Highly Active Air Electrode with Enhanced Proton Conduction via Isovalent Doping in a Layered Perovskite for Reversible Protonic Ceramic Cells

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Reversible protonic ceramic cells (R-PCCs) offer a compelling solution for efficient energy conversion and storage at intermediate temperatures (400–600 °C); however, their practical implementation and overall electrochemical performance are severely constrained by sluggish electrochemical reaction kinetics at the air electrode. Herein, a novel triple ionic–electronic conducting material is presented, the Ni-doped layered perovskite PrBa_{0.5}Sr_{0.5}Co_{1.8}Ni_{0.2}O_{5+ δ} (PBSCN20), to be utilized as an air electrode in R-PCCs. Thermogravimetric analysis and density functional theory calculations demonstrate that Ni doping at the Co site significantly promoted oxygen vacancy formation while simultaneously facilitating proton uptake and migration. Consequently, the R-PCCs with a PBSCN20 air electrode exhibited outstanding electrochemical performance, attaining peak power densities of 1.30 and 0.60 W cm⁻² in fuel cell mode, and current densities of -1.72 and -0.41 A cm⁻² at 1.3 V in electrolysis mode at 600 and 500 °C.

indiscriminate consumption of nonrenewable energy sources (e.g., fossil fuels).^[1,2] Ceramic-based reversible solid oxide cells (R-SOCs) have recently garnered significant attention as highly efficient and sustainable energy conversion devices. Furthermore, R-SOCs based on oxygen-ion (O^{2–})-conducting electrolytes can function reversibly, in which a water electrolysis device produces hydrogen in electrolysis cell (EC) mode, which is later converted back into electricity in fuel cell (FC) mode, thereby utilizing energy storage devices.^[3,4] Nonetheless, the operation of R-SOCs at high temperatures (800-1000 °C) has encounter significant challenges, including increased system costs, cell degradation, and thermomechanical incompatibility between the electrodes and electrolytes, which considerably impedes the commercialization of R-SOCs.^[5,6] Compared with R-SOCs, reversible protonic ceramic cells

1. Introduction

Renewable and clean devices for energy conversion and storage are crucial for addressing global climate deterioration due to the

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(R-PCCs) utilizing proton (H⁺)-conducting electrolytes play a key role in shifting toward lower operating temperatures (400–600 °C). In a R-PCC system, the use of protons, which are considerably smaller and lighter than oxide ions, leads to a decreased

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activation energy for ionic conduction, thereby providing high performance at lower operating temperatures due to the enhanced electrolyte conductivity.^[7,8] Furthermore, the FC mode inhibits fuel dilution, as protons are conveyed from the fuel electrode to the air electrode through the electrolyte, resulting in the production of water at the air electrode. In EC mode, steam (H₂O)-containing air is fed to the air electrode, whereas only pure hydrogen is produced at the fuel electrode, eliminating the need for a separate gas separator and thus reducing system complexity and costs.^[9,10]

Despite the substantial benefits of R-PCCs, the slow kinetics of electrochemical reactions at the air electrode, as expressed in Equation (1), particularly the oxygen reduction reaction (ORR, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) and the oxygen evolution reaction (OER, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), pose major barriers to realizing excellent electrochemical performance in the reduced-temperature regime.^[11,12]

$$2H^+$$
 (electrolyte) + $\frac{1}{2}O_2$ (gas) + $2e^-$ (air electrode) \leftrightarrow H₂O (gas) (1)

In the advancement of air electrode materials for R-PCCs, mixed ionic and electronic conducting (MIEC) materials, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF), La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), and $PrBaCo_2O_{5+\delta}$ (PBCO), have been demonstrated to be highly active and efficient air electrodes for R-SOCs.[13,14] However, when these air electrodes are utilized in R-PCCs, the inadequate proton transport ability restricts the electrochemically active sites to the triple phase boundaries (TPBs), where the air electrode, electrolyte, and gas converge. For this reason, ideal air electrodes for R-PCCs should be capable of simultaneous high $H^+/O^{2-}/e^$ triple conduction and should exhibit superior catalytic activities for the ORR/OER and chemically stable compatibility with other components. Such materials, known as triple ionic and electronic conductors (TIECs), demonstrate outstanding electrochemical performance because of their particularly appropriate proton conduction characteristics at the air electrode.^[15–19]

Given these advantages, several investigations have focused on enhancing the catalytic activity of perovskite oxides; in particular, doping has been extensively utilized as a simple and effective strategy.^[20-22] The effectiveness of the doping strategy is largely attributed to the remarkable compositional flexibility of perovskite lattices, which allows the structural integrity to be preserved despite doping with rare-earth or transitionmetal ions at the A and B sites.^[18,23,24] Among various transition metal-dopants, the effects of doping a small amount of Ni at the B site in perovskite-structured air electrodes have been recently investigated for R-PCC applications. For example, Liang et al. applied a Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Ni_{0.05}O_{3-δ} (BCFZYN) cathode for protonic ceramic fuel cells (PCFCs) based on $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb1711), which is a proton-conducting electrolyte, and demonstrated that partial substitution of Ni at the B site of perovskite-structured oxides enhanced the proton/oxygen ion conductivity and oxygen surface exchange kinetics.^[25] In addition, Wang et al. evaluated the proton-conducting ability of (La_{0.7}Ca_{0.3})(Co_{0.8}Ni_{0.2})O₃ (LCCN7382) via thermogravimetric curves, and the hydration energy of LCCN7382 was also evaluated to verify the validity of the hydration reaction obtained by density functional theory (DFT) calculations.^[26] The results demonstrated that the presence of Ni was beneficial for both the ORR/OER and the hydration reaction, leading to excellent electrochemical performance in reversible mode when this material was applied as an air electrode for R-PCCs. Most recently, Park et al. introduced an advanced layered perovskite-structured NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.45}Ni_{0.05}O_{5+ δ} (NBSCFN5) as an air electrode for R-PCCs.^[27] The incorporation of a small amount of Ni (5 mol.%) at the B site in NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+ δ} (NBSCF) enhanced its triple-conducting properties and electrocatalytic activity for air electrochemical performance of R-PCCs, which reached a peak power density of 0.74 W cm⁻² in FC mode and a current density of -0.66 A cm⁻² in EC mode at 600 °C.

In this study, we report a new triple ionic-electronic conducting material, the Ni-doped layered perovskite $PrBa_{0.5}Sr_{0.5}Co_{1.8}Ni_{0.2}O_{5+\delta}$ (PBSCN20), as a highly efficient air electrode for R-PCC applications. Experimental and theoretical approaches were employed to systematically elucidate the impact of Ni doping on the proton conduction and the related electrochemical properties. Thermogravimetric analysis (TGA) was conducted under both dry and wet ($pH_2O = 0.03$ atm) air conditions to assess the quantitative proton concentration and thermodynamic parameters. Further evaluation of the Gibbs free energy (ΔG_{hvdrat}) revealed that less energy was needed for the formation of protonic defects as Ni concentration increased. Moreover, the DFT results demonstrated that Ni doping effectively lowered the proton migration energy barrier, facilitating proton conduction within the lattice. Consequently, the R-PCC with the PBSCN20 air electrode delivered exceptional peak power densities of 1.30 and 0.60 W cm⁻² (FC mode) and current densities of -1.72 and -0.41 A cm⁻² at 1.3 V (EC mode) at 600 and 500 °C, respectively, along with superior long-term stability under reversible operating conditions.

2. Results and Discussion

2.1. Crystal Structure Analysis

The crystal structures of the PrBa_{0.5}Sr_{0.5}Co_{2.0-x}Ni_xO_{5+ δ} (x = 0, 0.1, 0.2, 0.3, and 0.4) air electrode powders were characterized via Xray diffraction (XRD) analysis. Reflecting increasing Ni concentration at the Co site, the compositions were abbreviated as PB-SCO, PBSCN10, PBSCN20, PBSCN30, and PBSCN40. As shown in Figure 1a, all of the electrodes exhibited a layered perovskite structure; however, PBSCN30 and PBSCN40 appeared to have undesired secondary peaks. This behavior is presumably due to Ni not being fully incorporated into the lattice, thereby suggesting that the Ni-doping threshold in PBSCO is ≈ 0.2 mol. Additionally, based on the Rietveld refinement results, the single phases of PBSCO, PBSCN10, and PBSCN20 air electrodes clearly presented a tetragonal structure, classified by the space group P4/mmm (Figure 1b; Figure S1, Supporting information). The lattice parameters and unit cell volume slightly increased as the Ni concentration increased, which can be attributed to the partial substitution of smaller Co ions (Co³⁺: 0.545 Å; Co⁴⁺: 0.530 Å) with larger Ni ions (Ni²⁺: 0.69 Å; Ni³⁺: 0.56 Å) (Table 1). To further verify the incorporation and distribution of Ni within the perovskite lattice, high-angle annular dark-field scanning www.advancedsciencenews.com

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Figure 1. a) XRD patterns of $PrBa_{0.5}Sr_{0.5}Co_{2.0-x}Ni_xO_{5+\delta}$ (x = 0, 0.1, 0.2, 0.3, and 0.4) powders. b) Rietveld refinement profiles of PBSCN20. c) HAADF-STEM image and corresponding EDS elemental mapping results of PBSCN20. d) In situ XRD patterns of PBSCN20 measured from 25 to 1000 °C in air. e) XRD patterns of the BZCYYb4411 electrolyte, PBSCN20 air electrode, and PBSCN–BZCYYb4411 composite after heat treatment at 950 °C in air for 4 h, as well as after an additional exposure to 20% H₂O/air at 500 °C for 100 h.

transmission electron microscopy (HAADF-STEM) combined with energy-dispersive X-ray spectroscopy (EDS) elemental mapping was performed on the PBSCN20 (Figure 1c). The results clearly demonstrated that each element (Pr, Ba, Sr, Co, Ni, and O) was homogeneously distributed in PBSCN20. In situ XRD was conducted to assess the structural stability under typical R- PCC operating temperatures, ranging from room temperature to 1000 °C. The main peaks near 33° slightly shifted toward a lower angle with increasing temperature, but the tetragonal structure was consistently preserved without an observable secondary phase formation at all temperatures (Figure 1d; Figure S2, Supporting information). The thermal expansion coefficients



Composition	Space group	a [Å]	b [Å]	c [Å]	V [Å ³]	oxygen content [5+ δ]
PBSCO	P4/mmm	3.8491	3.8491	7.6950	114.005	5.76
PBSCN10	P4/mmm	3.8512	3.8512	7.6989	114.188	5.71
PBSCN20	P4/mmm	3.8513	3.8513	7.6991	114.193	5.66

derived from lattice parameter changes were summarized in Figure S3 and Table S1 (Supporting information). In addition to thermodynamic stability, chemical stability under high steam concentrations is another crucial requirement for ensuring reversible and long-term operation in both the FC and EC modes. Thus, ex situ XRD was further conducted after annealing in 20% H₂O/air at 500 °C for 100 h (Figure S4, Supporting information). The results indicated that the PBSCO, PBSCN10, and PBSCN20 air electrodes exhibited excellent steam tolerance in a humidified environment. Next, we evaluated the chemical compatibility with the BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3- δ} (BZCYYb4411) electrolyte to validate the applicability of these materials as an air electrode in electrochemical cells. Each air electrode powder was mixed with BZCYYb4411 electrolyte powder at a 1:1 weight ratio and subjected to heat treatment in dry air at 950 °C, followed by treatment in 20% H₂O/air at 500 °C (Figure 1e; Figure S5, Supporting information). All heat-treated air electrode-BZCYYb4411 composite powders were chemically stable, which implies that the PBSCO, PBSCN10, and PBSCN20 air electrodes are appropriate materials for R-PCC air electrodes.

2.2. Hydration Properties

As previously highlighted, an ideal air electrode for R-PCCs should exhibit excellent ORR/OER catalytic activities and simultaneous triple conduction (H⁺/O^{2−}/e[−]) capabilities, particularly those related to proton transport (i.e., proton uptake and proton migration), which are essential for expanding the electrochemically active sites across the entire air electrode surface to beyond the TPBs. Proton uptake in an air electrode typically occurs through hydration processes under humidified conditions, wherein proton carriers (OH_o) are generated by the incorporation of dissociative water, oxygen vacancies (V_o[−]) and lattice oxygen (O_o[−]), resulting in proton uptake within the bulk of the air electrode, as described in Equation (2).

$$H_2O + V_O^{\cdot} + O_O^{\times} \leftrightarrow 2OH_O^{\cdot}$$
(2)

As the above properties are significantly influenced by the oxygen vacancy concentration, which is correlated with the oxidation state of transition metals,^[28] the oxidation states of the multivalent metal elements (i.e., Pr, Co, and Ni) in PBSCN were initially examined using X-ray photoelectron spectroscopy (XPS). The XPS spectra were fitted with Gaussian functions, and the average oxidation state of each element was calculated from the relative area ratios of the subpeaks within each doublet peak. As shown in Figure S6 (Supporting information) and summarized in Table S2 (Supporting information), the total metal oxidation state gradually decreased with increasing Ni content, accompanied by a corresponding reduction in the oxygen content $(5+\delta)$ to maintain charge neutrality. These changes in oxygen content were further reflected in the O 1s spectra (Figure 2a), which showed four distinct peaks corresponding to lattice oxygen species (O²⁻), oxidative oxygen species (O_2^{2-}/O^-) , hydroxyl groups (CO_3^{2-}/OH^-) , and adsorbed molecular water (H2O).^[29] The concentration of surface oxygen vacancies was quantitatively assessed using the O_{ads}/O_{lat} ratio, which represents the proportion of oxidative oxygen species (O_2^{2-}/O^-) relative to lattice oxygen (O^{2-}) .^[30] With increasing Ni content, the O_{ads}/O_{lat} ratio steadily increased from

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0.215 (for PBSCO) to 0.340 (for PBSCN20) (Table S3, Supporting information), indicating that oxygen vacancy formation becomes more favorable at higher Ni doping levels. This trend was further validated by iodometric titration (Figure S7, Supporting information). In parallel with the examination of average oxidation state of metal elements and oxygen vacancy concentration in PBSCN, electrical conductivity, encompassing both ionic and electronic transport, is an indispensable factor for evaluating air electrodes. The electrical conductivities of PBSCO, PBSCN10, and PBSCN20 air electrodes were measured using a 4-probe direct current (DC) method under wet (3% H₂O) air conditions. As illustrated in Figure S8 (Supporting information), the electrical conductivity slightly decreases with increasing Ni concentration at the Co site, primarily due to a decrease in hole concentration (Co^{3+}/Co^{4+}), as indicated in Table S2 (Supporting information). Nevertheless, all samples exhibited high values of exceeding 900 S cm⁻¹ within the typical R-PCC operation temperatures (400-600 °C). However, proton transport plays a more pivotal role in determining the overall electrochemical performances in R-PCCs.

To directly evaluate the proton uptake ability of the PBSCN materials, TGA as a function of temperature was subsequently conducted in dry ($pO_2 = 0.21$ atm) and wet ($pH_2O = 0.03$ atm) air environments. The initial oxygen contents obtained from iodometric titration were utilized to determine the temperaturedependent oxygen contents of PBSCO, PBSCN10, and PBSCN20 through TGA in dry air, and the results revealed a substantial increase in the oxygen vacancy concentration (Figure 2b), which potentially facilitates proton uptake during the hydration reaction. To quantitatively assess the proton uptake ability of the PBSCN materials, the weights were monitored under dry and wet air conditions, revealing distinct changes in weight closely related to proton uptake into the lattice (Figure S9, Supporting information). On the basis of Equation (3), the corresponding proton concentration of PBSCN20 was 2.74 mol.% per unit cell at 500 °C, which was higher than those of PBSCO and PBSCN10 at the same temperature: 1.80 and 2.39 mol.%, respectively (Figure 2c).

$$[OH^{\cdot}] = 2 \left[H_2O\right] = 2 \times \frac{M_{\text{sample}}}{m_{\text{sample}}} \times \frac{\Delta m}{M_{H_2O}}$$
(3)

Additionally, $[OH_{O}]/2[V_{O}]_{max}$, an indicator of the degree of hydration, was derived to further evaluate the correlation between the oxygen vacancy concentration and the proton concentration in PBSCN.^[31] The degree of hydration values of PBSCN10 and PBSCN20 were comparable, with both substantially exceeding that of PBSCO, suggesting considerable enhancement due to the presence of Ni at the Co site (see Figure 2d; Figure S10, Supporting information). Additional thermodynamic parameters for the hydration reaction in PBSCN can be derived from the equilibrium constant (K_{hydrat}) according to Equation (4):

$$K_{\text{hydrat}} = \frac{\left[\text{OH}_{\text{O}}^{*}\right]^{2}}{pH_{2}\text{O}\left[\text{V}_{\text{O}}^{*}\right]\left[\text{O}_{\text{O}}^{*}\right]} = \exp\left(\frac{\Delta S_{\text{hydrat}}}{\text{R}}\right)\exp\left(-\frac{\Delta H_{\text{hydrat}}}{\text{RT}}\right)$$
(4)

where $[OH_{O}^{\circ}]$, $[V_{O}^{\circ}]$, and $[O_{O}^{\circ}]$ are the proton concentration, oxygen vacancy concentration, and oxygen concentration under hydrated conditions, respectively. The concentrations of these defects under wet (hydrated) conditions can be obtained by Equations (5)

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Figure 2. a) O 1s XPS spectra for PBSCO, PBSCN10, and PBSCN20 air electrodes. b) Oxygen contents $(5+\delta)$ of PBSCO, PBSCN10, and PBSCN20 derived from TGA profiles in dry air. c) Mass changes of PBSCO, PBSCN10, and PBSCN20 at 500 °C under dry air and wet air conditions, along with the corresponding proton concentrations. d) Degree of hydration. e) Equilibrium constant and f) Gibbs free energy of the hydration reaction. g) Oxygen vacancy formation energy and hydration energy calculated using DFT simulations. h) Calculated COHP analysis of Co–O and Ni–O bonding interactions.

and (6) and are depicted in Figure S11 (Supporting information). The tiny change in the electron defect concentration due to steam was considered negligible.

$$\left[O_{O}^{\times}\right]_{wet} = \left[O_{O}^{\times}\right]_{dry} - \frac{1}{2}\left[OH_{O}^{\cdot}\right]$$
(5)

$$\left[V_{O}^{\cdot \cdot}\right]_{wet} = \left[V_{O}^{\cdot \cdot}\right]_{dry} - \frac{1}{2}\left[OH_{O}^{\cdot}\right]$$
(6)

Therefore, ΔH_{hydrat} and ΔS_{hydrat} were calculated from the van't Hoff plot of the equilibrium constant in Figure 2e and agreed well with those reported for perovskite-based air electrode materials (Figure S12, Supporting information). From these values, the Gibbs free energy (ΔG_{hydrat}) was subsequently calculated from Equation (7).

$$\Delta G_{\rm hydrat} = \Delta H_{\rm hydrat} - T\Delta S_{\rm hydrat}$$
(7)

The ΔG_{hydrat} of PBSCN decreased with increasing Ni concentration, as shown in Figure 2f and summarized in **Table 2**, unam-

biguously indicating that the Ni doping effect in PBSCO reduces the energy required for the hydration reaction.^[27]

To further support our findings, the oxygen vacancy formation energy (E_{vac}) and hydration energy (E_{hvd}) were determined through DFT calculations using constructed $(2\sqrt{2} \times 2\sqrt{2} \times 1)$ supercell models with Co:Ni ratios of 16:0 (x = 0 for PBSCO), 15:1 (*x* = 0.125 for PBSCN10), and 14:2 (*x* = 0.25 for PBSCN20) (Figures S13-15, Supporting information).^[32-34] As shown in Figure 2g and Table S4 (Supporting information), the E_{vac} values for PBSCO, PBSCN10, and PBSCN20 were calculated as 0.81, 0.54, and 0.22 eV, respectively, consistent with the experimental results in Figure 2a,b. As oxygen vacancy formation became more favorable, the E_{hvd} value decreased from 0.18 eV (for PBSCO) to -0.15 eV (for PBSCN20). Notably, upon Ni doping, E_{hvd} transitioned from positive to negative, indicating that proton uptake becomes thermodynamically favorable. Considering that oxygen vacancy formation involves breaking of the B-O chemical bonds in perovskite structures, a crystal orbital Hamilton population (COHP) analysis was conducted to elucidate the bonding characteristics. Negative -COHP values correspond to antibonding states, whereas positive values indicate bonding states.

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Material	$\Delta H_{ m hydrat}$ [kJ mol ⁻¹]	ΔS _{hydrat} [J mol ⁻¹ K ⁻¹] 450–600 °C	ΔG_{hydrat} [k] mol ⁻¹]				
	450–600 °C		450 °C	500 °C	550 °C	600 °C	
PBSCO	-12.1 ± 1.5	-59.3 ± 1.9	30.8 ± 2.9	33.8 ± 3.0	36.8 ± 3.1	39.7 ± 3.2	
PBSCN10	-11.6 ± 1.2	-55.0 ± 1.4	28.1 ± 2.2	30.9 ± 2.3	33.6 ± 2.3	36.4 ± 2.4	
PBSCN20	-11.0 ± 1.3	-53.1 ± 1.6	27.4 ± 2.5	30.0 ± 2.6	32.7 ± 2.7	35.4 ± 2.7	

Table 2. Summary of thermodynamic parameters for PBSCN calculated by van't Hoff plot. The errors of ΔH_{hydrat} and ΔS_{hydrat} were extracted from the regression line fitting. The errors of ΔG_{hydrat} were from the standard deviation by considering ΔH_{hydrat} and ΔS_{hydrat} .

Consequently, a lower integrated –COHP (–ICOHP) value up to the Fermi level indicates that more electrons occupy the antibonding states, indicating a weaker bond strength.^[35,36] As depicted in Figure 2h, the -ICOHP values for PBSCO, PB-SCN10, and PBSCN20 were calculated as 0.99, 0.80, and 0.76, respectively, demonstrating that Ni doping gradually weakens the B–O bond strength, thereby facilitating oxygen vacancy formation.

2.3. Electrochemical Performance

To assess the electrocatalytic activity of the air electrodes, electrochemical impedance spectroscopy (EIS) was initially conducted on BZCYYb4411-supported symmetric cells under wet air (pH_2O = 0.03 atm) conditions. As illustrated in the Arrhenius plot in **Figure 3**a, the PBSCN20 air electrode exhibited the lowest activation energy of 1.03 eV within the temperature range of 450– 700 °C. Notably, the lowest area-specific resistance (ASR) was 0.8 Ω cm² at 500 °C (Figure 3b), outperforming the other two air electrodes (EIS spectra at other temperatures are summarized in Figure S16, Supporting information). The reproducibility of this trend was further validated by duplicate symmetric cell measurements (Figure S17, Supporting information). Given that the microstructure of the air electrode remained unchanged regardless of the Ni content (Figure S18, Supporting information), the enhanced electrochemical performance can be attributed to the intrinsic electrocatalytic properties induced by Ni doping at the Co site. To gain deeper insight into the Ni doping effect, the EIS spectra in Figure 3b were further deconvoluted via distribution of relaxation time (DRT) analysis.^[37] The accuracy of DRT analysis highly depends on the quality of the impedance data, in which even minor deviations or erroneous measurement points may result in inaccurate interpretations of the electrochemical processes, rendering validation of the reliability of the impedance data.^[38] One widely established approach for ensuring data integrity is the linear Kramers-Kronig (Lin-KK) test,^[39-41] which verifies whether the impedance data meets the following requirements: causality, linearity, and time invariance. As shown in Figure S19 (Supporting information), the Lin-KK test results revealed that all the residuals of the EIS spectra in Figure 3b remained below 1%, confirming the reliability of the obtained



Figure 3. a) Arrhenius plot of the ASRs for BZCYYb4411 electrolyte-based symmetric cells with PBSCO, PBSCN10, and PBSCN20 air electrodes. b) EIS of the PBSCO, PBSCN10, and PBSCN20 air electrodes at 500 °C. c) DRT analysis using the EIS spectra of Figure 3b. d) Energy barrier for proton migration calculated using DFT simulations. e) Calculated COHP analysis of O–H bonding interactions.



impedance data. Figure 3c shows the DRT plots of the PBSCO, PBSCN10, and PBSCN20 air electrodes at 500 °C, where the predominant charge carrier is a proton. In DRT plots, the frequency ranges can be divided into three distinct regions: high frequencies (HF, $>10^4$ Hz), middle frequencies (MF, 10^{-1} – 10^4 Hz), and low frequencies (LF, $<10^{-1}$ Hz). Several studies indicate that these regions correspond sequentially to charge transfer (ion transfer at the air electrode-electrolyte interface), bulk and surface exchange (oxygen adsorption/desorption and proton/oxygen ion transport within the air electrode bulk), and mass transfer (i.e., gas diffusion).^[42] As depicted in Figure 3c and Figure S20 (Supporting information), the observed peaks in the middle frequency area were significantly suppressed with increasing Ni content, indicating that Ni doping effectively enhances the proton and oxygen ion exchange kinetics in the air electrode bulk and at the surface.

To further understand the enhanced proton transport behavior of PBSCN20, we also assessed the proton migration barriers utilizing DFT simulations. Since protons are well established to migrate along the octahedral faces of perovskite materials,^[43] possible proton migration paths were considered based on the octahedral symmetry of the layered perovskite structure (Figure S21, Supporting information). The proton migration pathways in all cases are oriented along the (100) plane of the perovskite lattice. In PBSCO, proton migration only occurs along a single pathway (i.e., Co-O-Co). However, the configurational diversity introduced by Ni doping at the B site offers an expanded array of proton migration pathways, resulting in multiple energetically favorable routes. As shown in Figure 3d, the proton migration barrier monotonically decreased with increasing Ni content, from 0.17 to 0.14 eV and 0.05 eV (Table S5, Supporting information). This reduction in the migration barrier indicates that Ni doping facilitates proton migration by weakening the O-H bond strength (Figure 3e), thereby creating energetically favorable pathways.

Beyond the investigating fundamental characteristics of PB-SCN air electrodes, to validate their electrochemical performance at the single-cell level, fuel electrode-supported R-PCCs were fabricated with dense electrolyte and porous air electrode layers ≈ 10 and 20 µm thick, respectively (Figure 4a). To evaluate the electrochemical performance under reversible operating conditions, humidified H₂ (3% H₂O) and humidified air (3% H_2O) were supplied to the cells. Figure 4b shows that all the air electrodes exhibited comparable ohmic resistances across all temperatures, implying identical electrolyte thickness and contact resistances between the air electrode and electrolyte. Unlike the ohmic resistance, the nonohmic resistance gradually decreased with increasing Ni concentration, eventually resulting in the lowest nonohmic resistance and the greatest increase in electrochemical performance for PBSCN20 (Figure 4c; Figure S22, Supporting information). The cell with the PBSCN20 air electrode achieved superior peak power densities of 1.30 and 0.60 W cm⁻² along with current densities (at 1.3 V) of -1.72and -0.41 A cm⁻² at 600 and 500 °C, respectively, surpassing those of most recently reported air electrodes (Figure 4d,e; Table S6, Supporting information).^[16,18,19,44–48] In electrolysis mode, a high current output may not entirely contribute to hydrogen production due to current leakage through the proton-conducting electrolyte, which exhibits the mixed ionic and electronic conducting properties.^[15–17] Therefore, we systematically evaluated the Faradaic efficiency and quantified the actual hydrogen production rate using gas chromatography (GC). To establish a calibration curve for quantifying hydrogen production, GC measurements were initially performed at open-circuit voltage (OCV) while gradually decreasing the hydrogen partial pressure from 14% to 6% H₂/Ar in 2% intervals at 500 °C (Figures S23a,b and Table **S7**, Supporting information). Figure 4f shows the *I*–*V* curve for the R-PCC with a PBSCN20 air electrode at 500 °C under 150 sccm of 10% H₂/Ar. As shown in Figure 4g, hydrogen production rates were measured at 500 °C under a sequence of applied voltages, including four attempts at 1.3 V, followed by 1.2, 1.1, and 1.2 V, and two more repetitions at 1.3 V. The theoretical hydrogen production rate was calculated from the observed current densities, assuming 100% Faradaic efficiency (black line), while the measured hydrogen production rate was determined from the obtained H₂/Ar area ratio with the pre-established calibration curve (black columns). The Faradaic efficiency was then calculated as the ratio of the measured hydrogen production rate to the theoretical value. The calculated Faradaic efficiency demonstrated over 60% at 1.3 V, which increased as the applied bias decreased. Moreover, Faradaic efficiency was assessed at various points at 1.3 V, yielding similar and reliable values for hydrogen production rate of all measurements (Table S8, Supporting information). Following the Faradaic efficiency measurements, we further verified electrochemical stability by re-performing the calibration under OCV conditions. As depicted in Figure S23c (Supporting information), the OCV remained stable at 1.039 V, which was identical to the value observed prior to the Faradaic efficiency measurements (Figure S23a, Supporting information). Additionally, the measured H_2/Ar area ratio (red point) closely matched the initial calibration value (Figure S23c, inset, Supporting information).

Furthermore, the PBSCN20 cell demonstrated remarkable long-term stability, maintaining stable performance for over 60 cycles in reversible operation mode (FC and EC modes, 250 h), followed by an additional 250 h in EC mode and 200 h in FC mode at 500 °C (Figure 4g). Post-XPS analysis (Figure S24, Supporting information) demonstrated that the oxidation states of PBSCN20 were substantially preserved after long-term stability measurement, suggesting good redox stability of PBSCN20 air electrode. Nevertheless, a slight degree of performance degradation was observed during each stability assessment, which is likely attributable to subtle microstructural changes in the air electrode rather than interfacial deterioration between the air electrode and electrolyte, as indicated in Figure S25 (Supporting information).

3. Conclusion

In summary, we successfully developed a highly efficient air electrode, $PrBa_{0.5}Sr_{0.5}Co_{2.0 \cdot x}Ni_xO_{5+\delta}$ (x = 0, 0.1, and 0.2), by partially doping Ni at the Co site in PBSCO for R-PCC applications. With respect to the hydration properties, TGA analyses and DFT simulations revealed that Ni doping effectively facilitated oxygen vacancy formation and proton uptake by reducing both the oxygen vacancy formation energy and the hydration energy near Ni cations. Moreover, Ni doping further reduced the energy barrier for proton migration, resulting in an exceptionally low ASR of 0.8

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Figure 4. a) Cross-sectional SEM image of the R-PCC with PBSCN20 air electrode. b) Arrhenius plot of ohmic and non-ohmic resistances for R-PCCs with PBSCO, PBSCN10, and PBSCN20 air electrodes between 450 and 600 °C. c) I-V and I-P curves of the R-PCC with the PBSCN20 air electrode. d,e) Comparison of the peak power densities and current densities at 1.3 V with those of previously reported air electrodes in a conventional single-cell configuration (fuel electrode/electrolyte/air electrode). f) I-V curve of the R-PCC with the PBSCN20 air electrode at 500 °C under 150 sccm of 10% H₂/Ar and 3% H₂O/air supply conditions. g) Hydrogen production rates and corresponding Faradaic efficiencies at 500 °C at various voltages. h) Long-term stability measurement at 500 °C for 700 h under various operating modes: reversible mode for 250 h, EC mode for 250 h, and FC mode for 200 h.

 Ω cm² at 500 °C in the BZCYYb4411-based symmetric cell. In reversible operations using R-PCCs, our cells with the PBSCN20 air electrode exhibited remarkable electrochemical performance in both the FC and the EC mode, achieving peak power densities of 1.30 and 0.60 W cm⁻² for the FC mode and current densities at 1.3 V of -1.72 and -0.41 A cm⁻² for the EC mode at 600 and 500 °C, respectively, along with outstanding long-term stability for over 700 h at 500 °C. Furthermore, a reliable Faradaic efficiency of over 60% was demonstrated at 1.3 V and 500 °C.

4. Experimental Section

Materials Preparation: BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3. δ} (BZCYYb4411) electrolyte powder was synthesized by the solid-state reaction (SSR). Stoichiometric amounts of BaCO₃ (Sigma Aldrich, 99%), ZrO₂ (Sigma Aldrich, 99%), CeO₂ (Alfa Aesar, 99.9%), Y₂O₃ (Alfa Aesar, 99.99%), and Yb₂O₃ (Alfa Aesar, 99.9%) were mixed with ethanol and ball-milled for 24 h. After removing the ethanol at 80 °C, the powder was pelletized and calcined at 1100 °C for 10 h in air. The above steps were repeated twice.^[49] PrBa_{0.5}Sr_{0.5}Co_{2.x}Ni_xO_{5+ δ} (PBSCN, x = 0, 0.1, 0.2, 0.3 and 0.4) air

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electrode powders were synthesized by the Pechini method. The corresponding compositions were denoted as PBSCO, PBSCN10, PBSCN20, PBSCN30, and PBSCN40, indicating Ni doping concentrations of x = 0, 0.1, 0.2, 0.3, and 0.4, respectively. Stoichiometric amounts of Pr(NO₃)₃·6H₂O (Sigma Aldrich, 99.9%), Ba(NO₃)₂ (Sigma Aldrich, 99+%), Sr(NO₃)₂ (Sigma Aldrich, 99.0%), Co(NO₃)₂·6H₂O (Sigma Aldrich, 98%), and Ni(NO₃)₂·6H₂O (Sigma Aldrich) were dissolved in distilled water. Then, citric acid (Alfa Aesar, 99.9+%) and ethylene glycol (Sigma Aldrich, 99.8%) were added as complexing agents. The nitrate solution was heated to 300 °C, followed by a self-combustion reaction to form the fine powder. The resultant powder was calcined at 600 °C for 4 h in air, ball-milled with acetone for 24 h, then dried in an 80 °C oven.

Cell Fabrication Procedure: The BZCYYb4411 electrolyte-based symmetric cells were prepared to investigate the area-specific resistances (ASRs) of PBSCN air electroles. To fabricate dense electrolyte support, the BZCYYb4411 electrolyte powder was compressed into pellets and sintered at 1600 °C for 24 h. The PBSCO, PBSCN10, and PBSCN20 air electrode slurries were prepared by mixing pre-calcined air electrode powders and the organic binder, ink vehicle (Fuel Cell Materials Inc.), in a weight ratio of 1:0.8. Each electrode slurry was screen-printed on both sides of the BZCYYb4411 electrolyte support, then sintered at 950 °C for 4 h in air.

The NiO-BZCYYb4411 fuel electrode powder was prepared by mixing NiO (Mechema, 99.9%), BZCYYb4411 electrolyte powder, and starch in a weight ratio of 65:35:5. Then, NiO-BZCYYb4411 fuel electrode powder was pelletized and lightly sintered at 800 °C for 4 h in air. To fabricate thin and dense BZCYYb4411 electrolyte layer, the BZCYYb4411 suspension was deposited on NiO-BZCYYb4411 layer by drop-coating method. The electrolyte suspension was prepared from BCZYYb4411 electrolyte powder and a multi-component organic fluid in a weight ratio of 0.9:10; the fluid was comprised of a mixture of 2-butanone (Alfa Aesar, 99%), ethyl alcohol (Sigma Aldrich, \geq 99.5%), polyvinyl butyral (Tape Casting Warehouse, TCW), butyl benzyl phthalate (TCW), polyalkylene glycol (TCW), and triethanolamine (Alfa Aesar). After drop-coating, the bi-layer (fuel electrode/electrolyte) was sintered at 1500 °C for 4 h. Then, the air electrode slurries were screen-printed on the BZCYYb4411 electrolyte layer and sintered at 950 °C for 4 h in air.

Characterization: The crystal structures of the PBSCO, PBSCN10, PB-SCN20, PBSCN30, and PBSCN40 air electrode powders were confirmed by an X-ray diffraction (XRD, Rigaku, SmartLab, Cu-Kα radiation, 40 k, 200 mA). The XRD patterns were collected over a 2theta range of 20 to 60° with a scanning rate of 2° min⁻¹. The lattice parameters were derived by the Rietveld refinement analysis of the XRD patterns using GSAS-II software. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and elemental energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were obtained by a Tecnai F20 G2 (ThermoFisher Scientific) with and Oxford Ultim Max TLE (Oxford) at 200 kV. To confirm the chemical stability of the air electrodes against chemical reaction with H₂O, each air electrode powder was annealed in 150 sccm of humidified air (20% H2O/air) at 500 °C for 100 h. And chemical compatibility with BZCYYb4411 electrolyte was verified by physical mixing the air electrode and BZCYYb4411 electrolyte powders, followed by heat treatment at 950 °C for 4 h. Additionally, mixed air electrode and BZ-CYYb4411 electrolyte composite powders were exposed to 150 sccm of humidified air (20% H_2O/air) at 500 °C for 100 h. In situ XRD (Malvern Panalytical, Empyrean, Cu Ka radiation) was conducted to assess thermodynamic phase stability of air electrodes against operating conditions. The PBSCO, PBSCN10, and PBSCN20 powders were placed in sample holder and heated up from room temperature to 1000 °C at a heating rate of 5 °C min⁻¹, with 100 °C intervals maintained for 30 min in air at each interval. The XRD patterns were recorded at 20 to 60 $^{\circ}$ within 2theta range, with at a scanning rate of 1 ° min⁻¹, after holding at each temperature for 30 min. The electrical conductivity of the PBSCO, PBSCN10, and PBSCN20 air electrodes was measured by 4-probe direct-current (DC) method under 3% humidified air conditions. Highly dense samples (relative density > 97%) were prepared by pelletizing each air electrode powder and sintering at 1100, 1150, and 1150 °C for 12 h, respectively. The microstructures of air electrodes and cross-sections of electrochemical cells were observed by field emission scanning electron microscopy (FE-SEM, Tescan MAIA III, 15 kV). The valence states of Pr, Co, Ni, and O in PBSCO, PBSCN10, and PBSCN20 air electrodes were characterized by X-ray photoelectron spectroscopy (XPS, ThermoFisher NEXSA) using a monochromatic Al $K\alpha$ source ($h\nu = 1486.6$ eV). The XPS spectra were acquired with a beam size of 400 µm, and a filament current of 6 mA under a vacuum pressure of 1.7 to 2.3×10^{-7} mbar. Survey and high-resolution spectra were collected with pass energies of 100 and 25 eV, and step sizes of 1.0 and 0.1 eV, respectively. To ensure data reliability, 25 acquisition cycles were applied for Co, Pr, and O. In particular, the number of cycles for Ni was further increased to 45 due to its relatively low atomic concentration. The initial oxygen contents $(5+\delta)$ for PBSCO, PBSCN10, and PBSCN20 were evaluated iodometric titration.^[50] Thermogravimetric analysis (TGA, SDT Q600) was performed to evaluate temperature-dependent oxygen non-stoichiometry (δ) and proton concentration. The powder samples (PBSCO, PBSCN10, and PBSCN20) were initially heated from room temperature to 800 °C under dry air conditions, and weight changes were recorded during cooling from 800 to 200 °C. After holding at 200 °C and dry air conditions for 1 h, the gas supply was switched from dry air to humidified air $(3\% H_2O/air)$. The weight changes in humidified air were recorded while powder samples were reheated from 200 to 800 °C. Consequently, the proton concentration was derived by the weight difference of the powder samples between dry and wet air conditions, using Equation (3).

Computational Details: Spin-polarized DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) software with projector-augmented wave (PAW) method to describe core-valence electron interactions.^[51,52] DFT-D3 method was applied to account for van der Waals corrections.^[53,54] The plane-wave cutoff energy of 500 eV was used. The energy and force convergence criteria were set to 10^{-4} eV and 0.01 eV Å⁻¹, respectively. The Brillouin zone was sampled using a 3×3 × 4 Monkhorst-Pack k-point grid. DFT+U approach was used to treat the Co-3d and Ni-3d orbitals with effective on-site Coulomb interaction parameters (U_{eff}) of 3.0 eV for Co and 5.5 eV for Ni $^{\left[55\right] }$ To model the structure of Ni-doped PBSCO, the lattice parameter of a ($\sqrt{2} \times \sqrt{2} \times 1$) PBSCO (a = 5.49 Å and c = 7.83 Å) were optimized as a host structure. The lattice constant optimization results are presented in Figure S13a (Supporting information). In the case of PBSCN20, the most stable configuration between two possible nearest neighbor sites of Ni dopants was used to focus on the effect of dopant concentrations on the material properties (Figures S13b,c, Supporting information).

The formation of hydroxide defects (OH_O) in perovskites was essential for proton diffusion because the proton transport occurs through the following steps: 1) dissociative adsorption of water molecules at oxygen vacancies, 2) dissociation of water forms hydroxide defects (H₂O + V_O⁻ + O_O[×] \rightarrow 2OH_O),^[56-58] and 3) hydrogen of the hydroxide defects (OH_O⁻) moves to another oxygen atom in perovskite. The oxygen vacancy formation energy (E_{vac}) was calculated as:^[59]

$$E_{vac} = E_{defect} - E_{bare} + \frac{1}{2}E_{O_2}$$
(8)

where E_{defect}, E_{bare} , and E_{O2} represent the energy of the system with an oxygen vacancy, the energy of the pristine system, and the energy of a gas phase oxygen molecule, respectively. The hydration energy (E_{hyd}) was calculated by:^[60]

$$E_{hyd} = E_{2OH} - E_{defect} + E_{H_2O}$$
(9)

where E_{2OH} , E_{H2O} represent the energy of the hydroxylated system, and the energy of a gas-phase water molecule, respectively. The climbing image nudged elastic band (CI-NEB) method was employed to calculate the proton migration barrier with a force convergence criterion of 0.03 eV Å^{-1,[61]} Crystal orbital Hamilton population (COHP) and integrated COHP (ICOHP) were calculated using the LOBSTER code.^[62]

Electrochemical Measurement: For electrochemical performance measurements, Ag wires (Good Fellow) and Ag paste (SPI supplies) were used as current collectors and attached to both electrodes. Then, the electrochemical (or symmetric) cells were fixed and sealed by a ceramic adhesive (Ceramabond 552, Aremco) onto an alumina tube. During the



electrochemical measurements, 150 sccm of humidified air (3% H₂O) was supplied to the air electrode. And 50 sccm of humidified H_2 (3% H_2O) was supplied to the fuel electrode. For area-specific resistance studies using symmetric cells, 150 sccm of humidified air (3% H₂O) was supplied to both electrodes. The electrochemical impedance spectra (EIS) and I-V curves were collected using a BioLogic VSP-300 potentiostat. EIS was performed under the open circuit voltage (OCV) condition with frequency range of 100 kHz to 0.1 Hz and an AC amplitude of 20 mV. The Faradaic efficiency of R-PCC was evaluated by quantifying the H₂ produced in the exhaust gas using gas chromatography (GC, Agilent 7890A) equipped with a thermal conductivity detector (TCD). Each GC measurements were performed for 10 min after the OCV (or current) stabilized. Minor disturbances were observed at the onset of GC measurement, but the OCV (or current) values were fully recovered to the respective initial levels. A linear calibration curve was established by the measured H_2/Ar peak area ratios under various hydrogen partial pressure (14% to 6% H₂/Ar) and OCV conditions (Figures S23a, Supporting information). During the GC measurement, 3% H₂O/air were supplied to the air electrodes. To further confirm the reliability of the calibration curve, the hydrogen partial pressure was increased again to $10\% H_2/Ar$, and the corresponding H_2/Ar area ratio was re-measured, showing excellent agreement with the initial value. Based on the obtained H₂/Ar area ratios, a calibration curve was established by linear fitting of five data points ($R^2 = 0.9983$, Figure S23b, Supporting information). The long-term stability measurement of the R-PCC was conducted at 500 °C at several voltages (reversible operation at 1.3 and 0.7 V for 250 h, EC mode at 1.3 V for 250 h, and FC mode at 0.7 V for 200 h).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

air electrode, hydration property, layered perovskite, Ni doping effect, proton migration, reversible protonic ceramic cells

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