED, and HR-TEM, these double perovskite oxides possess tetragonal lattice symmetry and a stable crystal structure. According to the information obtained from iodometric titration, TGA, and O_2-TPD measurements, an increase in oxygen vacancy concentration in the lattice with an increasing Ba cation deficiency (x value) is demonstrated. Additionally, oxygen permeation flux and electrical conductivity relaxation (ECR) measurements illustrate an improved oxygen ionic conductivity, chemical bulk diffusion coefficient (D_{chem}) and chemical surface exchange coefficient (K_{chem}) with the introduction of Ba deficiency, likely due to the increase in the concentration of oxygen vacancies. Tests at 700 °C of the electrochemical performance based on symmetrical cells show area specific resistances (ASRs) of 0.046, 0.042, and 0.038 Ω cm^2 for $PrBa_{1-x}Co_2O_{5+\delta}$ with x = 0.00, 0.05, and 0.10, respectively. These results are extremely promising; consequently, these oxides are worthy of further study and optimization as cathode materials for IT-SOFCs.

Keywords: double perovskite, $PrBaCo_2O_{5+\delta}$, cathode, oxygen reduction electrode, cation.

Introduction

Fuel cells, electrochemical energy-conversion devices that are typically composed of a porous cathode and anode with a dense electrolyte, have been considered as one of the most important power generation technologies of the near future. The most advantageous feature of fuel cells is the direct conversion of chemical energy in fuels to electric power at higher efficiency and with a lower environmental impact than conventional power plants. Among all types of fuel cells, solid oxide fuel cells (SOFCs) show additional advantages, such as excellent fuel flexibility, high-quality exhaust heat, and electrode materials composed of non-precious metals [1]. Lowering the operating temperature to an intermediate range (500-800 °C) can significantly mitigate the degradation rate of SOFC components, broaden the material choices and reduce the system costs [2]. However, reducing operating temperature often results in a remarkable decrease in the overall electrochemical performance, specifically the activity of the cathode for the oxygen reduction reaction (ORR) due to the large associated activation energy [3]. Accordingly, extensive efforts have been devoted to developing cathode materials with superior electrocatalytic activity and long-term durability at reduced temperatures [4-9].

The mixed conductivity of an electrode may extend the active sites for ORR from a conventional cathode-electrolyte-air triple phase boundary (TPB) region to the entire cathode surface, thus considerably improving electrode activity. Over the past decade, many mixed ionic-electronic conductors (MIECs) have been exploited as effective cathode materials for intermediate-temperature

SOFCs (IT-SOFCs). Among them, cobalt-containing perovskite oxides, including $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) [10], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [11], and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [12], have been extensively investigated. Recently, cobalt-containing oxides such as $LnBaCo_2O_{5+\delta}$ (Ln = lanthanide element) with a cation-ordered double perovskite structure have also received tremendous attention as a new family of MIEC oxides [13-17]. This family of compound structures can be described as a layered composite oxide with a stacking sequence of …$[LnO_\delta][CoO_2][BaO][CoO_2]$… along the c-axis [18]. The presence of a cation-ordered structure could effectively enhance oxygen transport properties compared to $Ln_{0.5}Ba_{0.5}CoO_{3-\delta}$ materials with the same nominal composition but containing a cation-disordered perovskite structure [19]. All oxygen vacancies in the cation-ordered $LnBaCo_2O_{5+\delta}$ are confined only to the $[LnO_\delta]$ plane forming channels along the a-axis. The particular distribution and high concentration of oxygen vacancies in these perovskites could dramatically improve the bulk diffusivity of oxygen ions, and supply surface defect sites with enhanced reactivity towards molecular oxygen. Furthermore, these double perovskite oxides have a wide range of oxygen nonstoichiometry and demonstrate attractive structural and electrocatalytic properties dependent on the oxygen concentration.

Among the various $LnBaCo_2O_{5+\delta}$ oxides, $PrBaCo_2O_{5+\delta}$ (PBCO) has received particular attention because of its fast oxygen bulk diffusion and surface exchange kinetics. Kim et al. demonstrated that the bulk diffusion coefficient and surface exchange coefficient for PBCO could be 2-3 orders of magnitude higher than those for $GdBaCo_2O_{5+\delta}$ (GBCO) at intermediate temperatures [20]. This implies that PBCO may perform well as a cathode material for IT-SOFCs. Indeed, a maximum power density as high as 620 mW cm^{-2} and an interfacial polarization resistance as low as 0.40 Ω cm^2 were achieved at 600 °C with a PBCO cathode and a samarium-doped ceria electrolyte [21]. Multiple efforts have been taken to ameliorate the structural and electrochemical properties of PBCO, such as A- and/or B-site doping [22], formation of a composite electrode with an ion-conducting electrolyte [23], preparation of a nano-structured or thin-film electrode [24], and so on. Some researchers have observed that introducing A-site cation deficiencies into the lattice structure of perovskite oxides could substantially affect the physicochemical properties of cathode materials [25-31]. For instance, Kharton et al. observed that the oxygen ionic conductivity of $Sr_{0.97}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ oxide increased when a deficiency was created in the A sublattice [25]. It was reported by Zhu et al. that A-site deficiency in $SrNb_{0.1}Co_{0.9}O_{3-\delta}$ could result in an increase in electrical conductivity [26]. Zhou et al. suggested that an increasing x value in $(Ba_{0.5}Sr_{0.5})_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ would give rise to a decrease in both electronic conductivity and thermal expansion coefficient [27]. In the A-site deficient perovskites, the charge compensation mechanism could be interpreted by the formation of oxygen vacancies and/or the oxidation of B-site cations. It is expected that additional oxygen vacancies are favorable to the oxygen bulk diffusion and surface exchange properties, and thereby to the electrocatalytic activity toward ORR. The superior electrochemical performance and operational stability of $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ was reported by Wang et al., who found that the polarization resistance and maximum power density at 650 °C were 0.029 Ω cm^2 and 955 mW cm^{-2}, respectively [28]. The primary results reported by Hansen et al. also indicated that A-site cation deficient perovskite $(Pr_{0.6}Sr_{0.4})_{0.95}Fe_{0.8}Co_{0.2}O_{3-\delta}$ exhibited a relatively low area specific resistance (ASR) value of 0.20 Ω cm^2 on a $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte at 700 °C [29].

A few studies on A-site deficient PBCO have primarily focused on the effect of A-site deficiency upon the electrochemical performance [30, 31]. However, minimal effort has been invested on achieving a thorough understanding of fundamental properties such as structure, oxygen content and transport properties of cation-deficient PBCO double perovskites. To the best of our knowledge, the effects of oxygen vacancy concentration and oxygen transportation on $PrBa_{1-x}Co_2O_{5+\delta}$ ($PB_{1-x}CO$) have not been discussed in the literature. These properties could provide, however, critical information in determining the suitability of electrodes prior to conducting tests in practical fuel cells.

In the present work, A-site barium-deficient PBCO double perovskite oxides with the composition of $PrBa_{1-x}Co_2O_{5+\delta}$ ($PB_{1-x}CO$, x = 0.00, 0.05, 0.10) were synthesized and systematically characterized, with main attention being focused on the phase structure, structural stability, oxygen vacancy concentration, electronic and ionic conductivity, and oxygen bulk diffusion and surface exchange. Symmetrical cell performance was also performed to further validate the potential of A-site Ba-deficient $PB_{1-x}CO$ oxides as cathode materials for IT-SOFCs.

Experimental

Materials Synthesis

$PrBa_{1-x}Co_2O_{5+\delta}$ ($PB_{1-x}CO$, x = 0.00, 0.05, 0.10) oxide powders were synthesized by a combined EDTA-citrate complexing sol-gel process, as detailed elsewhere [21]. Metal nitrates were used as the raw materials for the cation sources, and a combination of EDTA and citric acid was employed to assist in the complexing process. The as-obtained precursors were then calcined in stagnant air at 1050 °C for 10 h to acquire the desired perovskite phase.

Material Characterizations

The experimental products were characterized by powder X-ray diffraction (XRD) for phase identification on a Bruker D8 Advance diffractometer with filtered Cu-Kα radiation at 40 kV and 40 mA. The experimental diffraction patterns were collected at room temperature in a step-scan mode within the 2θ range of 20-80 ° at 0.05 ° per step. Crystal structure analysis was resolved via Rietveld refinements on the XRD patterns, employing the General Structure Analysis System (GSAS) software. Transmission electron microscopy (TEM) in conjunction with selected area electron diffraction (SAED) was conducted with a JEOL JEM-2100 field-emission instrument to examine the crystal structure of powdered samples. Specimens for TEM analysis were prepared by ultrasonically dispersing the powdered samples in ethanol and then applying several drops of the suspension onto a copper grid covered with a holey carbon film.

Iodometric titration was applied to chemically assess the initial average valence of the cobalt and oxygen content of the obtained $PB_{1-x}CO$ powders. Approximately 0.1 g of the powdered sample was accurately weighed and dissolved in ~20 mL of an aqueous HCl solution (~6 mol L^{-1}) together with ~3 g of KI powder. The I_2 liberated in the chemical reaction was then titrated with a standard thiosulfate $Na_2S_2O_3$ solution (~0.02 mol L^{-1}) using ~3 mL of starch solution as indicator. The average valence of the cobalt could be calculated based on the amount of $S_2O_3^{2-}$ consumed and the amount of oxide powder applied. The evolution of the weight (namely, oxygen concentration) of $PB_{1-x}CO$ samples was determined by thermal gravimetric analysis (TGA) with a Netzsch, STA 449 F3 instrument. Measurements were carried out under different atmospheres with a flow rate of 50 mL min^{-1}, within a temperature range from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}. The oxygen desorption properties of the powders were evaluated by oxygen temperature-programmed desorption (O_2-TPD) technique. Approximately 0.15 g of granular sample was loaded into a U-type quartz reactor, which was purged with argon at a flow rate of 15 mL min^{-1} at room temperature until the in situ monitored oxygen concentration achieved a relatively steady state. Afterward, a linear temperature program was used to ramp from room temperature to 930 °C at a rate of 10 °C min^{-1}. The molecular oxygen released from the oxide lattice was transported out by the flowing argon gas and monitored using an on-line mass spectrometer (Hiden QIC-20).

The transport properties of $PB_{1-x}CO$ specimens, including the electrical conductivity, chemical diffusion coefficient (D_{chem}) and chemical surface exchange coefficient (K_{chem}), were determined by the standard four-probe DC method on bar-shaped samples, which were previously processed to obtain a dense object in order to restrict the grain boundary contribution to the measurement. Silver paste (DAD-87, Shanghai, China) was painted onto the two rectangular cross-sectional edges and two circumferential surfaces of the bars to form the current and voltage electrodes, and four silver wires were attached to the electrodes as the lead wires. For the electrical conductivity measurement, the experimental temperature was performed over the range from 300 to 900 °C. At each temperature point, a cumulative current load was applied to the two current wires, and the corresponding voltage response on the two voltage wires was recorded with a Keithley 2420 source meter. Electrical conductivity values were then calculated from the slope of the obtained straight line. As for the determination of D_{chem} and K_{chem}, electrical conductivity relaxation (ECR) was conducted between 550 and 750 °C at an interval of 50 °C. The bars were first stabilized at the given temperatures for approximately 1 h to ensure that they completely equilibrated with the surrounding atmosphere (P_{O2} = 0.21 atm), which was then abruptly switched to an alternate atmosphere (P_{O2} = 0.1 atm), thereby leading to a change in electrical conductivity. The change in conductivity with time was plotted as $[\sigma(t)-\sigma(0)]/[\sigma(\infty)-\sigma(0)]$ and fitted to the solution of Fick's second law to obtain D_{chem} and K_{chem} under appropriate initial and boundary conditions as outlined in a previous study [32]. Oxygen permeation flux measurements were performed on a sintered membrane disk, which was polished to 1 mm thickness and sealed onto an alumina tube using silver paste. The operation was carried out over a temperature range of 700-900 °C by exposing the feed side of the sealed membrane to ambient air and the sweep side to pure helium. The composition of the effluent helium stream was analyzed by a Varian CP-3800 gas chromatograph equipped with a 5 Å molecular sieve capillary column. The ionic conductivity could be estimated using the Wagner relation based on the measured oxygen permeation flux.

Fabrication and Testing of Symmetrical Cells

Symmetrical cells with the configuration of $PB_{1-x}CO|Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)|$PB_{1-x}CO$ were prepared for electrochemical characterization. The as-prepared SDC powders were uniaxially pressed into disk-shaped pellets, followed by sintering at 1400 °C for 5 h in air to form dense electrolyte substrates. The $PB_{1-x}CO$ colloidal suspensions for spray deposition were mechanically mixed with organic additives (isopropyl alcohol, ethylene glycol and glycerol) through ball milling. The slurry was then symmetrically sprayed onto both sides of the SDC pellets and the resulting assemblies were subsequently fired at 1000 °C for 2 h in air to acquire symmetrical cells.

Electrochemical impedance spectroscopy (EIS) measurements of the obtained symmetrical cells were performed as a function of temperature between 550 and 750 °C at an increment of 50 °C in ambient air. AC impedance characteristics were recorded using a Solartron 1260A frequency response analyzer in combination with a Solartron 1287 potentiostat over a frequency range from 1 MHz to 0.01 Hz with a signal amplitude of 10 mV at open circuit voltage.

Results and Discussion

Phase Structure

Figure 1 shows the room temperature XRD patterns of the $PrBa_{1-x}Co_2O_{5+\delta}$ ($PB_{1-x}CO$, x = 0.00, 0.05, 0.10) series calcined at 1050 °C for 10 h under an air atmosphere. It can be seen that the as-prepared powders are well-crystallized, implying the sol-gel process is very effective in fabricating the layered structured perovskite oxides. **Figure 2** gives the Rietveld refinement data of $PB_{1-x}CO$ powders. The diffraction pattern of $PB_{1-x}CO$ samples were indexed using a tetragonal $\sim a_p \times a_p \times 2a_p$ sub-cell characteristic of the "112" structure (a_p being the cell parameter of cubic perovskite) in the P4/mmm space group. The reflected tetragonal structure in this study is somewhat different from the orthorhombic one as detailed elsewhere [31]. The structural disagreement primarily originates from the different oxygen content in the perovskite lattice since the crystal structure of $LnBaCo_2O_{5+\delta}$ depends strongly upon the oxygen nonstoichiometry, while synthesis conditions can have a significant effect on the oxygen content of oxides [33].

The refined lattice parameters and the obtained reliability factors of the refinements are listed in **Table 1**. The low reliability factors indicate an excellent agreement between the experimental data and the calculated profiles, suggesting that the cations are well-ordered between Pr^{3+} and Ba^{2+} ions in the layered perovskite lattice. The lattice parameters of $PB_{1-x}CO$ samples increased slightly with increasing Ba deficiency. Ba deficiency should cause structural shrinkage in the perovskite lattice, while the generation of more oxygen vacancies induced by Ba deficiency would result in lattice expansion. The resulting slightly increased lattice parameters may be ascribed to the dominating effect caused by the generation of oxygen vacancies.

The crystal structure of the $PB_{1-x}CO$ samples was further confirmed by TEM characterization. As an example, **Figure 3** demonstrates the SAED and high-resolution TEM (HR-TEM) images for the illustrated microstructure of $PB_{0.9}CO$. **Figure 3a** is a typical bright-field TEM image taken along the [010] zone axis, as confirmed by its corresponding SAED patterns. The corresponding HR-TEM image (**Figure 3b**) demonstrates the presence of crystalline fringes, corresponding to the (102) plane of the double perovskite structure, with a lattice fringes spacing of d_{102} = 0.263 nm, which is in accordance with the XRD results (d_{102} = 0.269 nm).

Structural Stability

The structural stability of the $PB_{1-x}CO$ samples was assessed by annealing the oxides at 700 °C for 400 h under an air atmosphere. The as-obtained samples were then examined by means of XRD analysis.

As shown in **Figure 4a**, after treatment the samples still maintained the favorable double perovskite lattice structure, characterized by an inconspicuous change in the position and shape of the diffraction peaks in the XRD patterns.

Taking cation stoichiometric PBCO oxide as an example, the phase structure was further characterized using Rietveld refinement, TEM observation and EIS measurement. Rietveld refinement fitting results, depicted in **Figure 4b**, revealed that the treated PBCO sample also presented a tetragonal structure (space group P4/mmm), which converged to the lattice parameters of a = 3.90(2) Å and c = 7.61(7) Å with the reliability factors of R_{wp} = 5.24 %, R_p = 4.18 %, and χ^2 = 1.139. By comparison, there was no significant change in the phase structure and space group of the sample after prolonged high-temperature calcination, except for a slight increase in the lattice parameters. The typical low-magnification TEM and corresponding HR-TEM images of the fresh powder and the treated one, through the long-playing calcination, are shown in **Figure 5**. The analogous TEM images and SAED patterns of the two investigated samples are displayed in **Figure 5a&c**. The characteristic (102) crystal plane corresponding to the most intense diffraction peak at the position of 2θ = 32.8 ° is also labeled in the SAED patterns. The electron diffraction spots in **Figure 5c** are not completely centrosymmetric. This is probably due to the uneven thickness of the sample caused by the preparation of specimens for TEM analysis; consequently, the intensity of the diffraction spots in the crystalline fringes could suffer. Analogous lattice spacing (d = ~0.26 nm) in the two different regions of crystalline fringes is observed in **Figure 5b&d**, which comes near to that of the (102) plane in the double perovskite structure with a tetragonal crystal system. On the basis of the above results, the crystal structure illustrates a remarkable stability when exposed to high temperatures for prolonged periods, embodied in the scarcely any changes observed in the microstructure after annealing at 700 °C for 400 h in air, in stark contrast to the simple perovskite cathode materials (e.g., BSCF or LSCF [34, 35]). To make further confirmation on the structural stability of the crystal lattice, symmetric cells were fabricated by applying the fresh and treated powders as cathodes. As shown in **Figure 6**, the ASR value (0.167 Ω cm^2) derived from the typical impedance spectra for the treated sample is slightly larger than the value (0.153 Ω cm^2) of the fresh one at 750 °C. The ASR results with respect to the temperature exhibit nearly identical activation energies (Ea), indicating the analogous nature of the electrode reaction mechanism and the unchanged electrode reaction process after prolonged high-temperature treatment. The results above clearly demonstrate that the synthesized oxides possess a stable double perovskite structure with a tetragonal crystal system, which is a desirable property for long-term durability.

Oxygen Content

As previously stated, the crystal structures of $LnBaCo_2O_{5+\delta}$ oxides rely on and are sensitive to the oxygen content. For the layered $LnBaCo_2O_{5+\delta}$ perovskite, a low concentration of oxygen vacancies normally gives rise to formation of the orthorhombic structure, whereas a high concentration of oxygen vacancies results in generation of the tetragonal structure [36]. A case in point is $YBaCo_2O_{5+\delta}$ [37], which presented an orthorhombic structure at $\delta \geq 0.50$ while maintaining a tetragonal structure at $0.25 \leq \delta \leq 0.44$. Hence, a high oxygen vacancy concentration in the crystal lattice may be a reasonable explanation for the resulting tetragonal phase of $PB_{1-x}CO$ oxides.

The iodometric titration technique was employed to examine the oxygen content of $PB_{1-x}CO$ oxides at room temperature, which were found to be 5.795, 5.761, and 5.685 (a decreasing trend) for samples with x = 0.00, 0.05, and 0.10, respectively, as also listed in **Table 2**. As expected, the introduction of Ba deficiency into double perovskites contributed to an increase in the concentration of oxygen vacancies, which is beneficial to enhancing the electrochemical activity toward ORR, since the oxygen vacancies supply active sites for oxygen adsorption, dissociation and diffusion on the surface of the cathode, as well as passages for oxygen-ion transporting inside the bulk of the cathode. **Figure 7a** depicts the variation in oxygen content with temperature in air for the $PB_{1-x}CO$ samples. The plots were derived by combining the initial oxygen content determined using the iodometric titration and TGA results (**Figure 7a** inset). A slight weight gain for the $PB_{1-x}CO$ samples from ~200 to ~300 °C indicates that the samples may be oxidized by the flowing air over this temperature range. It can be appreciated that the enlargement of δ evidences the absorption and diffusion of oxygen in PrO_δ planes at relatively low temperatures. A similar phenomenon was also observed in a previous study [38]. All of the $PB_{1-x}CO$ samples started to lose weight at temperatures above ~300 °C due to the thermal-driven release of interstitial oxygen from the lattice, accompanied by the reduction of Co ions. The $PB_{0.9}CO$ sample lost 0.386 oxygen atoms per formula upon heating to 1000 °C. The oxygen content value in the Ba-site deficient oxides (e.g., $PB_{0.9}CO$) decreased from 5.607 to 5.502 over a rise in temperature from 550 to 750 °C, whereas the corresponding one in the Ba-site stoichiometric oxide (PBCO) changed from 5.672 to 5.548 over the same temperature range. A set of measurements on the weight change of the selected $PB_{0.9}CO$ sample under atmospheres of oxygen, air or argon are plotted in **Figure 7b**. It can be seen that a pronounced oxygen gain occurs from approximately 200-300 °C under an oxygen atmosphere, whereas the characteristic of oxygen gain almost vanishes completely within the corresponding temperature range in argon due to the low oxygen partial pressure and lack of oxygen. Additionally, weight losses of 1.16, 1.30, and 2.09 % were observed from room temperature to 1000 °C under atmospheres of oxygen, air, and argon, respectively, which also favors the viewpoint of a small oxygen loss under oxygen-enriched atmospheres and a correspondingly large oxygen loss under oxygen-lean conditions.

The O_2-TPD technique was adopted to further evaluate the thermal behavior and interactions of oxygen in the oxides. The O_2-TPD profiles, measured for $PB_{1-x}CO$ oxides with varying Ba deficiency, are shown in **Figure 8**. It is worth noting that two types of oxygen desorption (denoted α and β) were discerned with the programmed increase in temperature. The α desorption, appearing at an onset temperature of approximately 300 °C, is ascribed to the oxygen vacancies formed, in which α oxygen is related to the formation of Co^{4+} ions or positive holes. The desorption of α oxygen may be expressed as $O_O^{\times} + 2h^{\bullet} \rightarrow V_O^{\bullet\bullet} + 1/2O_2$. On the other hand, the β desorption, occurring at a commencement temperature of approximately 800 °C, is accompanied by the reduction of Co ions to a lower valence state, described as $O_O^{\times} + 2Co_{Co}^{\times} \rightarrow V_O^{\bullet\bullet} + 2Co_{Co}^{'} + 1/2O_2$. The α desorption peaks are similar for all $PB_{1-x}CO$ samples, suggesting that α desorption is more specific to the Ba deficiency than β desorption. In contrast, a larger quantity of β oxygen was desorbed with increasing Ba deficiency, especially in the $PB_{0.9}CO$ oxide. A similar trend was also observed in A-site deficient BSCF and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) [39, 40]. Increasing the Ba deficiency was believed to contribute to the formation of more oxygen vacancies in the lattice. Moreover, according to the previous research [41], it was identified that the more exothermic reduction of Co ions could bring about a decline in the vacancy formation energy, which would make for the ease of oxygen bulk diffusion. These results are in turn of benefit to the ORR.

Transport Properties

An appropriate range in electrical conductivity is of importance for the practical application of cathode materials. Results on the variation in electrical conductivity of $PB_{1-x}CO$ samples with respect to temperature are displayed in **Figure 9**. The electrical conductivity of all samples initially almost maintains a plateau with temperature up to a transition temperature at approximately 450 °C, and then linearly decreases afterward, exhibiting a metallic nature. Similar behavior was also reported in a case study on the $NdBaCo_{1.6}Ni_{0.4}O_{5+\delta}$ double perovskite [42]. The electron hole conduction in cobalt compounds, including metallic conduction, originates from the presence of Co^{4+} ions and thermally generated charge disproportion where $2Co^{3+}$ transform into Co^{2+} and Co^{4+}. The decrease in electrical conductivity above a certain characteristic temperature could be mainly due to the creation of oxygen vacancies induced by the loss of oxygen from the lattice structure coupled with the reduction of Co ions, which is in well agreement with the observed TGA and O_2-TPD results. It can be noted that the generation of oxygen vacancies not only perturbs the Co-O-Co periodic potential resulting in introducing the carrier localization, but also alters the other defect concentrations leading to decreasing the charge carrier concentration.

As is evident in **Figure 9**, the electrical conductivities of $PB_{1-x}CO$ oxides demonstrate an initial increase with Ba deficiency (from x = 0 to 0.05) and then a decreasing trend when keeping raising x value. On the basis of the principle of charge balance, the negative charges introduced by Ba deficiency should be compensated through either one or both of the following two aspects: (1) ionic compensation by the formation of oxygen vacancies [43]; (2) electronic compensation by the generation of Co ions with high oxidation states (e.g., +4) [44], which works in the opposite direction for the electrical conductivity. A higher conductivity was obtained for $PB_{0.95}CO$ in contrast to PBCO, indicating the predominant role of the oxidation of Co ions, which may be evidenced by the higher valence state of Co ions based on the iodometric titration results. However, the higher Ba deficiency ($PB_{0.9}CO$) leading to a decreasing trend in conductivity suggests that the dominant effect is the formation of oxygen vacancies, which may be validated by the much higher concentration of oxygen vacancies in the $PB_{0.9}CO$ lattice structure.

Overall, favorable electrical conductivity (> 400 S cm^{-1} over the investigated temperature range) originating from the relatively high symmetry and layered structure of the $PB_{1-x}CO$ oxides is achieved, which is sufficiently acceptable for applications as IT-SOFC cathodes [45]. Furthermore, the relatively small difference in electrical conductivity (being sufficiently high) among the $PB_{1-x}CO$ oxides may play a less effect on the electrochemical performance.

Additionally, taking into account its important factor, the oxygen ionic conductivity was also determined by oxygen permeability measurements. The oxygen permeation flux [$J(O_2)$] through the membrane was calculated using the following equation:

$$J_{O_2}(mL \cdot cm^{-2} \cdot \min^{-1}, [STP]) = (C_O - \frac{0.21}{0.79} \cdot C_N \cdot \sqrt{\frac{28}{32}}) \cdot \frac{Q}{S}$$

where C_O and C_N are the measured gas-phase concentrations of oxygen and nitrogen in the penetrative stream, respectively; Q is the flow rate (mL min^{-1}) of the penetrative stream and S is the effective surface area (cm^2) of the disk exposed to the sweeping gas. For MIEC ceramic membranes, assuming that the bulk diffusion of oxygen ions is the rate-limiting step in 1 mm thick disk and the electronic conductivity is overwhelmingly higher than the ionic conductivity, the average ionic conductivity can be expressed by the Wagner relation as follows [46]:

$$\sigma_i = J_{O_2} \frac{16F^2L}{RT} \left(\ln \frac{p_h}{p_l} \right)^{-1}$$

where R is the gas constant, T is the absolute temperature, F is Faraday's constant, L is the membrane thickness, p_h and p_l are the equivalent oxygen partial pressures at the feed side and sweep side, respectively. The temperature dependence of nominal ionic conductivity for the $PB_{1-x}CO$ oxides is plotted in **Figure 10**. The average ionic conductivities are 0.118, 0.142, and 0.162 S cm^{-1} at 900 °C for x = 0.00, 0.05, and 0.10, respectively. The values of cation-stoichiometric PBCO are comparable to those reported by Zhang et al. [14]. Increasing Ba deficiency from x = 0.00 to 0.10 resulted in an increase in the oxygen ionic conductivity. This effect might be related to the increase in oxygen vacancies through which the ionic diffusion takes place. This is also supported by the relationship between the oxygen ionic conductivity and oxygen vacancy concentration expressed by the Einstein relation in the following manner: $\sigma_i \infty C_V$, where Cv is the concentration of oxygen vacancies. The favorable oxygen ionic conductivity may be in turn beneficial for the chemical diffusion and surface exchange properties.

In addition to the electrical conductivity, the electrocatalytic performance of electrode materials is also closely associated with the oxygen bulk diffusion and surface exchange properties. The values of D_{chem} and K_{chem}, derived from the ECR measurement, are shown in **Figure 11**. The resulting D_{chem} and K_{chem} values of the $PB_{1-x}CO$ oxides are analogous to those previously reported for related materials [47]. Fitting to the Arrhenius equation provides activation energies of ~86-121 and ~88-123 kJ mol^{-1} for D_{chem} and K_{chem}, respectively, which approach those obtained in Ref. 48. Generally, a tetragonal structure is characterized by faster oxygen diffusion through the bulk and surface with higher electrocatalytic activity for ORR in contrast with an orthorhombic structure [49]. It is clear that the $PB_{1-x}CO$ double perovskite materials exhibit high activity for oxygen mobility and activation. Additionally, experimental results achieve higher D_{chem} and K_{chem} values with an increase in Ba deficiency, which are an indication that the corresponding increase in oxygen vacancies in the structure could lead to enhanced diffusivity of oxygen ions inside the bulk and more surface defect sites with increased reactivity towards molecular oxygen.

Electrocatalytic Activity

The electrocatalytic activity for ORR of the $PB_{1-x}CO$ oxides was evaluated in symmetrical cells using EIS characterization on a $PB_{1-x}CO|SDC|PB_{1-x}CO$ configuration. **Figure 12a** shows the typical impedance spectra measured under open circuit conditions at 700 °C. The ohmic resistances were normalized to zero in order to clearly illustrate and compare the cathodic polarization resistances, which were normalized by the geometric electrode area (ASR) and could be roughly derived from the intercept of the spectra with the real axis. The ASR values are 0.046, 0.042, and 0.038 Ω cm^2 for x = 0.00, 0.05, and 0.10, respectively, which are comparable to those obtained for other double perovskites, such as $PrBaCo_{2-x}Sc_xO_{6-\delta}$ [50] and $Ba_2Bi_{0.1}Sc_{0.2}Co_{1.7}O_{6-x}$ [51]. It was observed that an increase in Ba deficiency concentration caused a decrease in the ASR values. The higher concentration of mobile oxygen defects in the Pr-O layer originating from the increased Ba deficiency contributes to faster oxygen kinetics (namely, oxygen bulk diffusion and surface exchange) and thus better electrochemical performance. The Arrhenius-type plots of ASR for the $PB_{1-x}CO$ electrodes are depicted in **Figure 12b**. The relatively low activation energies obtained, 112.0-123.5 kJ mol^{-1}, are of interest for intermediate-temperature operations. Additionally, considering the polycrystalline structure of $PB_{1-x}CO$ oxides, it is also pointed out that the activity for ORR might be further improved by microstructure optimization such as incorporation of electrolytes to form composite electrodes.

Conclusions

To summarize, A-site barium-deficient composites of $PrBa_{1-x}Co_2O_{5+\delta}$ ($PB_{1-x}CO$, x = 0.00, 0.05, 0.10) were systematically characterized with respect to their application as oxygen reduction electrodes. The characterization primarily focused on crystal structure, structural stability, oxygen nonstoichiometry and transport properties. The synthesized $PB_{1-x}CO$ oxides adopted a tetragonal structure in the P4/mmm space group, and the introduction of Ba deficiency through the formation of oxygen vacancies resulted in slightly increased lattice parameters. It is also noted that the crystal structure of these oxides illustrated a superior stability after prolonged high-temperature treatment. Moreover, favorable transport properties, including oxygen-ion conductivity, chemical bulk diffusion coefficient and chemical surface exchange coefficient, were obtained, which could be rationalized based on the increasing concentration of oxygen vacancies, resulting from the introduction of Ba deficiency into the lattice. To put it simply, the $PB_{1-x}CO$ double perovskites featured a number of promising properties, such as stable crystal structure, high oxygen nonstoichiometry, sufficient electrical conductivity, and fast bulk diffusion coefficient and surface exchange coefficient. These results could account for the remarkable electrocatalytic activity: low polarization resistances of 0.046, 0.042, and 0.038 Ω cm^2 for $x = 0.00$, 0.05, and 0.10, respectively, at 700 °C, which demonstrates that these oxides warrant further research as a prospective cathode materials for IT-SOFCs. In particular, the more competitive activity for ORR may be achieved by microstructure optimization of the electrode processing.

Acknowledgements

Feifei Dong wishes to thank The Hong Kong Polytechnic University for a visiting scholarship. The authors also acknowledge the Australian Research Council (ARC) future fellowship under contract FT100100134.

References

(1) Wachsman, E. D.; Marlowe, C. A.; Lee, K. T. Role of Solid Oxide Fuel Cells in a Balanced Energy Strategy. *Energy Environ. Sci.* **2012**, *5*, 5498-5509.

(2) Shao, Z. P.; Zhou, W.; Zhu, Z. H. Advanced Synthesis of Materials for Intermediate-Temperature Solid Oxide Fuel Cells. *Prog. Mater. Sci.* **2012**, *57*, 804-874.

(3) Adler, S. B. Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes. *Chem. Rev.* **2004**, *104*, 4791-4844.

(4) Lynch, M. E.; Yang, L.; Qin, W. T.; Choi, J. -J.; Liu, M. F.; Blinn, K.; Liu, M. L. Enhancement of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Durability and Surface Electrocatalytic Activity by $La_{0.85}Sr_{0.15}MnO_{3\pm\delta}$ Investigated Using a New Test Electrode Platform. *Energy Environ. Sci.* **2011**, *4*, 2249-2258.

(5) Zhou, W.; Sunarso, J.; Motuzas, J.; Liang, F. L.; Chen, Z. G.; Ge, L.; Liu, S. M.; Julbe, A.; Zhu, Z. H. Deactivation and Regeneration of Oxygen Reduction Reactivity on Double Perovskite $Ba_2Bi_{0.1}Sc_{0.2}Co_{1.7}O_{6-x}$ Cathode for Intermediate-Temperature Solid Oxide Fuel Cells. *Chem. Mater.* **2011**, *23*, 1618-1624.

(6) Dong, F. F.; Chen, D. J.; Chen, Y. B.; Zhao, Q.; Shao, Z. P. La-Doped $BaFeO_{3-\delta}$ Perovskite as a Cobalt-Free Oxygen Reduction Electrode for Solid Oxide Fuel Cells with Oxygen-Ion Conducting Electrolyte. *J. Mater. Chem.* **2012**, *22*, 15071-15079.

(7) Dong, F. F.; Chen, Y. B.; Ran, R.; Chen, D. J.; Tade, M. O.; Liu, S. M.; Shao, Z. P. $BaNb_{0.05}Fe_{0.95}O_{3-\delta}$ as a New Oxygen Reduction Electrocatalyst for Intermediate Temperature Solid Oxide Fuel Cells. *J. Mater. Chem. A* **2013**, *1*, 9781-9791.

(8) Li, M.; Wang, Y.; Wang, Y. L.; Chen, F. L.; Xia, C. R. Bismuth Doped Lanthanum Ferrite Perovskites as Novel Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11286-11294.

(9) Dong, F. F.; Chen, Y. B.; Chen, D. J.; Shao, Z. P. Surprisingly High Activity for Oxygen Reduction Reaction of Selected Oxides Lacking Long Oxygen-Ion Diffusion Paths at Intermediate Temperatures: A Case Study of Cobalt-Free $BaFeO_{3-\delta}$. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11180-11189.

(10) Xia, C. R.; Rauch, W.; Chen, F. L.; Liu, M. L. $Sm_{0.5}Sr_{0.5}CoO_3$ Cathodes for Low-Temperature SOFCs. *Solid State Ionics* **2002**, *149*, 11-19.

(11) Dusastre, V.; Kilner, J. A. Optimisation of Composite Cathodes for Intermediate Temperature SOFC Applications. *Solid State Ionics* **1999**, *126*, 163-174.

(12) Shao, Z. P.; Haile, S. M. A High-Performance Cathode for the Next Generation of Solid-Oxide Fuel Cells. *Nature* **2004**, *431*, 170-173.

(13) Tarancon, A.; Skinner, S. J.; Chater, R. J.; Hernandez-Ramirez, F.; Kilner, J. A. Layered Perovskites as Promising Cathodes for Intermediate Temperature Solid Oxide Fuel Cells. *J. Mater. Chem.* **2007**, *17*, 3175-3181.

(14) Zhang, K.; Ge, L.; Ran, R.; Shao, Z. P.; Liu, S. M. Synthesis, Characterization and Evaluation of Cation-Ordered $LnBaCo_2O_{5+\delta}$ as Materials of Oxygen Permeation Membranes and Cathodes of SOFCs. *Acta Mater.* **2008**, *56*, 4876-4889.

(15) Kim, J. H.; Cassidy, M.; Irvine, J. T. S.; Bae, J. Electrochemical Investigation of Composite Cathodes with $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ Cathodes for Intermediate Temperature-Operating Solid Oxide Fuel Cell. *Chem. Mater.* **2010**, *22*, 883-892.

(16) Parfitt, D.; Chroneos, A.; Tarancon, A.; Kilner, J. A. Oxygen Ion Diffusion in Cation Ordered/Disordered $GdBaCo_2O_{5+\delta}$. *J. Mater. Chem.* **2011**, *21*, 2183-2186.

(17) Ma, C. R.; Liu, M.; Collins, G.; Wang, H. B.; Bao, S. Y.; Xu, X.; Enriquez, E.; Lin, Y.; Whangbo, M. -H. Magnetic and Electrical Transport Properties of $LaBaCo_2O_{5.5+\delta}$ Thin Films on Vicinal (001) $SrTiO_3$ Surfaces. *ACS Appl. Mater. Interfaces* **2013**, *5*, 451-455.

(18) Choi, S.; Shin, J.; Kim, G. The Electrochemical and Thermodynamic Characterization of $PrBaCo_{2-x}Fe_xO_{5+\delta}$ (x = 0, 0.5, 1) Infiltrated into Yttria-Stabilized Zirconia Scaffold as Cathodes for Solid Oxide Fuel Cells. *J. Power Sources* **2012**, *201*, 10-17.

(19) Taskin, A. A.; Lavrov, A. N.; Ando, Y. Achieving Fast Oxygen Diffusion in Perovskites by Cation

Ordering. *Appl. Phys. Lett.* **2005**, *86*, 091910-091910-3.

(20) Kim, G.; Wang, S.; Jacobson, A. J.; Reimus, L.; Brodersen, P.; Mims, C. A. Rapid Oxygen Ion Diffusion and Surface Exchange Kinetics in $PrBaCo_2O_{5+x}$ with a Perovskite Related Structure and Ordered A Cations. *J. Mater. Chem.* **2007**, *17*, 2500-2505.

(21) Chen, D. J.; Ran, R.; Zhang, K.; Wang, J.; Shao, Z. P. Intermediate-Temperature Electrochemical Performance of a Polycrystalline $PrBaCo_2O_{5+\delta}$ Cathode on Samarium-Doped Ceria Electrolyte. *J. Power Sources* **2009**, *188*, 96-105.

(22) Choi, S.; Yoo, S.; Kim, J.; Park, S.; Jun, A.; Sengodan, S.; Kim, J.; Shin, J.; Jeong, H. Y.; Choi, Y.; Kim, G.; Liu, M. L. Highly Efficient and Robust Cathode Materials for Low-Temperature Solid Oxide Fuel Cells: $PrBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+\delta}$. *Sci. Rep.* **2013**, *3*, 2426-2431.

(23) Chen, D. J.; Ran, R.; Shao, Z. P. Assessment of $PrBaCo_2O_{5+\delta}$+ $Sm_{0.2}Ce_{0.8}O_{1.9}$ Composites Prepared by Physical Mixing as Electrodes of Solid Oxide Fuel Cells. *J. Power Sources* **2010**, *195*, 7187-7195.

(24) Liu, J.; Collins, G.; Liu, M.; Chen, C. L.; He, J.; Jiang, J. C.; Meletis, E. I. Ultrafast Oxygen Exchange Kinetics on Highly Epitaxial $PrBaCo_2O_{5+\delta}$ Thin Films. *Appl. Phys. Lett.* **2012**, *100*, 193903-193903-4.

(25) Kharton, V. V.; Kovalevsky, A. V.; Tsipis, E. V.; Viskup, A. P.; Naumovich, E. N.; Jurado, J. R.; Frade, J. R. Mixed Conductivity and Stability of A-Site-Deficient $Sr(Fe,Ti)O_{3-\delta}$ Perovskites. *J. Solid State Electrochem.* **2002**, *7*, 30-36.

(26) Zhu, Y. L.; Chen, Z. -G.; Zhou, W.; Jiang, S. S.; Zou, J.; Shao, Z. P. An A-Site-Deficient Perovskite Offers High Activity and Stability for Low-Temperature Solid-Oxide Fuel Cells. *ChemSusChem* **2013**, *6*,

2249-2254.

(27) Zhou, W.; Ran, R.; Shao, Z. P.; Jin, W. Q.; Xu, N. P. Evaluation of A-Site Cation-Deficient $(Ba_{0.5}Sr_{0.5})_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (x>0) Perovskite as a Solid-Oxide Fuel Cell Cathode. *J. Power Sources* **2008**, *182*, 24-31.

(28) Wang, F. C.; Chen, D. J.; Shao, Z. P. Composition and Microstructure Optimization and Operation Stability of Barium Deficient $Ba_{1-x}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ Perovskite Oxide Electrodes. *Electrochim. Acta* **2013**, *103*, 23-31.

(29) Hansen, K. K. A-Site Deficient $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$ Perovskites as Solid Oxide Fuel Cell Cathodes. *J. Electrochem. Soc.* **2009**, *156*, B1257-B1260.

(30) Pang, S. L.; Jiang, X. N.; Li, X. N.; Wang, Q.; Su, Z. X.; Zhang, Q. Y. Highly Enhanced Electrochemical Performance of $PrBa_{0.92}Co_2O_{5+\delta}$ Cathode by Introducing Ba Cationic-Deficiency. *Int. J. Hydrogen Energy* **2012**, *37*, 3998-4001.

(31) Pang, S. L.; Jiang, X. N.; Li, X. N.; Wang, Q.; Su, Z. X. Characterization of Ba-Deficient $PrBa_{1-x}Co_2O_{5+\delta}$ as Cathode Material for Intermediate Temperature Solid Oxide Fuel Cells. *J. Power Sources* **2012**, *204*, 53-59.

(32) Chen, D. J.; Shao, Z. P. Surface Exchange and Bulk Diffusion Properties of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Mixed Conductor. *Int. J. Hydrogen Energy* **2011**, *36*, 6948-6956.

(33) Seikh, M. M.; Simon, C.; Caignaert, V.; Pralong, V.; Lepetit, M. B.; Boudin, S.; Raveau, B. New Magnetic Transitions in the Ordered Oxygen-Deficient Perovskite $LnBaCo_2O_{5.50+\delta}$. *Chem. Mater.* **2008**, *20*, 231-238.

(34) Svarcova, S.; Wiik, K.; Tolchard, J.; Bouwmeester, H. J. M.; Grande, T. Structural Instability of Cubic Perovskite $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$. *Solid State Ionics* **2008**, *178*, 1787-1791.

(35) Simner, S. P.; Anderson, M. D.; Engelhard, M. H.; Stevenson, J. W. Degradation Mechanisms of La-Sr-Co-Fe-O_3 SOFC Cathodes. *Electrochem. Solid-State Lett.* **2006**, *9*, A478-A481.

(36) Aksenova, T. V.; Gavrilova, L. Y.; Tsvetkov, D. S.; Voronin, V. I.; Cherepanov, V. A. Crystal Structure and Physicochemical Properties of Layered Perovskite-Like Phases $LnBaCo_2O_{5+\delta}$. *Russ. J. Phys. Chem. A* **2011**, *85*, 427-432.

(37) Akahoshi, D.; Ueda, Y. Oxygen Nonstoichiometry, Structures, and Physical Properties of $YBaCo_2O_{5+x}$ ($0.00 \leq x \leq 0.52$). *J. Solid State Chem.* **2001**, *156*, 355-363.

(38) Frontera, C.; Caneiro, A.; Carrillo, A. E.; Oro-Sole, J.; Garcia-Munoz, J. L. Tailoring Oxygen Content on $PrBaCo_2O_{5+\delta}$ Layered Cobaltites. *Chem. Mater.* **2005**, *17*, 5439-5445.

(39) Ge, L.; Zhou, W.; Ran, R.; Liu, S. M.; Shao, Z. P.; Jin, W. Q.; Xu, N. P. Properties and Performance of A-Site Deficient $(Ba_{0.5}Sr_{0.5})_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ for Oxygen Permeating Membrane. *J. Membr. Sci.* **2007**, *306*, 318-328.

(40) He, Y. F.; Zhu, X. F.; Yang, W. S. The Role of A-Site Ion Nonstoichiometry in the Oxygen Absorption Properties of $Sr_{1+x}Co_{0.8}Fe_{0.2}O_3$ Oxides. *AIChE J.* **2011**, *57*, 87-95.

(41) Pavone, M.; Ritzmann, A. M.; Carter, E. A. Quantum-Mechanics-Based Design Principles for Solid Oxide Fuel Cell Cathode Materials. *Energy Environ. Sci.* **2011**, *4*, 4933-4937.

(42) Che, X. L.; Shen, Y.; Li, H.; He, T. M. Assessment of $LnBaCo_{1.6}Ni_{0.4}O_{5+\delta}$ (Ln = Pr, Nd, and Sm) Double-Perovskites as Cathodes for Intermediate-Temperature Solid-Oxide Fuel Cells. *J. Power Sources*

2013, *222*, 288-293.

(43) Kostogloudis, G. C.; Ftikos, C. Properties of A-Site-Deficient $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-Based Perovskite Oxides. *Solid State Ionics* **1999**, *126*, 143-151.

(44) Yang, Z. B.; Han, M. F.; Zhu, P. Y.; Zhao, F.; Chen, F. L. $Ba_{1-x}Co_{0.9-y}Fe_{y}Nb_{0.1}O_{3-\delta}$ (x = 0-0.15, y = 0-0.9) as Cathode Materials for Solid Oxide Fuel Cells. *Int. J. Hydrogen Energy* **2011**, *36*, 9162-9168.

(45) Carter, S.; Selcuk, A.; Chater, R. J.; Kajda, J.; Kilner, J. A.; Steele, B. C. H. Oxygen Transport in Selected Nonstoichiometric Perovskite-Structure Oxides. *Solid State Ionics* **1992**, *53-56*, 597-605.

(46) Vente, J. F.; Haije, W. G.; Rak, Z. S. Performance of Functional Perovskite Membranes for Oxygen Production. *J. Membr. Sci.* **2006**, *276*, 178-184.

(47) Grimaud, A.; Bassat, J. -M.; Mauvy, F.; Pollet, M.; Wattiaux, A.; Marrony, M.; Grenier, J. -C. Oxygen Reduction Reaction of $PrBaCo_{2-x}Fe_{x}O_{5+\delta}$ Compounds as H^{+}-SOFC Cathodes: Correlation with Physical Properties. *J. Mater. Chem. A* **2014**, *2*, 3594-3604.

(48) Burriel, M.; Pena-Martinez, J.; Chater, R. J.; Fearn, S.; Berenov, A. V.; Skinner, S. J.; Kilner, J. A. Anisotropic Oxygen Ion Diffusion in Layered $PrBaCo_{2}O_{5+\delta}$. *Chem. Mater.* **2012**, *24*, 613-621.

(49) Kim, J. -H.; Prado, F.; Manthiram, A. Characterization of $GdBa_{1-x}Sr_{x}Co_{2}O_{5+\delta}$ ($0 \leq x \leq 1.0$) Double Perovskites as Cathodes for Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **2008**, *155*, B1023-B1028.

(50) Li, X. N.; Jiang, X. N.; Xu, H. X.; Xu, Q. L.; Jiang, L.; Shi, Y. C.; Zhang, Q. Y. Scandium-Doped $PrBaCo_{2-x}Sc_{x}O_{6-\delta}$ Oxides as Cathode Material for Intermediate-Temperature Solid Oxide Fuel Cells. *Int. J. Hydrogen Energy* **2013**, *38*, 12035-12042.

(51) Zhou, W.; Sunarso, J.; Chen, Z. -G.; Ge, L.; Motuzas, J.; Zou, J.; Wang, G. X.; Julbe, A.; Zhu, Z. H.

Novel B-Site Ordered Double Perovskite $Ba_2Bi_{0.1}Sc_{0.2}Co_{1.7}O_{6-x}$ for Highly Efficient Oxygen Reduction Reaction. *Energy Environ. Sci.* **2011**, *4*, 872-875.