Article
Rational A/B Site Ion Doping to Design Efficient and Stable \( Pr_{0.5}Ba_{0.4}Ca_{0.1}Fe_{1-x}Co_xO_{3-\delta} \) Perovskites as Zinc–Air Batteries Cathode

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Abstract: The development of robust and efficient electrocatalysts for use in fuel cells and metal–air batteries has garnered a great deal of interest due to the quest for clean and renewable energy sources. In this paper, a promising Co-doped \( Pr_{0.5}Ba_{0.4}Ca_{0.1}Fe_{1-x}Co_xO_{3-\delta} \) \((x = 0, 0.2, 0.4, 0.6, 0.8; \text{denoted as PBCFC-x, } x = 0, 2, 4, 6, 8)\) with enhanced durability and electrocatalytic ORR/OER activity for zinc–air battery cathode catalysts is presented. Particularly, PBCFC-6 exhibits the best bifunctional catalytic activity in alkaline media among several materials, according to research using the RDE. The zinc–air battery with PBCFC-6 as the cathode catalyst delivered the smallest discharge–charge voltage difference at the current density of 10 mA \( \cdot \) cm\(^{-2}\) and only increased by 0.031 V after 220 cycles (220 h), demonstrating its superior bifunctional catalytic activity and durability. The optimized electrochemical performance of both OER and ORR as well as stability in zinc–air batteries might result from the higher electrical conductivity, increasing concentration of adsorbed oxygen, and the greater proportion of Fe\(^{4+}\) \((t_2g^3e_g^1)\) with optimal electron occupancy, owing to the partial replacement of Fe with Co.

Keywords: \( Pr_{0.5}Ba_{0.4}Ca_{0.1}Fe_{1-x}Co_xO_{3-\delta} \); rechargeable zinc–air batteries; ORR/OER; bifunctional catalyst

1. Introduction

Given the complicated global situation and the ongoing depletion of fossil energy sources, there is urgency in researching and developing sustainable and environmentally friendly conversion and storage devices, such as fuel cells and metal–air batteries [1–11]. A growing number of studies on zinc–air batteries have been conducted due to their superior chemical reversibility and greater safety compared to other types of metal–air batteries. The study and innovation of air electrode catalysts for zinc–air batteries are mainly centered on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [12–15]. Until now, the best materials for OER/ORR catalysis have been the noble metals represented by Pt/C and RuO\(_2\), etc. [8]. However, the limited stability, poor catalytic efficacy, and expensive price of precious metal materials prevent their wider application [16–18]. Thanks to the flexibility of the B-site and A-site cations and the O-site anion, ABO\(_3\)-type perovskites typically exhibit a variety of structural and physicochemical features [19–25]. In addition, given their relatively low cost and abundant deposits, they are anticipated to take the replacement of precious metal catalysts in zinc–air battery cathode catalysts [20,26–29]. Therefore, to handle the obstacles of sluggish ORR and OER kinetics and facilitate the commercial scale-up of zinc–air batteries, it is vital to develop low-cost perovskite catalysts with excellent catalytic performance and durability.

Alexis et al. reported a range of \((Ln_{0.5}Ba_{0.5})CoO_{3-\delta}\) \((Ln = Sm, Pr, Ho, and Gd)\) as OER high-activity catalysts, with samples where Pr was present in the Ln position demonstrating the best performance [30]. Numerous researchers have studied the \( Pr_{0.5}Ba_{0.5}Co_{3-\delta} \)-based perovskite extensively using surface modification, ion doping, and nanosizing [31–37].
He et al. reported that minimal doping of Ca increases the corrosion resistance of perovskite oxides by preventing Ba leaching and surface degradation, thereby improving their structural stability to provide enduring OER performance [38]. According to Li et al., the Co-Fe of BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ doped with Co ions at the B-site would have lower defect formation energy, modulating its oxygen vacancy concentration and enhancing its catalytic activity [39]. Due to their affordable price and acceptable catalytic activity, Fe-based perovskites have drawn a lot of attention lately [34,40–43]. Since the lower electrical conductivity of Fe-based perovskites is not favorable for charge transfers during catalytic reactions, their catalytic activity is relatively poor compared to that of Co-based perovskites. Previously, the bifunctional catalytic activity of PrFeO$_{3-δ}$-based perovskites has been poorly investigated. Therefore, a thorough understanding of the characteristics of PrFeO$_{3-δ}$-based perovskites is crucial to enhance their bifunctional catalytic activity through rational design.

Herein, we designed a series of PBCFC-x (x = 0, 2, 4, 6, 8) by a citrate–nitrate combustion process with trace Ca ion doping at the A-site and Co ion substitution at the B-site to probe the highly catalytically active and durable perovskite oxides. The catalytic activity of the obtained catalyst materials was then investigated in 0.1 M KOH solution. The aforementioned materials’ physicochemical characteristics, including surface shape, crystal structure, surface species, and elemental valence, were investigated using XRD, SEM, EDS, and XPS to figure out the altered ORR/OER activity. Additionally, the bifunctional catalytic performance and the durability of a series of perovskite materials as cathode catalysts was evaluated via a homemade zinc–air battery at room temperature in constant current discharge and long-term cycle tests.

2. Experimental Section

2.1. The Synthesis of Material

A range of PBCFC-x (x = 0, 2, 4, 6, 8) perovskite materials was prepared by applying the citrate–nitrate combustion process. All drugs were analytically pure from Aladdin and were not further purified before conducting the experiments. First, in order of ease of dissolution, specific amounts of Pr$_6$O$_{11}$, Ba(CO$_3$)$_2$, Ca(CO$_3$)$_2$, Fe(NO$_3$)$_3$·9H$_2$O, and Co(NO$_3$)$_3$·6H$_2$O were dissolved in a vigorously magnetically stirred dilute nitric acid solution. Citric acid and ethylenediaminetetraacetic acid were added as complexing agents in a 1:2:1 ratio of AC: EDTA: metal ions and the solution’s pH was controlled at around 7 by the addition of ammonia dropwise. The solution was stirred in a 60 °C water bath for 24 h until the metal cations were fully complex. The complexed solution was then heated on an evaporating dish in an electric furnace until spontaneous combustion of the precursors was obtained. The precursors were heated to 900 °C for 5 h and annealed at a rate of 2 °C/min under air conditions to obtain the corresponding perovskite materials.

2.2. Characterizations

The purity and crystal structures of perovskite catalysts were determined over the scanning angular range of 10° to 90° by X-ray diffraction (XRD, 40 kV and 15 mA, λ = 1.5418 Å, Cu-Kα radiation, PANalytical Aeris, Melbourne, Australia). The field emission scanning electron microscope (SEM, Hitachi S-4800, Tokyo, Japan) equipped with energy dispersive X-ray spectroscopy (EDS) was performed to deeply examine the elemental composition and surface morphology of the as-prepared catalysts. The Brunauer–Emmett–Teller (BET, ASAP2460, Norcross, GA, USA) method was used to determine the specific surface area of the prepared perovskite oxides. The surface cation valence states and oxygen-related species were explored using X-ray photoelectron spectroscopy (XPS, Al Ka radiation, AXIS-His spectrometer, Waltham, MA, USA). The measured XPS binding energy was calibrated regarding the peak of the standard C 1s at 284.8 eV. To examine the as-prepared material’s conductivity, the PBCFC-x samples were pressed into strips and sintered in an air atmosphere at 1100 °C for 10 h to ensure their denseness and were tested at room temperature using the four-probe method.
2.3. Electrochemical Measurements

To make the uniform electrocatalyst slurry, 5 mg of conductive carbon black (XC72R), 5 mg of catalyst, and 50 µL of Nafion solution (5 wt %) were added to a mixture of isopropanol (400 µL) and deionized water (100 µL), followed by sonication for 2 h. The homogenized slurry was then transferred in 5 µL to a polished glassy carbon (GC, 0.196 cm² area) electrode and allowed to dry at room temperature for an entire night, with a catalyst loading of 0.232 mg·cm⁻². In addition, commercially available Pt/C (20 wt.%) and IrO₂ were tested using the same preparation process as a reference catalyst.

The ORR and OER tests were carried out using rotating disc electrodes (RDE) in a three-electrode system. A Pt wire, GC electrodes coated with catalyst films, and SCE were employed as the counter, the work, and the reference electrodes. All electrochemical tests were performed using the CHI760E electrochemical station in an O₂-saturated 0.1M KOH aqueous solution at room temperature. It should be mentioned that all potentials tested vs. SCE were handled with IR corrected and converted to the potential vs. RHE. The LSV (1600 rpm, 10 mV·s⁻¹) for OER and ORR was recorded over a potential range of 0 to 1 V and −0.9 to 0.2 V (vs. SEC), respectively. It is necessary to maintain oxygen saturation in the electrolyte utilized during the ORR and OER test.

The following Koutecky–Levich (K–L) equation was employed to determine the electron transfer number to examine the dominated pathway in ORR of the as-prepared perovskite materials [42]:

\[
j = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{j_k} + \frac{1}{f_0 \omega^{1/2}} = \frac{1}{j_k} + \frac{1}{0.62 F \Delta Q_2 D \nu^{-1/2} \omega^{1/2}} \tag{1}\]

where, \(j\), \(j_k\), and \(j_l\) in the above equations respond to the measured, kinetic, and diffusion-limiting current density, respectively. \(v\), \(F\), \(\omega\), \(D\), \(\nu\), and \(\Delta Q_2\) are the kinetic viscosity of 0.1 M KOH solution, Faraday constant, rotating rate, the diffusion coefficient of oxygen, electron transfer number, and saturated bulk concentration of oxygen, respectively.

2.4. Characterization and Preparation of Zinc–Air Batteries

To evaluate both the stability and catalytic performance of as-prepared materials as cathode catalysts under practical working conditions, a homemade zinc–air battery was assembled. To prepare the catalytic layer for the air electrode, a mixture of acetylene black (Li-2060): catalyst: activated carbon (YP50F): polytetrafluoroethylene emulsion (PTFE, 60 wt%, teflon) at a ratio of 1:3:3:3 was stirred vigorously in alcohol for at least 3 h to produce a homogeneous suspension. The homogeneous mixture was then loaded to one side of the flattened nickel foam after being dried to a gel-like solid at 80 °C, resulting in a loading of approximately 5 mg·cm⁻² (only perovskite). The gas diffusion layer was coated to another side of the nickel foam, except that the weight ratio of PTFE: acetylene black was 7:3. The area of the positive and negative electrodes were 4 cm² and 6.25 cm², respectively. To realize the durability and the catalytic properties of the prepared samples, a cycle (30 min for discharge, 30 min for charge) and constant current discharge experiment was carried out at room temperature for zinc–air batteries with different perovskite oxides as air electrode catalysts. There are some differences between the negative electrode and electrolyte used in homemade rechargeable and primary zinc–air batteries. The former uses 1 mm thick polished zinc flakes and a 6M KOH + 0.2M zinc acetate solution, while the latter uses zinc powder pressed into flakes and a 6M KOH solution. Both constant current discharge and cycling tests of the batteries were carried out at a current density of 10 mA·cm⁻² using the NEWARE battery system (Fujian, China).

3. Results and Discussion

According to the XRD patterns of Figure 1, a series of Co-doped PBCFC-x (x = 0, 2, 4, 6, 8) demonstrate a well-crystallized phase of perovskite. The diffraction peaks of PBCFC-x reveal a tetragonal phase with a space group of P4mm, proving that there was no phase
change after Co doping [40,44,45]. As can be seen, the peak positions of PBCFC-x shift to the right since element Co is doped, indicating a contraction in lattice volume. The positive movement of the PBCFC-x diffraction peak can be directly traced to the position of the Fe$^{3+}$/Fe$^{4+}$ (0.645/0.585 Å) occupied by the Co$^{3+}$/Co$^{4+}$ (0.615/0.53 Å) with a smaller ionic radius. The refinement profile and pertinent crystalline parameters for the as-prepared PBCFC-x (x = 0, 2, 4, 6, 8) samples analyzed using the Rietveld method are shown in Figure S1 and Table S1, respectively. The lattice parameters obtained from the refinement correspond to the XRD data obtained from the testing of the PBCFC-x (x = 0, 2, 4, 6, 8) samples. The trend of cell volume reduction of the above Co-doped samples coincides well with the positive shift of its peak position.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of PBCFC-x (x = 0, 2, 4, 6, 8) (a), their magnified diffraction peaks (b).

SEM images of PBCFC-x (x = 0, 2, 4, 6, 8) powder samples were employed to identify its morphology since there is a meaningful relationship between the quantity of its catalytically active sites and its particle size. As can be seen in Figure 2, all samples were not uniform in size and partial agglomerates, with the most pronounced agglomeration occurring in PBCFC-0. Furthermore, the Scherrer Equation was employed to analyze the XRD images of PBCFC-x (x = 0, 2, 4, 6, 8) samples analyzed using the Rietveld method are shown in Figure S1 and Table S1, respectively. The lattice parameters obtained from the refinement correspond to the XRD data obtained from the testing of the PBCFC-x (x = 0, 2, 4, 6, 8) samples. The trend of cell volume reduction of the above Co-doped samples coincides well with the relatively homogeneous distribution of each element in the EDS pattern.

Rotating disk electrode technique measurements were carried out in O$_2$-saturated 0.1 M KOH solutions to assess the ORR electrocatalytic performance of PBCFC-x (x = 0, 2, 4, 6, 8) samples with different Co contents. The Linear scanning voltammetry(LSV) curves of various catalyst samples at 1600 rpm were compared to evaluate their ORR catalytic performance, as shown in Figure 3a. In comparison to other catalyst materials with various Co compositions, the onset potential of PBCFC-6 is significantly shifted in a more positive direction. The half-wave potential of the as-prepared catalyst materials follows the order of PBCFC-6 (0.59 V vs. RHE) > PBCFC-8 (0.568 V vs. RHE) > PBCFC-4 (0.566 V vs. RHE) > PBCFC-2 (0.563 V vs. RHE) > PBCFC-0 (0.524 V vs. RHE). Furthermore, PBCFC-6 possesses the highest limiting current density when compared to other materials, which means that the right amount of Co doping helps increase the ORR catalytic activity. As shown in Figure 3b, the electron transfer pathway of perovskites doped with different Co components was further investigated by fitting LSV pictures (Figure S3) over a range of different speeds (225–2500 rpm) using a K–L equation. Apparently, the values of electrons transferred by Co-doped PBCFC-2 (3.92), PBCFC-4 (3.72), PBCFC-6 (3.83), and PBCFC-8 (3.75) were closer to four relative to the 2.78 of PBCFC-0, demonstrating that a four-electron
dominated pathway to reduce oxygen to OH⁻ in the ORR is more likely to be used when Fe is partially replaced with Co in perovskite oxides [46,47].

![Figure 2. SEM images of PBCFC-0 (a), PBCFC-2 (b), PBCFC-4 (c), PBCFC-6 (d), and PBCFC-8 (e) samples.](image)

![Figure 3. ORR polarization curves of PBCFC-x (x = 0, 2, 4, 6, 8) at 1600 rpm (a); The value of electrons transferred for PBCFC-x (x = 0, 2, 4, 6, 8) at 0.4 V vs. RHE (b).](image)

To explore more about the bifunctional performance of PBCFC-x (x = 0, 2, 4, 6, 8) catalysts, the OER catalytic activity of the prepared materials was examined in 0.1 M O₂-saturated KOH solution by LSVs at 1600 rpm. It is worth mentioning that PBCFC-6 had the lowest potential (1.621 V vs. RHE) among other materials at a current density of 10mA·cm⁻² and was lower than the 1.63 V vs. RHE of precious metal material RuO₂ (Figure 4). The overpotentials (η) of PBCFC-0, PBCFC-2, PBCFC-4, PBCFC-6, and PBCFC-8 were 439 mV, 415 mV, 415 mV, 391 mV, and 408 mV, respectively. As shown in Figure 4, the kinetics toward the OER activity of perovskites doped with different Co components were further investigated by the Tafel plot. The Tafel slopes of OER for PBCFC-0, PBCFC-2, PBCFC-4, PBCFC-6, and PBCFC-8 were 89, 89, 87.3, 85.7, and 96·dec⁻¹mV·dec⁻¹, respectively. The minimum Tafel slopes of PBCFC-6 responded to the significant increase in OER intrinsic activity following Co doping. The PBCFC-6 had the lowest polarization resistance, as seen in Figure 4c, which highlights its improved capacity for charge transfer during the OER [48]. Figure S3 depicts CV curves for various scan speeds (20–120 mV·s⁻¹) in the non-Faraday region, and from this, the double-layer capacitance (Cdl) values were calculated for perovskite materials with different Co-doping compositions. The obtained Cdl of PBCFC-0, PBCFC-2, PBCFC-4, PBCFC-6, and PBCFC-8 were 2.6mF·cm⁻², 2.29 mF·cm⁻², 2.69 mF·cm⁻², 4.49 mF·cm⁻², and 3.9 mF·cm⁻², respectively. The maximum Cdl of PBCFC-
6 demonstrates a wider electrochemically active surface area (ECSA), which undoubtedly helped strengthen the efficiency of OER. As can be seen in Figures S5 and S6, the amperometric i-t curve and CV tests were utilized to verify the OER stability of the PBCFC-0 and PBCFC-6. The overpotentials (\( \eta \)) of the PBCFC-6 diminish by just 13 mV after 500 CV tests and does not continue to decay after 1000 cycles when compared to the undoped PBCFC-0. The amperometric i-t curve of the two materials also demonstrates the significance of Co doping in improving the OER stability of PBCFC-x.

The bifunctional catalytic activity of the as-prepared PBCFC-x (x = 0, 2, 4, 6, 8) was evaluated by calculating the difference (\( \Delta E \)) between the half-wave potential and 10 mA cm\(^{-2} \) in the LSV curves of the ORR and OER. As shown in Table S2, the bifunctional catalytic performance of as-prepared catalyst materials follows the order of PBCFC-6 (\( \Delta E = 1.03 \) V) > PBCFC-8 (\( \Delta E = 1.06 \) V) > PBCFC-4 (\( \Delta E = 1.07 \) V) > PBCFC-2 (\( \Delta E = 1.08 \) V) > PBCFC-0 (\( \Delta E = 1.14 \) V). Particularly, PBCFC-6 exhibits the best bifunctional catalytic activity in alkaline media among several materials and even can compare to the noble metal catalyst Pt/C (\( \Delta E = 1.03 \) V), according to research using the rotating disk electrode technique.

The surface oxygen species and the transition metal ion state of PBCFC-0 and PBCFC-6 were examined by XPS since there is a significant relationship between the catalytic activity of OER/ORR and the chemical makeup on the surface of the perovskite. The survey spectrum of the as-prepared PBCFC-6 reveals clear Pr 3d, C 1s, Co 2p and Ba 3d, O 1s, Ca 3d, and Fe 2p peaks, as illustrated in Figure 5a. The O 1s spectra were deconvoluted into four distinct diffraction peaks, A (lattice oxygen species, O\(^{2-} \)), B (highly oxidative oxygen, O\(^{2-}/O^2- \)), C (surface adsorbed oxygen/hydroxyl groups, O\(_2^2-/OH^- \)), and D (molecular water/carbonates, H\(_2\)O/CO\(_3^{2-} \)) [49,50]. By fitting the peak areas, it was revealed that PBCFC-6 represented a comparatively higher amount of adsorbed oxygen, which will contribute to increasing the strength of the B-O bond and thus speeding up the rate-limiting O\(_2^{2-}/OH^- \) substitution and OH\(^- \) regeneration during the ORR [51]. Accordingly, it is

Figure 4. OER polarization profiles (1600 rpm) of PBCFC-x (x = 0, 2, 4, 6, 8) perovskites (a); The Tafel slope derived from the OER plots (b); The EIS at 0.6 V vs. SCE (c); The function of different scan rates and the current densities at 0.25 V vs. SCE for the PBCFC-x (x = 0, 2, 4, 6, 8) materials (d).
predicted that the improved O$_2^{2-}$/OH$^-$ percentage in PBCFC-6 will have a positive effect on ORR efficiency. Additionally, the rising hydroxyl oxygen concentration encourages the chemisorbed OOH$^-$ formation during the OER process, thus boosting its OER catalytic efficiency. Compared to PBCFC-0 (18.3%), the relatively higher proportion of adsorbed surface water of PBCFC-6 (21.1%) means that it is more hydrophilic, which facilitates better wettability of the catalyst sample with the electrolyte, thus positively affecting the OER/ORR performance [52].

Upon deconvolution, the presence of Fe$^{4+}$ and Fe$^{3+}$ was confirmed to be around 711.86 and 710.14 eV in the Fe 2p$_{3/2}$ region of the spectrum [53]. The percentages of Fe$^{4+}$ for PBCFC-0 and PBCFC-6 were determined to be 52.8% and 59.8% by calculating the regions of the peaks separately. Given the optimal $e_g$ orbital filling ($t_{2g}^3e_g^1$) of Fe$^{4+}$, the slightly increased amount of Fe$^{4+}$ ions in PBCFC-6 is estimated to lead to improved OER properties [52–56]. As shown in Figure 5d, the peaks of Ba3d and Co2p overlapped heavily in their spectra due to their very close positions, while some previous reports have confirmed the presence of Co$^{3+}$ and Co$^{2+}$ to be around 779.7eV and 781.1 eV, respectively [34]. Therefore, the presence of Co$^{3+}$ ions in PBCFC-6 is also estimated to positively affect the OER/ORR performance owing to the optimal $e_g$ orbital filling of Co$^{3+}$ [22,55].

Numerous catalysts’ bifunctional catalytic activity in 0.1 M KOH solution was characterized by RDE, and a homemade zinc–air cell operating at room temperature was used to evaluate both the stability and catalytic performance of these materials in practical working conditions. A primary zinc–air battery’s working mechanism is depicted in Figure 6a. For a homemade primary zinc–air battery, the electrolyte and negative electrode are a 6M KOH solution and zinc powder pressed into flakes, respectively. The power density and LSV curves for the primary zinc–air batteries using PBCFC-x as the air cathode catalyst are depicted in Figure 6b. The maximum power densities of PBCFC-0, PBCFC-2, PBCFC-4, PBCFC-6, and PBCFC-8 were 55.85, 67.1, 66.33, 74.76, and 62.68 mW·cm$^{-2}$, respectively. As is noticeable, PBCFC-6 exhibited the best ORR performance among several perovskite
materials with a peak power density 1.34 times greater than that of undoped PBCFC-0. To assess the cathode’s performance when using various materials as catalysts, EIS was measured at a cell voltage of 1 V. To further investigate the reasons for the improved performance of the Co-doped catalysts, their impedance spectra were fitted separately by Zview. Figure 6c illustrates the equivalent circuit’s five parts: \( R_s \), \( R_{ct} \), \( R_{int} \), \( Q_{dl} \), and \( Q_{int} \) where \( Q_{int} \) and \( Q_{dl} \) stand for the capacitances produced by the electrode–electrolyte interface [56]. \( R_s \) is associated with the concentration of the electrolyte and the distance between the positive and negative electrodes, which corresponds to the electrolyte and contact resistance. The \( R_{int} \) and \( R_{ct} \) are defined as the solid electrolyte interface resistance and the air electrode charge transfer impedance, respectively [57]. Table 1 lists the aforementioned parameters that were obtained through fitting. Since the electrolyte and positive and negative pole spacing in the tests were similar, PBCFC-x had a relatively similar ohmic resistance of around 0.88. As \( R_{int} \) is tightly dependent on the intrinsic conductivity of the perovskite catalyst, we tested its conductivity at room temperature by the four-probe method. The conductivity of PBCFC-0, PBCFC-2, PBCFC-4, PBCFC-6, and PBCFC-8 were 8.931 \( \times \) 10\(^{-6} \) S cm\(^{-1} \), 0.186 S cm\(^{-1} \), 0.369 S cm\(^{-1} \), 4.193 S cm\(^{-1} \), and 2.945 S cm\(^{-1} \). It was revealed that the appropriate Co doping increases the electrical conductivity of perovskite oxide significantly. In comparison to PBCFC-0 (0.31 \( \Omega \)), the lower \( R_{int} \) of PBCFC-6 (0.20 \( \Omega \)) benefits from its superior hydrophilicity, which corresponds to the relatively higher proportion of water adsorbed on its surface, as determined by XPS data. Among several materials, the zinc–air battery with PBCFC-6 as an air electrode catalyst possessed the smallest \( R_{ct} \) of 0.47, suggesting that it has a higher intrinsic ORR catalytic activity. Furthermore, the zinc–air battery with PBCFC-6 as a cathode catalyst had the lowest polarization resistance compared to any of the samples tested. As shown in Figure 6, the long-term output performance of primary zinc–air batteries with different materials as air electrode catalysts was tested at room temperature at a current density of 10 mA cm\(^{-2} \). Obviously, the primary zinc–air batteries adopted PBCFC-x (x = 2, 4, 6, 8) as the air cathode catalyst displays a higher discharge voltage and discharge time than undoped PBCFC-0. In comparison to PBCFC-0, PBCFC-2, PBCFC-4 and PBCFC-8, the zinc–air battery utilizing PBCFC-6 as the air cathode catalyst expressed the greatest discharge voltage across the discharge process.

To realize the cycle capabilities of as-prepared perovskite oxides, a cycle (30 min for discharge, 30 min for charge, 10 mA cm\(^{-2} \)) experiment was carried out at room temperature for zinc–air batteries with different air electrode catalysts. For homemade rechargeable zinc–air batteries, the electrolyte and negative electrode are 6M KOH + 0.2 M acetate zinc solution and a 1 mm-thick polished zinc plate, respectively. Figure 7a,b presents the discharge cut-off voltage and charge cut-off voltage curves for the discharge–charge cycle of batteries with different perovskites as air cathode catalysts, respectively. Apparently, PBCFC-6 displays higher discharge voltages and lower charging voltages than the other four perovskites during the discharge–charge cycle test, demonstrating its superior energy efficiency. The variation of the discharge–charge voltage difference during the cycle test for the batteries with PBCFC-x (x = 0, 2, 4, 6, 8) as the oxygen electrode catalysts was shown in Table S3 where \( \Delta E_1 \), \( \Delta E_{100} \), and \( \Delta E_d \) represent the difference in discharge–charge cut-off voltage for the first cycle, the 100th cycle, and the difference between them, respectively. In comparison with other materials, PBCFC-6 possessed a lower \( \Delta E_1 \) of 0.827 V, which corresponds to its excellent ORR and OER activity. As shown in Figure 7, the voltage difference after 220 cycles (220 h) of batteries with PBCFC-6 as the oxygen electrode catalyst was 0.861 V, an increase of only 0.031 V compared to the first cycle, demonstrating the superior stability of PBCFC-6. Table S4 shows a comparison of the cycle life of PBCFC-x and other published materials used as cathode catalysts for zinc–air batteries. The comparison with previous materials indicated that PBCFC-6 is a durable cathode catalyst. All the above studies show that Co-doped PBCFC-6 possesses excellent bifunctional catalytic activity as well as high stability and might be an efficacious bifunctional catalyst.
Comparison of cycling curves for PBCFC-x (x = 0, 2, 4, 6, 8) as the oxygen electrode catalyst. The cycling curves for PBCFC-6 showed higher discharge voltages and lower charging voltages than the other materials, demonstrating its superior bifunctional catalytic activity and high stability in zinc–air batteries. As shown in Figure 6, the long circuit components produced by the EIS values of different materials as air electrode catalysts might result from the higher electrical conductivity, which corresponds to the excellent OER and ORR activity of PBCFC as the air cathode catalyst.

The optimized air electrode catalyst for zinc–air batteries utilizing PBCFC-x (x = 0, 2, 4, 6, 8) is presented and used in zinc–air batteries, resulting in higher energy efficiency. The variation of the discharge voltage difference during the cycle for PBCFC-6 during 220 cycles (220 h) of batteries with PBCFC-6 as the air cathode catalyst expressed the greatest discharge voltage across the discharge cycle test, demonstrating its superior activity as well as high stability and might be an efficacious bifunctional catalyst.

Table 1. Power density and LSV profiles for PBCFC-x (x = 0, 2, 4, 6, 8) air electrode. The power density and LSV profiles for zinc–air batteries with PBCFC-6 as the air cathode catalyst disfavorably affects the ORR/OER electrocatalytic activity. In comparison with other materials, PBCFC-6 displays higher discharge voltages and lower charging voltages than the other materials, which plays a higher discharge voltage and a lower charging potential.

Figure 7. Constant current discharge cut-off voltage (a); Constant current charge cut-off voltage (b) of per cycle for a rechargeable zinc vacant battery with PBCFC-x as the oxygen electrode at 10 mA cm\(^{-2}\); Comparison of cycling curves for PBCFC-x (c); Cycling curves for PBCFC-6 (d).
Table 1. The equivalent circuit components produced by the EIS values of PBCFC-x (x = 0, 2, 4, 6, 8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>R_S (Ω)</th>
<th>R_{int} (Ω)</th>
<th>R_{ct} (Ω)</th>
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<td>PBCFC-0</td>
<td>0.89</td>
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<td>0.83</td>
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</table>

4. Conclusions

In summary, a promising Co-doped Pr_{0.5}Ba_{0.4}Ca_{0.1}Fe_{1-x}Co_{x}O_{3-δ} (x = 0, 2, 4, 6, 8) is presented and used in zinc–air batteries as an air electrode catalyst to verify its durability and ORR/OER electrocatalytic activity. As an air electrode catalyst for zinc–air batteries, PBCFC-6 demonstrated a higher peak power density (74.76 mW/cm²) and longer cycle time than other materials, demonstrating its superior bifunctional catalytic activity and durability. The optimized electrochemical performance of both OER and ORR as well as stability in zinc–air batteries might result from the higher electrical conductivity, increasing concentration of adsorbed oxygen, and the greater proportion of Fe^{4+} with optimal electron occupancy, owing to the partial replacement of Fe with Co. All these results provide a reasonable strategy for designing more efficient and stable perovskite oxides as an air electrode catalyst for rechargeable zinc–air batteries.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/batteries8120259/s1, Figure S1: Rietveld refinement of X-ray powder diffraction pattern of PBCFC-0 (a), PBCFC-2 (b), PBCFC-4 (c), PBCFC-6 (d), PBCFC-8 (e) samples; Figure S2 EDX images of PBCFC-0 (a), PBCFC-2 (b), PBCFC4 (c), PBCFC-6 (d), PBCFC-8 (e); Figure S3: The N_{2} adsorption/desorption isotherms for PBCFCx (x = 0, 2, 4, 6, 8) catalysts. The inset shows the BET surface area for all perovskite materials; Figure S5: LSV curves for PBCFC-0 and PBCFC-6 catalysts before and after 500th and1000th CV (100 mV·s^{-1}) cycles test; Figure S6: The amperometric i-t curve for PBCFC-0 and PBCFC-6 catalysts at an initial current of 10 mA·cm^{-2}; Figure S7 SEM photographs of the zinc negative electrode before (a) and after (b–d) cyclic charging and discharging; Table S1: List of Calculated Lattice Parameters of PBCFC-x through a Rietveld Refinement Method; Table S2: the bifunctional catalytic activity of various materials; Figure S4: CV curves of PBCFC-0 (a), PBCFC-2 (b), PBCFC-4 (c), PBCFC-6 (d) and PSFM-8 (e) at scan rates from 20 to 100 mV·s^{-1} and linear fitting of the current density difference versus the scan rates at 1.25 vs. RHE; Table S3: The variation of the charge/discharge voltage difference during the cycle of a zinc-air battery with PBCFC-x as the oxygen electrode; Table S4: Cycle testing comparison of materials used as zinc air battery cathode catalysts in the literature [58–72].

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